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POLYMERIZATION AND COPOLYMERIZATION OF VINYLFERROCENE

by

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A thesis presented for the Degree of Doctor of Philosophy
in the University of London.

June 1974.



To Mary

' No man is an Iland, intire of it selfe '

Devotions XVll

John Donne (1572-1631)

ABSTRACT

The free radical polymerization of vinylferrocene is shown to be distinct from other vinyl monomers.

The rate of polymerization is proportional to the monomer and initiator concentration raised to a power 1.1. The overall activation energy for the polymerization is unusually high whilst the average degree of polymerization in any given experiment is dependent upon the monomer concentration only and independent of the initiator concentration.

Vinylferrocene is shown to be very susceptible to transfer reactions and also to initiate its own polymerization in chloroform in the absence of any added initiator. Solutions of polyvinylferrocene exhibit aggregation phenomena whilst polymers isolated at high conversions become insoluble in all solvents except chloroform. Vinylferrocene readily copolymerizes with butadiene to form 'ideal copolymers'.

Polyvinylferrocene and its copolymers are shown to contain a paramagnetic species which is identified as an ionically bound complex of Fe(III) in a high spin configuration.

The unusual features observed in the radical polymerization of vinylferrocene are explained by direct participation of the ferrocene nucleus in the polymerization reactions, in particular, in the termination step. The mechanism for the termination step is shown to occur by an intramolecular electron transfer from a ferrocene nucleus to the growing chain radical. This reaction terminates the polymer chain and produces an Fe(III) complex in the polymer.

Intramolecular electron transfer termination has not been observed before in radical polymerizations of vinyl monomers. The term 'intraelectran' is suggested to describe this type of termination.

ACKNOWLEDGEMENTS

The research for this thesis was undertaken at the Rocket Propulsion Establishment, Westcott, Buckinghamshire and Imperial College of Science and Technology, London, between December 1970 and December 1973 under the Public Research Institutions Scheme. I am grateful to the Director of RPE, Mr. J.P. Dunning for allowing me to register as an internal student at Imperial College, and Professor R.M. Barrer for allowing me to work in his department.

I am extremely grateful to my Director of Studies at Imperial College, Dr. M.H. George for his constant help and guidance during the course of this study. I am also indebted to my Supervisor at RPE, Dr. D. Sutton for his unfailing support and encouragement.

My appreciation is given to Mr. J.R. McLean and Mr. D.A.R. Herrick (RPE) for iron analyses and glassblowing respectively; Dr. A.V. Cunliffe and Mr. E.J. Gallacher (Explosives Research and Development Establishment, Waltham Abbey, Essex) for NMR analysis and GPC data; Mr. G.C. Goode (Atomic Weapons Research Establishment, Aldermaston, Berks) for Activation Analysis of polymer samples; and personnel at Imperial College especially the glassblowers and my fellow research workers in Physical Chemistry. I also thank Drs. B.W. Dale and R.K. Webster (Atomic Energy Research Establishment, Harwell, Berks.) for helpful discussions on Mössbauer and ESR spectroscopy.

Finally, my deepest thanks is due to my wife Mary, for typing this manuscript whilst attending Teacher Training College and looking after our home and three children.

G.F. Hayes

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INTRODUCTION

Since the discovery of ferrocene in 1951, the chemistry of this Π - bonded metal complex and its derivatives and congeners, ruthenocene and osmocene, has been extensively investigated.¹⁻⁶

In comparison, research on polymers based on these compounds is relatively recent and has mainly been concerned with synthetic and structural aspects. Thus, Neuse and Rosenberg⁷ concluded from their recent review of metallocene polymers that, 'as expected in any novel field of chemical research very little is known about the kinetic or thermodynamic aspects of the processes studied in the preparation of these polymers'. Similarly, other reviews of metallocene polymers⁸⁻¹⁵ are mainly compilations of the synthesis, properties and structures of polymers based on ferrocene.

Moreover, the prime emphasis of research on metallocene polymers has been on condensation polymers containing ferrocene as an integral part of the polymer backbone and research on addition polymers containing pendent ferrocene groups is even more sparse. Again, the majority of papers dealing with addition polymers are concerned with the synthesis, structures and properties of homo- and copolymers based on unsaturated ferrocene derivatives.^{16-36,81-84,136} Commensurate with the scientific and technological importance of the vinyl group, the major part of this research has been concerned with vinylferrocene,^{25-36,81-84} Pittman and his co-workers^{33,34,36,82-84,136} being especially active with this monomer.

However, even for vinylferrocene, its polymerization kinetics have not been studied in detail. For example, the only report on the kinetics of the radical polymerization of vinylferrocene contains three experiments.³⁰ On the basis of this paper, it has been claimed that vinylferrocene is analogous to styrene in free radical polymerizations.

Unfortunately, there are some anomalies in this paper which indicate that vinylferrocene does not behave like styrene in radical polymerizations. In fact, the chemistry of ferrocene, particularly the effect of the nucleus on its reactions, suggests that simple comparisons between ferrocene derivatives and benzene analogues are not possible. For example, vinylferrocene is unique amongst mono substituted ethylenes in its reactivity towards electrophillic reagents.^{53,58}

The Rocket Propulsion Establishment in collaboration with the Explosives Research and Development Establishment is interested in the properties of copolymers of vinylferrocene. In view of the imprecise knowledge concerning the polymerization of vinylferrocene by free radicals, the reactions of this monomer in free radical polymerizations have been investigated.

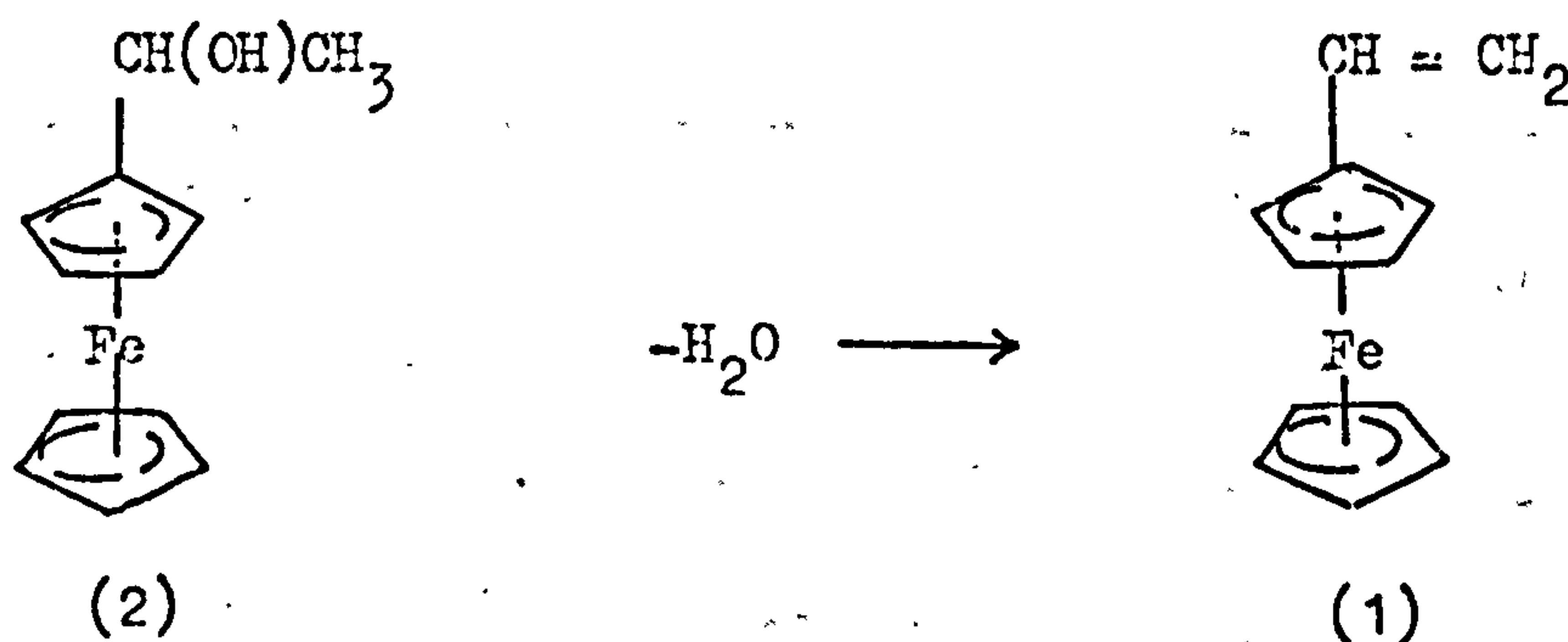
This thesis records the results of these studies.

1 LITERATURE REVIEW OF THE POLYMERIZATION OF VINYLFERROCENE

There has been a tendency to regard vinylferrocene and styrene as comparable monomers in free radical polymerizations. However, the influence of the ferrocene nucleus on the chemical reactions of vinylferrocene suggest that a simple analogy between these two monomers is not justified.

1.1 Chemical and Physical Properties of Vinylferrocene

Vinylferrocene (1) was first synthesized by Arimoto and Haven²⁵ in 1955 by pyrolysis of α - hydroxyethylferrocene (2)



The experimental conditions have been optimized by Fitzgerald,³⁷ Rausch and Siegel³⁸ and Pascal and Borecki³⁹. The lability of the hydroxyl group is such that dehydration can be achieved by simply shaking a benzene solution of (2) in the presence of excess acidic alumina.⁴⁰ Vinylferrocene is also available from other pyrolysis³⁷ and reduction reactions^{37,41-43} as well as via the Wittig olefin synthesis.⁴⁴

The monomer is a red-brown solid with a strong camphor-like odour. Its melting point has been recorded over a temperature range of 46.5 °C to 56 °C. It sublimes readily and is soluble in most

organic solvents. The ultraviolet absorption spectrum of vinylferrocene is given in Table 1-1.

Table 1 - 1

Electronic Spectra of Vinylferrocene⁴⁶ and Ferrocene¹

	$\lambda_{\max}$ (nm)	ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	solvent
Vinylferrocene	333 ^a	505	ethanol
	446	250	ethanol
ferrocene	325	52	95% ethanol
	440	91	

a appears as a shoulder on the tail of an intense uv band

The infrared spectrum is recorded in Table 1-2 and shows the characteristic bands of ferrocene⁴⁵ together with the bands associated with the vinyl group.

The oxidation-reduction potential is $E_f = -0.280 \text{ V}$ ⁴⁷ (vs normal calomel electrode) whilst the quarter wave potential (vs standard calomel electrode) was found to be $+0.325 \pm 0.002 \text{ V}$ ⁴⁸. This value is 0.018 volt higher than ferrocene indicating the enhanced oxidative stability of vinylferrocene compared with the parent compound. This is expected since electron withdrawing substituents in the ferrocene ring decrease ease of oxidation whilst electron releasing groups have the reverse effect.⁴⁹

Vinylferrocene is stable in the crystalline state in air, but rapidly decomposes in halogenated solvents.^{35,38} to give an ionic species.

Ferrocene is decomposed likewise in halogenated solvents. In the case of ferrocene, Brand and Snedden⁵⁰ have shown that it forms a charge transfer complex with CCl_4 .

Table 1 - 2

Infrared Frequency Assignments for Vinylferrocene ^a

Assignment	Frequency cm^{-1}
ferrocene ring C - H stretch	3090
aliphatic C - H stretch	3004
vinyl group C = C stretch	1631
ferrocene ring antisymmetric C - C stretch	1411
vinyl group CH_2 in - plane deformation	1240
ferrocene ring antisymmetric ring breathing	1103
ferrocene ring C - H bend (11) ^b	1002
vinyl group = C - H wag	899
ferrocene ring C - H bend ($\perp$) ^c	815

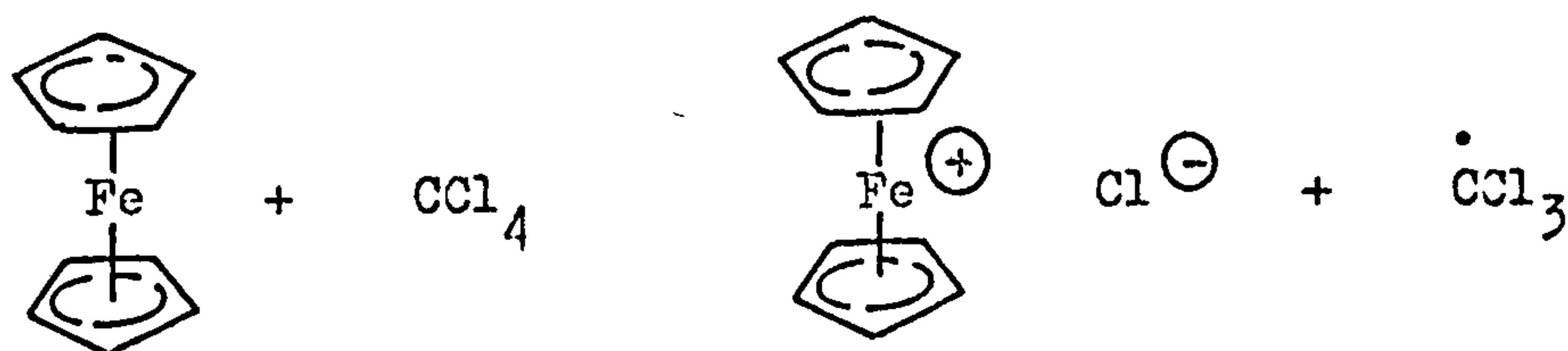
a determined in CHCl_3 solution

b parallel to the plane of the cyclopentadienyl ring

c perpendicular to the plane of the cyclopentadienyl ring

Golding and Orgel⁵¹ have also shown that the species formed by electron transfer from ferrocene is unstable in organic solvents and decomposes into an ionic species. In accordance with these observations, Rosenblum⁵² has suggested the following two step mechanism to account for the decomposition of ferrocene in carbon tetrachloride:

i) electron transfer to form the ferricenium cation



ii) decomposition of the ferricenium cation to an ionic species.

Since vinylferrocene decomposes in a similar manner to ferrocene, the same mechanism may also apply to the unsubstituted derivative. The significance of the above mechanism is that free radicals are released as a result of the initial electron transfer reaction. Hence, vinylferrocene could possibly initiate its own polymerization in halogenated solvents.

The chemical reactions of vinylferrocene have been compiled⁴ and as expected, it undergoes many of the reactions characteristic of mono-substituted ethylenes. However, vinylferrocene is unique amongst this class of compounds in its reactivity towards electrophilic reagents. For example, it will undergo addition reactions with weak electrophiles such as hydrogen azide and acetic acid even at low temperatures⁵³, whereas uncatalysed addition of weak acids to olefins does not generally occur readily.^{54,55} Similarly, many other ferrocene derivatives show unusual reactivity.^{40,56,57} This unusual reactivity has been shown to be due to direct participation of the ferrocene nucleus with the formation of stable ferrocenyl carbonium ions. The formation, stability and influence of these intermediates on the reactions of ferrocene derivatives are well documented and have been recently reviewed.⁵⁸

As well as the influence of ferrocenyl carbonium ions on the reactions of ferrocene derivatives, the iron atom can undergo direct protonation⁵⁹ and also participate in hydrogen bonding.⁶⁰

1.2 Homopolymerization of Vinylferrocene

Vinylferrocene has been shown to polymerize readily by anionic, cationic and free radical mechanisms in bulk, solution and emulsion systems^{25-36,81-83} The polymer obtained by free radical initiation was a yellow powder melting at 280 °C to 285 °C, soluble in benzene and chloroform but insoluble in methanol.²⁵ The polymer demonstrated the same reversible oxidation-reduction reactions characteristic of ferrocene.¹

Thus, polyvinylferrocene can be classified as a redox polymer. The electronic spectra of polyvinylferrocene and its oxidised form are shown in Table 1-3. The absorption at 632 nm suggests that the electronic structure of the oxidised polymer is essentially the same as the monomeric molecules.⁶⁹

Table 1 - 3

Electronic Spectra of Polyvinylferrocene³³ and its Oxidised Form³²

	$\lambda_{\text{max.}}$ (nm)	ϵ ($\text{dm}^3 \text{g}^{-1} \text{cm}^{-1}$)	Solvent
Polyvinylferrocene	232	6,460	methylene dichloride ³³
	260	6,660	" "
	323 ^a	496	" "
	440	109	" "
	446	120	Benzene ³²
Oxidised form	474 ^b	230	conc. H_2SO_4
	452 ^b	240	" "
	632	420	" "

a shoulder

b these bands did not disappear on dilution, indicating that they were not due to incomplete oxidation.

Vinylferrocene is not polymerized by benzoyl peroxide³⁰ except in the presence of ultraviolet light.²⁷ Benzoyl radicals have been shown to oxidise ferrocene to the ferricenium species which is then decomposed to ferric benzoate.⁶¹⁻⁶³ A similar reaction probably occurs with vinylferrocene. Since the ferricenium cation is very reactive towards free radicals,⁶⁴ normal vinyl polymerization is prevented. Photolytically, benzoyl peroxide decomposes to produce mainly aryl radicals and CO₂.⁶⁵ Presumably, these radicals do not oxidise the ferrocene nucleus but attack the olefinic double bond and initiate addition polymerization.

Baldwin and Johnson³⁰ have reported the only kinetic study of the polymerization of vinylferrocene. They concluded that vinylferrocene followed normal vinyl polymerization mechanisms and emphasized its similarity to styrene. The rate constants obtained were:-

$$k(\text{vinylferrocene}) = R_p / [M] [AIEN]^{0.5} = 1.1 - 1.8 \times 10^{-4} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1}$$

$$k(\text{styrene}) = R_p / [M] [AIEN]^{0.5} = 1.65 \times 10^{-4} \text{ dm}^{3/2} \text{ mol}^{-1/2} \text{ s}^{-1}$$

Their results are shown in Table 1-4 and reveal some apparent anomalies. Firstly, the molecular weight obtained for the polystyrene appears to be low.

The degree of polymerization $\bar{D}_p$ is only 51 whereas normally under these conditions $\bar{D}_p$ for polystyrene is of the order of 10^2 to 10^3 . George⁶⁶ obtained a value of 176 for polystyrene prepared in experiments in DMF using similar monomer and initiator concentrations.

Also a log-log plot of Baldwin and Johnson's values of rate against initiator concentration using the method of least mean squares gives a straight line whose slope is 1.15. This value is not in accord with a rate dependence on the square root of the initiator concentration.

In addition to the dilatometric study at low conversions, Baldwin and Johnson examined the polymerization to high conversions using an NMR technique. No degradative transfer reactions were observed and the polymerization was not inhibited.

Table 1 - 4

Homopolymerization of Vinylferrocene and Styrene in Benzene at 70 °C
Initiated by AIBN³⁰

monomer	$[M]$ mol dm ⁻³	$[In] \times 10^{-2}$ mol dm ⁻³	$R_p \times 10^4$ mol dm ⁻³ s ⁻¹	$\frac{R_p}{[M][In]}^{0.5}$	$\bar{M}_n^a$
styrene	1.6	1.02	2.64	1.65	5,400
vinyl-ferrocene	1.6	0.51	1.24	1.1	-
	1.6	1.02	1.90	1.2	-
	1.6	2.04	4.01	1.8	6,000

a number average molecular weight determined by vapour pressure osmometry in benzene solution at 37 °C.

Vinylferrocene also undergoes fairly facile cationic polymerization at 0 °C³². However, the molecular weights of the polymers obtained were low. Surprisingly, at - 78 °C, no polymer was formed and only dimeric and tetrameric products were obtained. However, the ferrocene nucleus is very reactive towards electrophilic substitution.⁶⁷ Therefore, since the propagation step in cationic polymerization is considered to be attack by an α -ferrocenyl cation on another ferrocene molecule, nuclear substitution may successfully

compete with vinyl addition at low temperatures. Nuclear substitution does not proceed alongside vinyl addition as the infrared spectrum of the polymers shows the presence of homoannular substitution only.⁶⁸

The melting points and solubility of the cationically-prepared polymers were identical to those prepared by free radical initiation.

Pittman et al^{33,34} have characterized PVF in some detail. Low molecular weights ($\bar{M}_n < 12,000$) were obtained in all their experiments. The molecular weights distributions were examined by gel permeation chromatography using a Q - factor^{70,71} of 88. The inaccuracies of interpreting GPC curves by this method has been discussed and its use is not recommended.⁷² Hence the results quoted by Pittman et al may be in error. (Pittman et al³⁶ in a later publication have, themselves drawn attention to these errors.)

These workers recorded the Mössbauer spectrum of PVF at 77 K. The spectrum showed a quadrupole doublet, isomer shift (relative to nitroprusside) = 0.78 mm s^{-1} and a quadrupole splitting = 2.44 mm s^{-1} . Similar results are obtained for ferrocene.⁷³ The glass transition temperature of the polymers was observed between 184°C to 196°C .

Polyvinylferricenium salts have been obtained with electron attracting compounds such as dichlorodicyanoquinone, o-chloranil and tetracyanoethylene. The Mössbauer spectra of these salts indicated complete electron transfer had occurred.⁷⁴ Collins and Pettit⁷³ and Brandon et al⁷⁴ only obtained a charge transfer complex between ferrocene and TCNE. Charge transfer is expected with TCNE because of its lower oxidation-reduction potential compared to DDQ. The structure of the PVF/TCNE complex is therefore not certain.

Vinylferrocene has been successfully polymerized by soluble Ziegler catalysts, typified by $\text{Al Et}_2 \text{ Cl/Cu(acac)}_2$ ³⁵. Attempts to

polymerize the monomer by the isobutyl derivative, $\text{Al}(\text{iso-Bu})_3 \cdot \text{Cu}(\text{acac})_2$ did not succeed. Substituted phosphine - $\text{Ni}(\text{II})$ complexes typical of those used to polymerize acetylenes,⁷⁵ were also unsuccessful. However, substituted phosphine - $\text{Ni}(\text{II})$ complexes obtained in-situ in chloroform proved to be highly effective. They concluded that the polymerization occurred by an anionic-co-ordinative mechanism. Hiraki et al⁷⁶ have proposed a radical mechanism for a similar catalytic system. Since vinylferrocene is decomposed in chloroform more work is required to support an anionic - co-ordinative mechanism.

The effect of experimental conditions on the properties of PVF prepared by radical initiation has been studied.³⁶ The molecular weights obtained for soluble polymers varied from $\bar{M}_n = 4,000$ to $\bar{M}_n = 382,000$. These are the highest reported for PVF. The GPC data was interpreted using a standard calibration curve. The relationship between $[\eta]$ and $\bar{M}_n$ of fractionated PVF samples is recorded in Table 1-5.

Table 1 - 5

Molecular Weights and Intrinsic Viscosities of Fractionated Polyvinylferrocene

$\bar{M}_n^a$	$[\eta]$ ($100\text{cm}^3\text{g}^{-1}$) benzene 30 °C	$[\eta]$ ($100\text{cm}^3\text{g}^{-1}$) THF 30 °C
23,000	0.0729	0.0959
15,400	0.0574	0.0693
9,800	0.0507	0.0523
9,250	0.0484	0.0487
5,920	0.0373	0.0361

a determined by VPO at 37 °C benzene.

The constants for the Mark Houwink equation were found to be $K = 6.64 \times 10^{-4}$, $\alpha = 0.48$ in benzene; and $K = 7.20 \times 10^{-5}$, $\alpha = 0.72$ in THF. They concluded from the low value of α , that the PVF molecule is relatively coiled in benzene solution.

For a randomly coiled polymer, the lower limit of α theoretically is 0.5 at the Theta temperature when precipitation will occur.⁷⁷ Pittman et al³⁶ point out that lower values have been observed e.g. polyvinylchloride in dioxan exhibits $\alpha = 0.2$ ⁷⁸. However, PVC in dioxan is a well-known system where aggregation is important.⁷⁹ The low value of α for PVF in benzene might therefore be an indication of polymer-polymer aggregation.

This view is supported by the unusually high molecular weights ($M_n > 10^6$) which Pittman et al obtained since anomalously high molecular weights are observed when aggregation phenomena are present.⁸⁰ Pittman and his colleagues also noticed that the normal relationship between molecular weight and intrinsic viscosities was frequently not obeyed. Aggregation affects molecular weight more than intrinsic viscosities and may account for this anomaly as well. Unfortunately, the Huggins slope constant was not recorded. Values above 0.5 are a clear indication of aggregation.⁸⁰

Benzene-insoluble polymers were obtained at high conversions and the authors concluded that abstraction and branching reactions occur which ultimately lead to cross-linking.

1.3 Copolymerization of Vinylferrocene

Vinylferrocene readily copolymerizes with a large number of diverse olefinic compounds which include methyl methacrylate, 25,26,30,34 ethyl acrylate³⁰ styrene,^{25,26,30,32,34,81} acrylonitrile,^{26,34} methyl acrylate³⁴ vinyl isobutylether³² chloroprene^{25,26} butadiene⁸² maleic anhydride,⁸³

and N - vinyl -2- pyrrolidone.⁸⁴ Vinylferrocene does not copolymerize with vinyl acetate.^{26,30,34} Results obtained with isoprene are conflicting. Pittman et al³⁴ reported that copolymerization does not occur whereas Reed⁸⁵ reported successful copolymers. Reed emphasized that impure vinylferrocene polymerized poorly and showed anomalous behaviour in copolymerizations.

Similarly, there are conflicting reports concerning the Q and e values for vinylferrocene. Pittman et al³⁴ calculated e to be positive ($e = + 0.47$). They suggested that the apparently low vinyl reactivity was because the ferrocene nucleus tended to destabilize adjacent radical centres.⁸⁶

Aso et al⁸¹ obtained a large negative e value for vinylferrocene ($e = - 1.3$). Roche and Price⁸⁷ have demonstrated that a close relationship exists between the e value of a monomer and the rate of bromine addition to the double bond. Monomers with negative values brominate much more rapidly than those with positive values. Since bromine adds readily to vinylferrocene,⁸⁸ the value reported by Aso et al, appears more accurate.

Their result is also supported by the exceptional electron releasing capacity of the ferrocene nucleus⁸⁹ since vinyl monomers containing electron-releasing substituents tend to have negative e values.

Concomitant with a negative value, vinylferrocene is much more reactive than styrene in cationically initiated copolymerizations.³² This is expected because of the enhanced stability of α -ferrocenylcarbonium ions in comparison to aromatic carbonium ions.⁵⁸

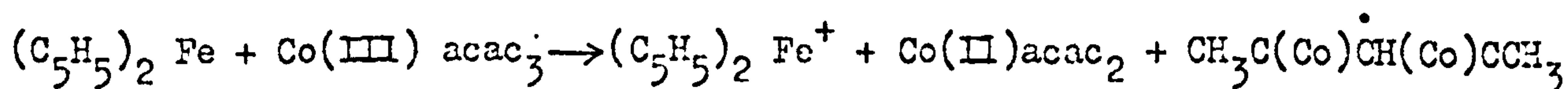
From copolymerizations of acrylonitrile and vinylferrocene Pittman et al calculated e values of $+ 1.2$ and $+ 0.73$ respectively. However, these values are inconsistent with the low value for the product of their reactivity ratios ($r_1 r_2 = 0.024$). Although the $Q - e$ scheme is

only semi-empirical, it is sufficiently precise to predict that low values of $r_1 r_2$ are associated with large differences in the respective e values⁹⁰

With maleic anhydride, Pittman et al⁸³ observed that vinylferrocene formed an alternating copolymer ($r_1 r_2 = 0.0042$). This result reflects a large difference in polar properties of the two monomers in accordance with the electron-releasing effect of the ferrocene substituent and the electron withdrawing effect of the anhydride group. Since this result is also at variance with their previous work,³⁴ the authors suggest that a charge transfer complex may operate in the copolymerization mechanism. However, all their results can be rationalized if the values of Q and e for vinylferrocene ($Q = 0.4$, $e = -1.3$) from the work of Aso et al are used.

Vinylferrocene was found to be much less reactive than vinyl isobutyl ether in cationic polymerizations,³² the reactivity ratios being r_1 (vinylferrocene) = 0.1 ± 0.1 and r_2 (vinyl isobutyl ether) = 9.7 ± 1.0 . Ferrocenyl substituents have been found to markedly increase the rate of solvolysis of chlorides in comparison to methoxy substituents.⁹¹ The apparently smaller influence of the ferrocenyl group in cationic polymerizations with the isobutyl ether was ascribed to steric hindrance with the bulky ferrocene monomer.

Pittman has reported that vinylferrocene does not copolymerize with butadiene using free radical initiators.⁸² Attempted polymerizations with AIBN, benzoyl peroxide and cyclohexanone peroxide were unsuccessful. However, he prepared copolymers using metal acetylacetonates as initiators. This is quite a general reaction and others⁹²⁻⁹⁴ have shown that vinyl monomers in the presence of acetylacetonates and metallocenes polymerize by free radical mechanisms. The general scheme involves an electron transfer reaction, which liberates free radicals:-



These radicals then initiate polymerization of the vinyl monomer. Since a similar reaction can occur between vinylferrocene and an acetyl-acetonate, a radical mechanism has probably occurred in the copolymerization of vinylferrocene and butadiene. Pittman's conclusion that free radicals are ineffective for copolymerizing vinylferrocene and butadiene, may be premature.

1.4. Summary of Review and Conclusions.

Seventeen papers have been published up to June 1973 on the homo- and copolymerization of vinylferrocene. This relatively small number reflects the available knowledge concerning the polymerization of this monomer. It is, perhaps unfortunate that the only paper on the kinetics of the homopolymerization of vinylferrocene contained such few experimental results. An examination of these results has indicated some apparent anomalies. It is also evident that conflicting results about the copolymerization and reactivity of vinylferrocene have been recorded.

These papers have been critically examined and discussed in terms of the basic chemistry of ferrocene as well as the chemistry of vinyl polymerizations. The review has suggested that vinylferrocene does not polymerize in accordance with well established polymerization mechanisms. It appears that vinylferrocene should not be considered simply as an analogue of styrene.

2. KINETICS OF FREE RADICAL POLYMERIZATION OF VINYLFERROCENE IN BENZENE

2.1 MATERIALS

2.1.1. Vinylferrocene

Vinylferrocene from Research Organic/Inorganic Chem. Corp. California, was used for the major part of the polymerization study. The melting point of initial samples was 47-48°C, whilst for later samples it was 52.5 - 53.5°C. All samples were purified by successive sublimation at 30°C and 0.1 mmHg. Successive sublimations achieved a constant melting point of 53-54°C (Lit values 46.5 - 53.5°C^{25-36,37-43}). A large scale sublimator, similar to that described by Elvidge and Sammes⁹⁵ was used. Approximately 20g of vinylferrocene could be purified per day in this manner.

The purity of the monomer after each sublimation was checked by gas chromatographic analysis (Pye Unicam 101, carbo-wax column / 20M KOH at 200°C). Impurity peaks which could be observed at high sensitivity were removed after the second sublimation. The chromatograms are shown in Fig. 2-1 and confirm the purity of the vinylferrocene. Thin layer chromatography on Alumina G (Woelm, Eschwege, Germany) also demonstrated that the monomer was pure.

Gotzmer⁹⁶ has reported that vinylferrocene from Research Organic/Inorganic contains α - hydroxyethylferrocene as an impurity (up to 50 %). TLC of all samples received for the present study, do not substantiate this report. Gotzmer identified the impurity by eluting vinylferrocene from an alumina column with benzene. Since the carbinol is dehydrated to produce vinylferrocene by simply shaking in benzene in the presence of alumina,⁴⁰ the reverse reaction may have occurred in Gotzmer's study.

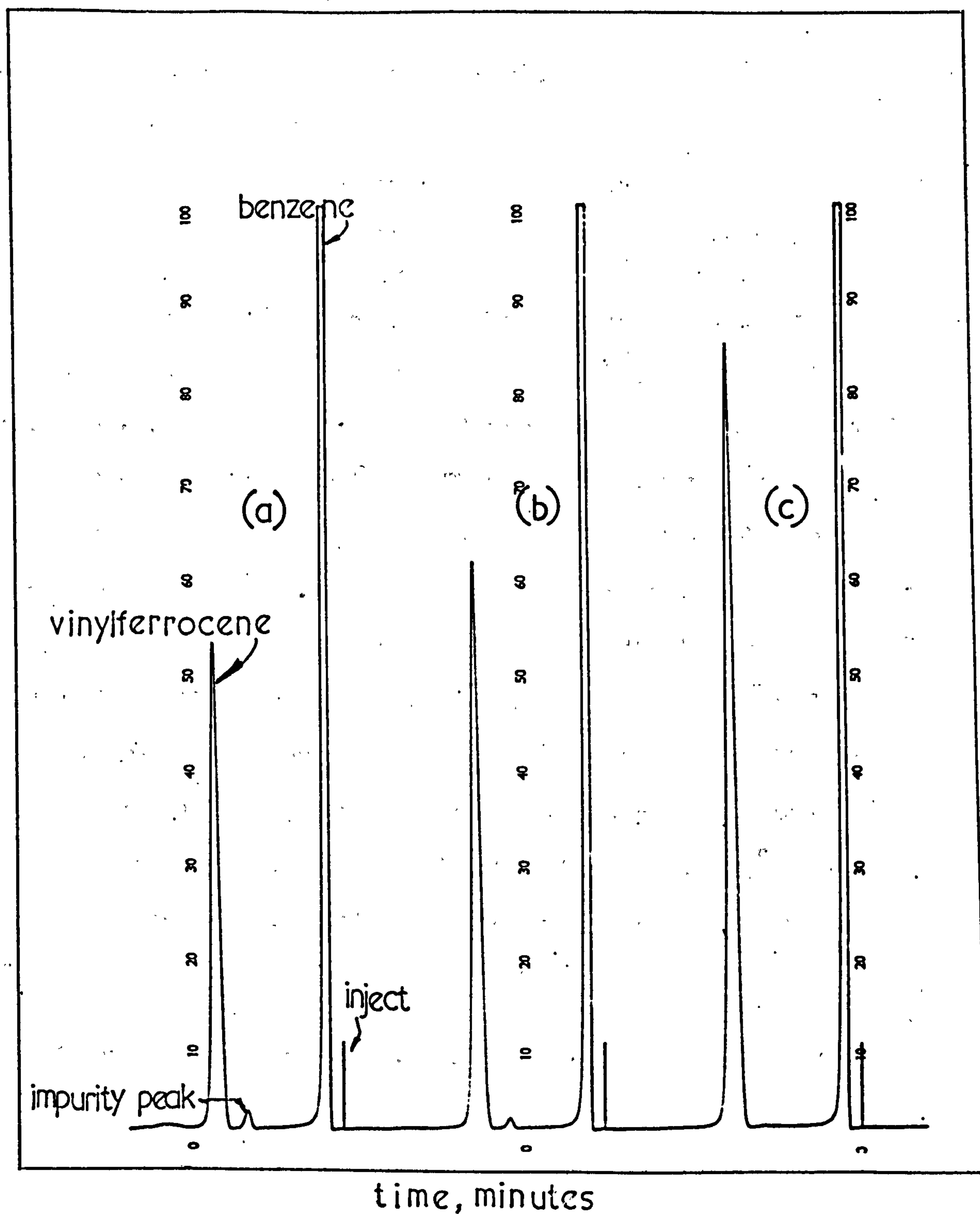


Fig 2-1. Gas chromatographic analysis of vinylferrocene examined at 200°C in benzene on a carbowax column. The impurity peak observed at high sensitivity is removed after the second sublimation (a) as-received (b) 1st sublimation (c) 2nd sublimation.

Vinylferrocene was also synthesized by reduction of acetylferrocene and subsequent dehydration of the alcohol. The use of lithium aluminiumhydride described by Arimoto and Haven²⁵ was found to be unnecessary. Potassium borohydride was equally effective and avoided the problems of moisture sensitivity associated with handling LiAlH_4 ⁹⁷.

3.0 acetylferrocene (Koch-Light Laboratories Ltd., Colnbrook) in 40 cm³ dry methanol was treated with 1.2g KBH_4 (BDH Chemicals Ltd., Poole). Reduction was judged to be complete when the initial red solution had turned yellow. This occurred after about fifteen minutes shaking. Unreacted KBH_4 was filtered off and destroyed with dilute acetic acid. The alcohol was precipitated by dilution of the solution with 100 cm³ water, collected and dried (m.pt 72 °C to 74 °C, 81 % yield) 10g α -hydroxyethylferrocene and 30g activated alumina (CAMAG neutral, Alfa Inorganics, Beverly, Mass. heated for 24 hours at 200 °C) were intimately mixed and placed in a vacuum sublimator. The sublimator was evacuated to 10 mmHg and heated at 155 °C for 20 hours. An 86 % yield of vinylferrocene was obtained m.p. 52 °C - 53 °C.

Calculated for vinylferrocene, $\text{C}_{12}\text{H}_{12}\text{Fe}$;

carbon	67.96 %
hydrogen	5.71 %
iron	26.33 %

Found;

carbon	67.86 %	67.65 %
hydrogen	5.85 %	5.65 %
iron	26.40 %	26.38 %

Samples of purified vinylferrocene were stored in sealed flasks at -22 °C. No changes in the melting points or the infrared spectra of the samples were observed during storage.

2.1.2 2,2'-Azobisisobutyronitrile (AIBN)

AIBN $(\text{CH}_3)_2\text{C}(\text{CN})\text{N}=\text{N}(\text{CN})\text{C}(\text{CH}_3)_2$ (Aldrich Chem. Co. Inc. Milwaukee) was recrystallized three times from AnalaR methanol (m.p. 101-102 °C with decomposition identical with lit values⁹⁸) Its ultraviolet spectrum (in methanol; Pye Unicam SP500 Spectrophotometer) was consistent with a pure compound. (λ_{max} 347 nm; $\epsilon = 13.94 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$; lit value⁹⁹ λ_{max} 350; $\epsilon = 14.07 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) The initiator was stored in sealed flasks under oxygen-free nitrogen at -22 °C

2.1.3 Solvents

AnalaR benzene was refluxed with P_2O_5 for four hours and then fractionally distilled from fresh P_2O_5 at reduced pressure. The middle fraction was collected and stored in sealed flasks in the dark at room temperature. AnalaR chloroform was shaken with concentrated sulphuric acid, concentrated potassium hydroxide and finally water. It was then dried over anhydrous calcium sulphate and fractionally distilled. The middle fraction was collected and used as soon as possible.

2.2 Apparatus

2.2.1 High Vacuum Line

Oxygen must be excluded from all kinetic experiments in order to obtain reproducible results.¹⁰⁰ The high vacuum line (Fig.2-1) used to degas the reactants, consisted of a mercury vapour diffusion pump (Speedivac Model EMG, Edwards) backed by a two-stage mechanical rotary pump (Speedivac 2SC, Edwards High Vacuum Ltd., Crawley) fitted with a gas ballast. The main manifold was connected to the intake port of the diffusion pump via a cold trap cooled with liquid nitrogen. A by-pass line allowed the vapour pump to be isolated whilst the system was pumped to a backing pressure of 10^{-3} mmHg. A reservoir of 10 dm^3 between the mechanical pump and the diffusion pump provided the necessary volume maintained at backing pressure against which the vapour pump operated when isolated. Backing pressures were measured with a Pirani vacuum gauge (model 8/2 Edwards High Vacuum Ltd) and low pressures were recorded by Penning gauge (Penning 8 Edwards). Both gauge heads were protected by liquid nitrogen cooled traps. Operating procedures have been described elsewhere. 101

2.2.2 Dilatometers

The dilatometers consisted of a length (ca. 120 mm) of 1.0 mm precision bore tubing (Veridia Ltd., London) attached to bulbs of volumes between 1 cm³ and 5 cm³. Tubes employed for filling the dilatometers had a volume of ~40 cm³ and a side arm and B19 socket for attachment to the vacuum line. The dilatometers were attached to the tubes for the filling and degassing procedures. The volume and capillary radius of each dilatometer were determined before use by calibrating with distilled water.

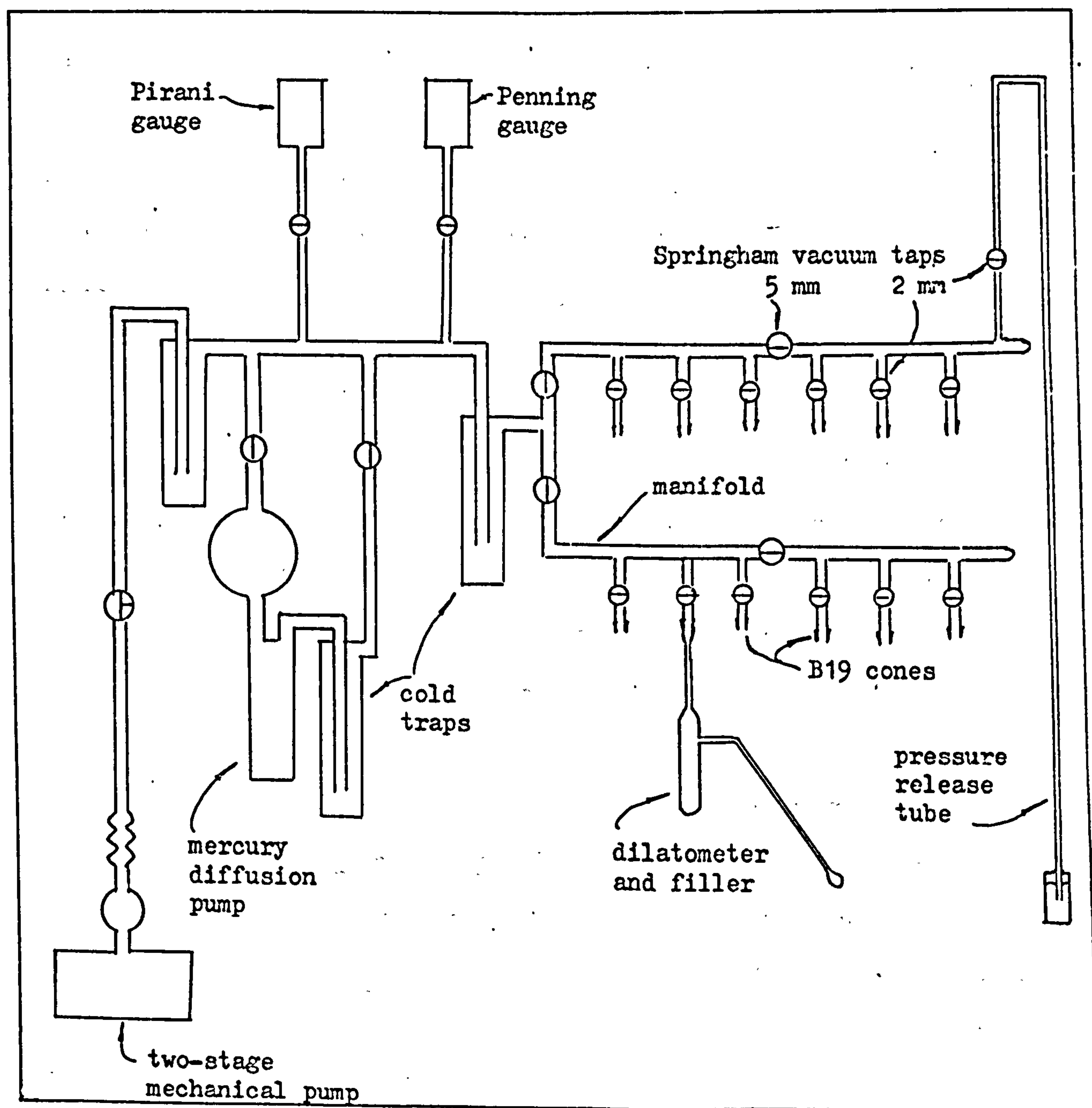


Fig.2-2 High Vacuum Line for Degassing Reactants Used in the Polymerization Studies of Vinylferrocene.

2.3 EXPERIMENTAL TECHNIQUES.

2.3.1 Dilatometric procedure

A solution of initiator in AnalaR benzene was measured from a micro-burette and allowed to drain through a drawn-out capillary so as to lay evenly on the bottom of the filling-tube. The benzene was immediately and carefully evaporated, at room temperature under reduced pressure, leaving the required amount of initiator as a fine deposit on the bottom of the filling-tube. A number of tubes were prepared in this manner and stored under oxygen-free nitrogen at -22°C until required. Vinylferrocene was then weighed into the tubes, benzene added, and the tubes attached to a high vacuum line and the contents degassed by three freeze-pump-thaw cycles at 10^{-4} mm Hg. The filling-tube was separated from the vacuum line whilst still pumping by sealing the constriction in the neck. The contents of the tube were warmed to room temperature, shaken to ensure a homogeneous solution and then the tube was tilted to allow the required amount of solution to run from the tube into the attached dilatometer. The solutions in the bulb of the dilatometer and that remaining in the filling-tube were simultaneously frozen in liquid nitrogen and the dilatometer separated from the filler by sealing at the constriction in the side-arm. The dilatometer was then placed in a water bath (Townson and Mercer Ltd) at $60^{\circ}\text{C} \pm 0.01$ and the change in height of the meniscus followed with a cathetometer (Precision Tool and Instrument Co. Ltd.) accurate to 0.01 mm.

The effects of temperature on the rate of polymerization was examined by employing a range of temperatures for the kinetic experiments.

2.3.2 Determination of density of vinylferrocene and polyvinylferrocene

The variation in the density of vinylferrocene with temperature was determined by standard dilatometric techniques.¹⁰² The density of polyvinylferrocene was determined by three methods; displacement, density gradient column and weighing a known volume. The first two methods presented some difficulties with this polymer and a scatter in the experimental results was obtained. The third method was easily performed and produced consistent results. A sample of the polymer was placed in a

die (13 mm Specac, London) and degassed. Pressure was applied at room temperature in stages up to 27.6 MNm^{-2} (4,000 psi). The polymer fused under these conditions to give a compressed disc similar to the potassium bromide discs used for infra red spectroscopy. The disc was weighed and its height and diameter measured with a comparator (Sigma Instruments Ltd) accurate to $\pm 0.0025 \text{ mm}$ from which a value for the density was obtained.

The method employed to determine the apparent density of vinylferrocene and polyvinylferrocene in benzene was based on that of Matheson.¹⁰³ It was modified to a smaller scale because of the relatively small amounts of polymer available. A solution of monomer or polymer was introduced into a calibrated dilatometer from a syringe fitted with a fine needle. The volume of the solution was then measured at different temperatures. The apparent density was obtained from the expression:-

$$\text{apparent density of solute} = \frac{\text{weight of solute}}{\text{volume of solution} - \text{volume of solvent}}$$

The volume additivity of vinylferrocene in benzene was checked by adding known weights to a calibrated dilatometer and measuring the resultant volumes.

2.3.3 Isolation of polymers

The polymerizations were stopped at $\sim 5\%$ conversion by pouring the contents of the dilatometer into 500 cm^3 of methanol containing a trace of hydroquinone (Ralph N. Emanuel Ltd). The precipitated polymer was filtered out, redissolved in benzene and reprecipitated into methanol. It was finally collected on a sintered crucible (porosity No 4) and dried to a constant weight at 70°C and 0.1 mm Hg .

2.4 CHARACTERIZATION OF POLYMERS

Carbon, hydrogen and nitrogen contents were determined by combustion analysis. (Elemental Analyser Model 240 Perkin Elmer Ltd, Beaconsfield). Iron analysis was performed separately by polarography using standard techniques,¹⁰⁴ with a Davis Differential Cathode Ray Polarograph (Southern Analytical Instruments Ltd., Camberley).

Number average molecular weights below 20,000 were measured by vapour

pressure osmometry in benzene solution at 37 °C. (Molecular Weight Apparatus, Model 115, Hitachi Perkin-Elmer Ltd). Values of $\bar{M}_n$ above 20,000 were measured with a membrane osmometer in chloroform solution at 40 °C. (Recording Osmometer Model CSM -1, Melabs Inc. California) The theory and experimental techniques for determining molecular weights of polymers have been discussed in detail elsewhere.^{105,106}

Molecular weight distributions were examined by gel permeation chromatography of THF solutions of the polymers on a Waters GPC Model ALC 100. (Waters Associates, Stockport).

Infrared spectra of PVF films and solutions were recorded on a Perkin Elmer 157G spectrophotometer. Ultraviolet and visible spectra were examined in benzene and chloroform solution with a SP 700 spectrophotometer (Pye Unicam Ltd., Cambridge).

Nuclear magnetic resonance spectra of PVF samples at room temperature were obtained in ortho-dichlorobenzene and carbon disulphide on a Perkin Elmer R10 60MHz_z spectrometer. Samples were also examined over a range of temperatures up to 150 °C in ortho-dichlorobenzene on a Perkin Elmer R32 90MHz_z spectrometer.

Mössbauer data for PVF were obtained at liquid nitrogen temperatures, room temperature and 400K by the Mössbauer Group, Harwell, Berks, on a Mössbauer spectrometer described by Cranshaw.¹⁰⁷

Electron spin resonance was examined with a Varian V-4500 spectrometer (Varian Associates Ltd. Walton-on-Thames) operated at X - band frequency (9500 MHz_z) with an applied modulation field of 100 kHz_z. Polymer samples were investigated as powders and as solutions in benzene. Spectra were recorded at room temperature and at 77K.

Magnetic susceptibility measurements were made by the Faraday method¹⁰⁸ at ten temperatures down to 77K. Force measurements were made at four field strengths for each temperature.

Intrinsic viscosities were determined in benzene and chloroform solutions and mixtures of these solvents at 25 °C. A suspended-level dilution viscometer was used. The experimental technique has been fully described by Billmeyer¹⁰⁹

Glass transition temperatures of PVF samples were determined by differential scanning calorimetry (DSC 1-B Perkin Elmer Ltd.) at four heating rates on samples in sealed pans.

2.5 RESULTS OF KINETIC EXPERIMENTS

2.5.1 Dilatometry

Dilatometry provides a reliable and extremely accurate method for observing the kinetics of vinyl polymerizations.¹¹⁰ It is based on following the change in volume which occurs when the olefinic double bond is saturated. Since the density of the polymer is greater than that of the monomer, a contraction in volume takes place during the polymerization reaction. Starkweather and Taylor¹¹¹ first demonstrated a linear relationship between the per cent volume contraction and the per cent conversion. Hence it is possible to calculate the per cent conversion as follows.

Let V_m = volume of monomer

V_p = " " polymer after time t

ρ_m = density of monomer

ρ_p = " " polymer

mass of monomer converted = mass of polymer formed

$$= V_p \rho_p$$

but

$$V_p = V_m \rho_m$$

therefore mass of
monomer converted

$$= V_m \rho_m / \rho_p$$

Now the contraction in volume in the capillary is equal to the difference between the volume of monomer converted and the volume of polymer formed.

$$\text{i.e. } \pi r^2 h = V_m - V_p$$

where h is the observed contraction in the dilatometer and r is the radius of the capillary

$$\text{therefore } \pi r^2 h = V_m - \left\{ V_m \rho_m / \rho_p \right\}$$

$$\text{therefore } V_m = \pi r^2 h \rho_p / (\rho_p - \rho_m)$$

$$\begin{aligned} \text{The per cent conversion} &= \frac{\text{mass of monomer converted}}{\text{initial mass of monomer}} \\ &= \left(V_m / V_o \right) 100 \end{aligned}$$

where V_o is the initial volume of monomer.

$$\text{but } V_o = \rho_m / m_o$$

where m_o is the initial mass of monomer.

$$\text{therefore \% conversion} = \left(V_m \rho_m / m_o \right) 100$$

and substituting for V_m

$$\text{per cent conversion} = \left\{ \pi r^2 h \rho_p \rho_m / (\rho_p - \rho_m) m_o \right\} 100$$

A plot of per cent conversion of monomer to polymer against time is found to be linear for vinyl polymerizations at low conversions. The rate of polymerization can be obtained from the slope of this plot, for example in per cent polymerization per minute. The rate is then usually expressed in $\text{mol dm}^{-3} \text{ s}^{-1}$

$$\text{i.e. } R_p = \text{slope} \times [M] / (100 \times 60) \text{ mol dm}^{-3} \text{ s}^{-1}$$

where R_p is the initial rate of polymerization, and $[M]$ is the monomer concentration in mol dm^{-3} and the slope is expressed in % polymerization/minute.

The contraction in the dilatometer, h , is obtained by plotting meniscus height against time. The initial volume, and hence m_o , is found by extrapolation to zero time.

In dilatometric determinations of the extent of a polymerization reaction, the observed volume contraction is due to the difference between the partial specific volumes of the reactant and product. The partial specific volumes cannot be assumed to be equal to the specific volumes of the respective pure components.

Calculation of the volume contraction from the densities of the pure monomer and polymer is probably only completely valid for the bulk polymerization of a monomer immiscible with its polymer. In any system

containing a solvent for the monomer and polymer, the volume contraction accompanying polymerization cannot be calculated from the bulk densities of polymer and monomer, since this assumes that the partial specific volumes of the components are the same in bulk as in solution.¹¹² Treloar¹¹³ has discussed the errors which can be introduced into conversion factors by relying on bulk densities. Moreover, it is often assumed that linearity exists between the density of homogeneous mixtures and their concentration. This relationship is not fulfilled when the volumes are additive.¹¹⁴ Also, Morris and Parts¹¹⁴ have examined conversion factors in dilatometry and concluded that with concentrated monomer solutions, the conversion factor is not a constant, but varies with the composition of the mixture, i.e. on the extent of polymerization.

Matheson et al¹⁰³ have shown that for accurate results, the 'apparent density' of the monomer and polymer must be determined in the solvent used for the polymerization reaction. A knowledge of these values at the reaction temperature and in a similar concentration to that used in the experiments is also required.

Of course, much of the uncertainty associated with a conversion factor may be precluded by calibrating the dilatometric procedure for a given system by an absolute technique such as gravimetric determinations.

2.5.2 Densities and Apparent Densities of Vinylferrocene and Polyvinylferrocene

The density and apparent density of the monomer and polymer are recorded in Table 2-1. The density and apparent density of vinylferrocene varied linearly with temperature and plots are shown in Fig. 2-3 and 2-4. The density of vinylferrocene was obtained below its melting point since the monomer remained liquid down to 34 °C with

Table 2 - 1

Density of Vinylferrocene and 'Apparent' Density of Vinylferrocene
when Dissolved in Benzene

temperature °C	density of vinylferrocene g cm ⁻³	'apparent' density of vinylferrocene as a 40 % solution in benzene, g cm ⁻³
34.1	1.284	1.281
36.5	1.282	-
38.5	1.281	-
40.0	-	1.284
50.0	-	- 1.276
55.8	1.262	-
60.0	1.258	1.268
66.1	1.253	-
70.0	-	1.262
70.5	1.249	-
75.0	-	1.259
75.8	1.244	-
80.2	1.240	-

slow cooling. The extrapolated value at room temperature lies on the observed plot. The difference between the density and apparent density of PVF at low concentrations was very small, and did not alter significantly with temperature.

The volumes of vinylferrocene and benzene were found to be additive within experimental error. Values are recorded in Table 2-2.

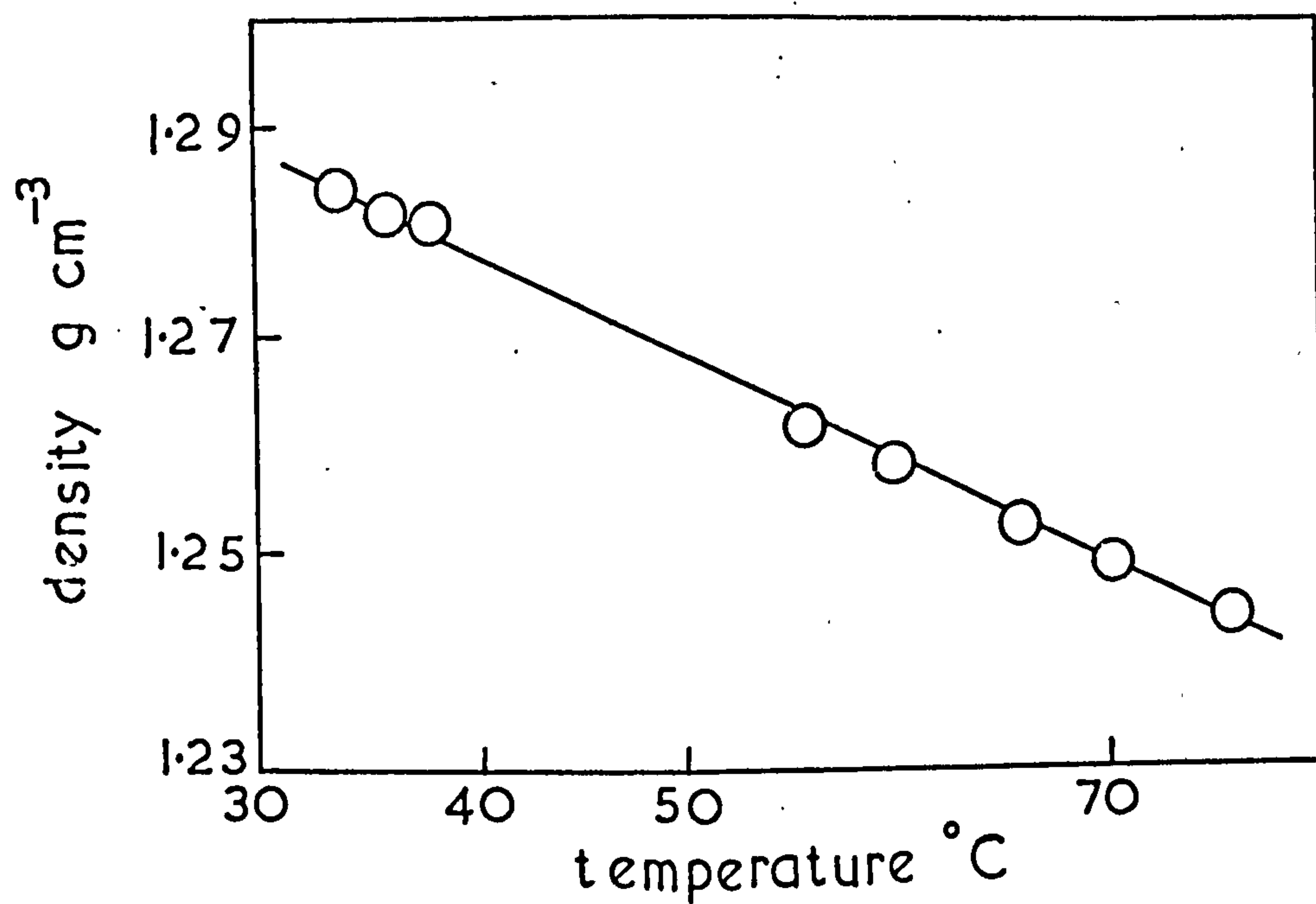


Fig. 2-3 Plot of Density of Vinylferrocene as a Function of Temperature.

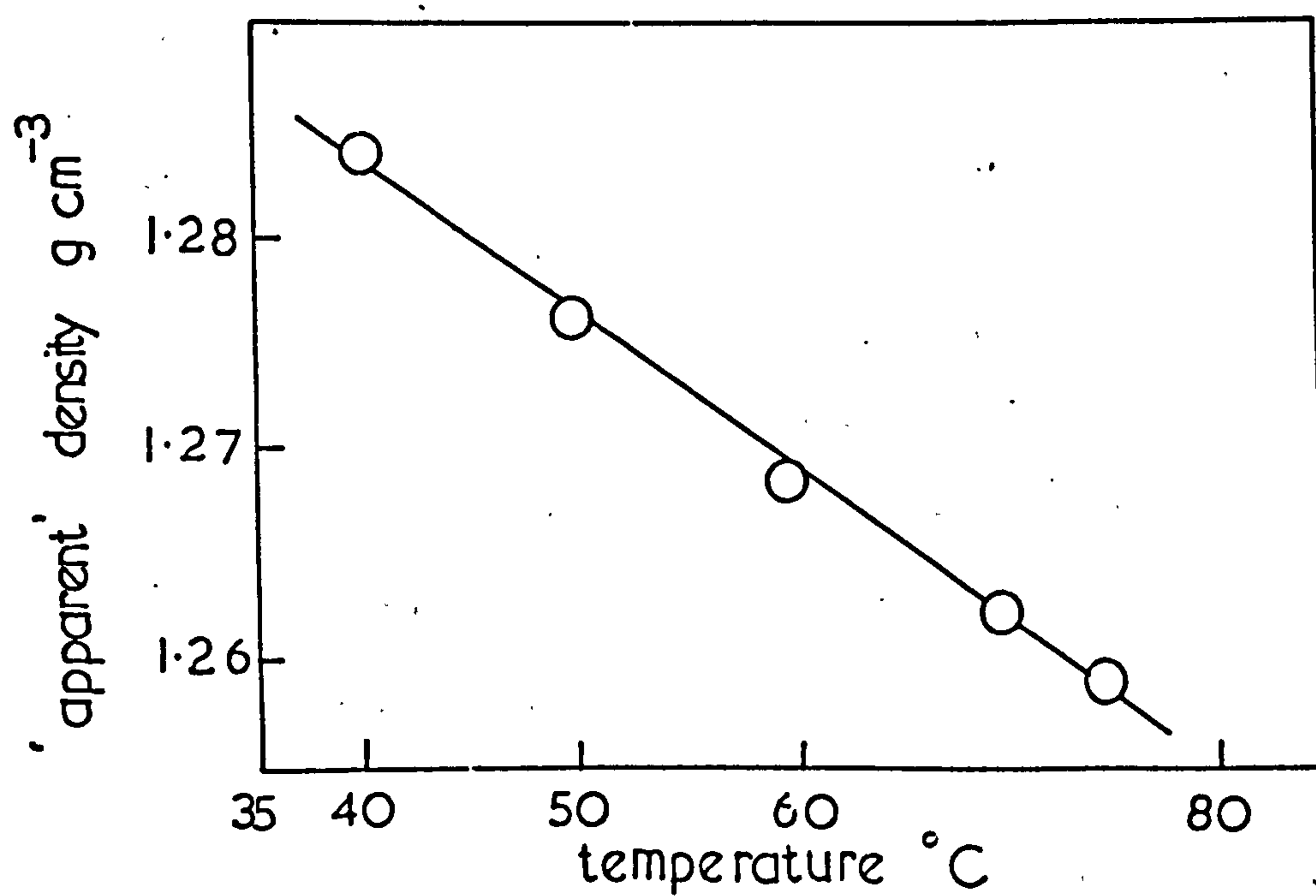


Fig. 2-4 Plot of 'Apparent' Density of Vinylferrocene as a Function of Temperature. 40 % Solution in Benzene.

Volume additivity of vinylferrocene and benzene.

temperature °C	vinylferrocene cm ³	benzene	calculated volume for additivity cm ³	observed volume cm ³
15	1.44	1.29	2.73	2.78
20	1.31	1.11	2.42	2.40
25	3.18	2.19	5.37	5.31
30	2.04	1.21	3.25	3.31

The values for the apparent density of vinylferrocene and PVF at 60 °C used to calculate the per cent conversion of monomer to polymer were:-

$$\rho_{\text{vinylferrocene}} = 1.268 \text{ g cm}^{-3}$$

$$\rho_{\text{polyvinylferrocene}} = 1.403 \text{ g cm}^{-3}$$

These values were estimated to be accurate to ± 0.004 .

The per cent conversions calculated with these values were checked by gravimetric determination of the amount of polymer formed in the dilatometer. The per cent conversions found were in reasonable agreement with those calculated. Hence at the low conversions employed for these experiments the dilatometric technique was acceptable. Representative results for calculated and observed conversions are shown in Table 2 - 3.

Percentage conversions calculated by using density values for the bulk monomer and polymer were approximately 10% below those obtained with the corrected values. Bulk density values for vinylferrocene and polyvinylferrocene therefore do not appear to be acceptable for calculating rates of polymerization by dilatometry. The errors produced would be expected to increase at higher conversions. The estimated errors for the dilatometric technique used in this study were approximately 5% which is within the acceptable limits for dilatometry.

The percentage conversions were found to be linear with time at

the conversions studied. A plot of some representative results of per cent conversion against time is shown in Fig. 2-5.

Table 2 - 3

Per cent conversion at 60 °C observed by dilatometry and found gravimetrically.

$[I]_0 \times 10^2$ mol dm ⁻³	$[M]_0$ mol dm ⁻³	% conversion observed by dilatometry	% conversion found gravimetrically
0.4	4.0	0.6	0.44
1.0	4.0	1.8	1.65
1.8	4.0	3.1	2.90
2.0	4.0	3.2	2.89
1.0	2.0	1.1	0.87
1.0	3.0	1.9	1.61

2.5.3 Rate of Polymerization of Vinylferrocene

The results of the kinetic experiments are recorded in Tables 2-4 and 2-5, and 2-6. The dilatometric technique was an extremely sensitive method for observing any inconsistencies in the rate experiments. Inhibition, retardation and in one case acceleration of the polymerization of vinylferrocene can be ascribed to traces of oxygen in the systems. Oxygen is known to have pronounced and often unpredictable effects on the rates of vinyl polymerizations.¹¹⁵⁻¹¹⁷ Vinylferrocene seems to be particularly susceptible to induced decomposition reactions with oxygen-containing compounds.²³ The presence of oxygen in some of the experiments in the present study is supported by the fact that all these experiments were performed in relatively thin walled glassware. This glassware tended to collapse on sealing under vacuum, allowing air to be sucked into the system. Pinholes were, in fact found in some cases.

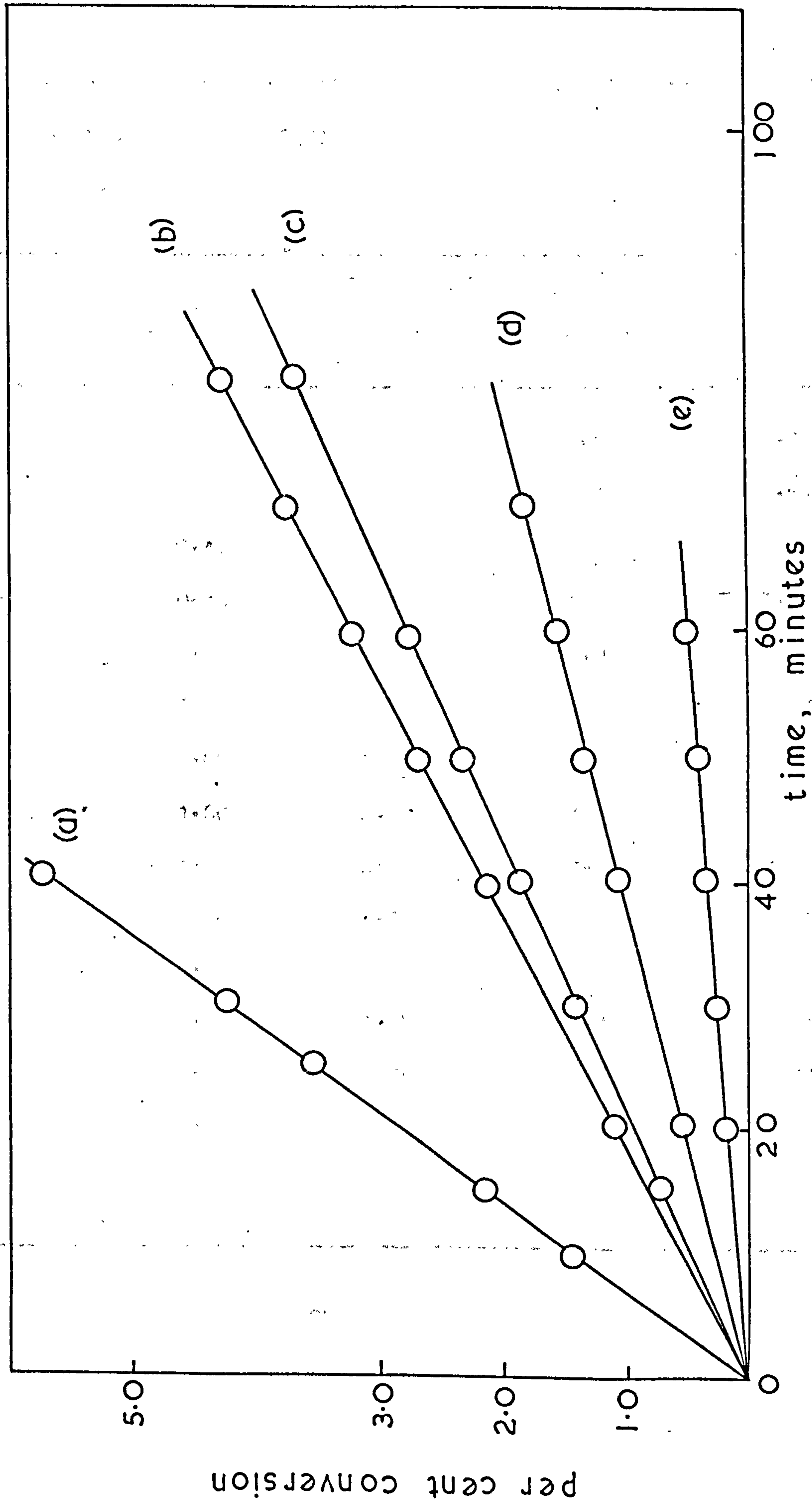


Fig 2-5. Plot of per cent conversion as a function of time for the polymerization of vinylferrocene in benzene in the presence of AIBN. (a) $[M]_0 = 4.0$, $[In]_0 = 0.4 \times 10^{-2}$, $T^\circ C = 78$; (b) $[M]_0 = 4.0$, $[In]_0 = 0.4 \times 10^{-2}$, $T^\circ C = 70$; (c) $[M]_0 = 4.0$, $[In]_0 = 2.0 \times 10^{-2}$, $T^\circ C = 60$; (d) $[M]_0 = 4.0$, $[In]_0 = 1.0 \times 10^{-2}$, $T^\circ C = 60$; (e) $[M]_0 = 4.0$, $[In]_0 = 0.4 \times 10^{-2}$, $T^\circ C = 60$; all concentrations in mol dm⁻³.

Table 2 - 4

Homopolymerization of Vinylferrocene in Benzene Initiated by AIBN.

All Reactions at $60 \pm 0.01^\circ \text{C}$ and Constant Monomer Concentration,

$$[M]_0 = 4.0 \text{ mol dm}^{-3}$$

reaction number	$[I_2]_0 \times 10^2$ mol dm ⁻³	$[In] \times 10^2$ mol dm ⁻³	per cent conversion	$R_p \times 10^5$ mol dm ⁻³ s ⁻¹	$\bar{M}_n$
20	0.1	0.098	0.1	0.07	
4	0.40	0.39	1.1	0.51	
12	0.40	0.39	1.2	0.55	5,900
18	0.40	0.39	0.6	0.54	
16	0.50	0.49	0.9	0.79	
10	1.00	0.97	1.6	1.51	
14	1.00	0.97	1.8	1.62	
15	1.00	0.97	1.8	1.61	5,600
22	1.00	0.97	1.8	1.71	
30	1.50	1.46	2.4	2.30	
6 ^a	1.69	1.64	2.1	1.07	
11	1.8	1.75	3.1	2.90	6,800
17	2.0	1.94	3.2	3.20	7,900
7	2.5	2.43	4.7	4.24	

^a 45 minutes inhibition

Table 2 - 5

Homopolymerization of Vinylferrocene in Benzene Initiated by AIBN. All Reactions at $60 \pm 0.01^\circ\text{C}$ and Constant Initiator Concentration, $[\text{In}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

reaction number	$[\text{M}]_0$ mol dm^{-3}	$[\bar{\text{M}}]$ mol dm^{-3}	per cent conversion	$R_p \times 10^5$ $\text{mol dm}^{-3} \text{s}^{-1}$	$\bar{M}_n$
38 ^a	1.0		3.9	0.81 ^a	
45	1.0	0.99	1.1	0.42	6,100
47 ^b	1.0		-	-	
49	1.0	0.99	1.3	0.38	
21 ^b	2.0		-	-	
24	2.0	1.98	1.6	0.78	2,700
23 ^c	3.0		4.9	3.61	
25	3.0	2.97	1.9	1.34	5,800
13	4.0	3.96	2.1	1.91	8,500
14	4.0	3.96	1.8	1.62	
22	4.0	3.96	1.8	1.71	6,300

a accelerated rate but no polymer obtained

b complete inhibition

c reacted at 70°C

Table 2 - 6

Homopolymerization of Vinylferrocene in Benzene Initiated by AIBN. All Reactions at Constant Monomer Concentration, $[\text{M}]_0 = 4.0 \text{ mol dm}^{-3}$ and Constant Initiator Concentration, $[\text{In}]_0 = 0.4 \times 10^{-2} \text{ mol dm}^{-3}$

reaction number	T $^\circ\text{C}$ ± 0.01	per cent conversion	$R_p \times 10^5$ $\text{mol dm}^{-3} \text{s}^{-1}$	$\bar{M}_n$
33 ^a	55	-	-	
34	60	1.0	0.58	-
27	70	4.3	3.35	3,400
29	75	3.5	5.87	6,900
28	78	5.8	9.54	6,600

a complete inhibition

The rates of polymerization were calculated as described in section 2.3.1. The reproducibility of the rates in replicate experiments was well within the limits of experimental errors in the majority of cases.

2.5.4 Dependence of Rate on Initiator Concentration.

The order of reaction with respect to the initiator concentration was obtained from the slope of a log-log plot of the initial rate of polymerization against the initiator concentration at constant monomer concentration and temperature. The initiator concentration is assumed to remain constant, at low conversions of monomer to polymer in order to derive kinetic expressions to describe the polymerization reaction. In practice however, a mean value of the initiator concentration is usually employed and is given by:

$$[\bar{\text{In}}] = [\bar{\text{In}}]_0 + [\text{In}]_t$$

where $[\text{In}]_0$ is the initial concentration and $[\text{In}]_t$ is the concentration after time t .

AIBN has been shown to decompose by strictly first-order kinetics in benzene.¹¹⁸

$$-d [\text{AIBN}] / dt = k_d [\text{AIBN}]$$

where $k_d = 1.13 \times 10^{-5} \text{ s}^{-1}$

Therefore the value of $[\text{In}]_t$ can be found by substitution into the integrated form of the rate equation. Values of the mean initiator concentrations are given in Table 2-4.

The log-log plot of initial rate of polymerization against $[\bar{\text{In}}]$ is shown in Fig. 2 - 6. The straight line obtained by the method of least squares had a slope of 1.11. The standard error of estimate from the least squares fit was 2.4 %. However, the experimental errors in

determining the rates of polymerization are more likely to be nearer 5 % .

The order of the polymerization reaction with respect to the initiator concentration is therefore between 1.05 and 1.16 with 95 % confidence limits.

Table 2-7 records values of the $[\overline{\text{In}}]^{1.1}$ and Fig. 2-7 shows a plot of these values against the rate of polymerization.

Table 2 - 7

Values of R_p and $[\overline{\text{In}}]^{1.1}$ for Homopolymerization of Vinylferrocene in Benzene at 60°C in the Presence of AIBN. $[M]_0 = 4.0 \text{ mol dm}^{-3}$ in all reactions.

reaction number	$[\overline{\text{In}}]^{1.1} \times 10^2$ mol dm^{-3}	$R_p \times 10^5$ $\text{mol dm}^{-3} \text{ s}^{-1}$
4	0.22	0.51
18	0.22	0.54
16	0.29	0.79
10	0.61	1.51
14	0.61	1.62
22	0.61	1.71
30	0.96	2.30
11	1.17	2.90
17	1.31	3.20
7	1.67	4.24

The straight line obtained from this plot supports the relationship between the initial rate of polymerization and the initiator concentration found by the log-log plot (Fig.2-6). The rate of polymerization of vinyl ferrocene is proportional to the initiator concentration to a power 1.1.

Thus, $R_p \propto [\overline{\text{In}}]^{1.1}$ for $[\overline{\text{In}}]^{1.1}$ between 0.39 and $2.43 \times 10^{-2} \text{ mol dm}^{-3}$.

2.5.5 Dependence of Rate on Monomer Concentration

The order of reaction with respect to the monomer concentration was obtained from the slope of a log-log plot of the initial rate of

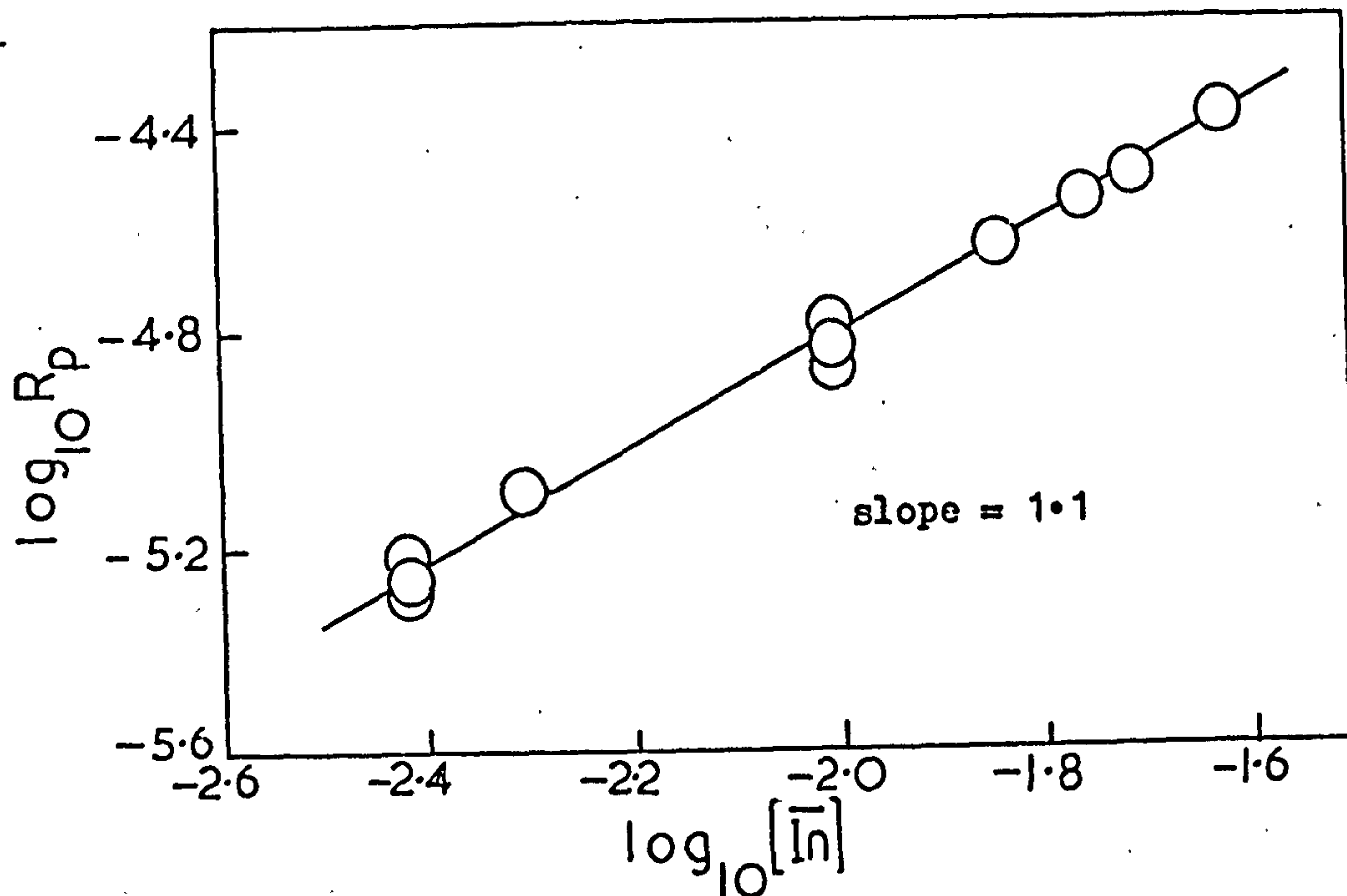


Fig. 2-6 Plot of $\log R_p$ as a function of $\log [\text{In}]$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN. $[M]_0 = 4.0 \text{ mol dm}^{-3}$ in all experiments.

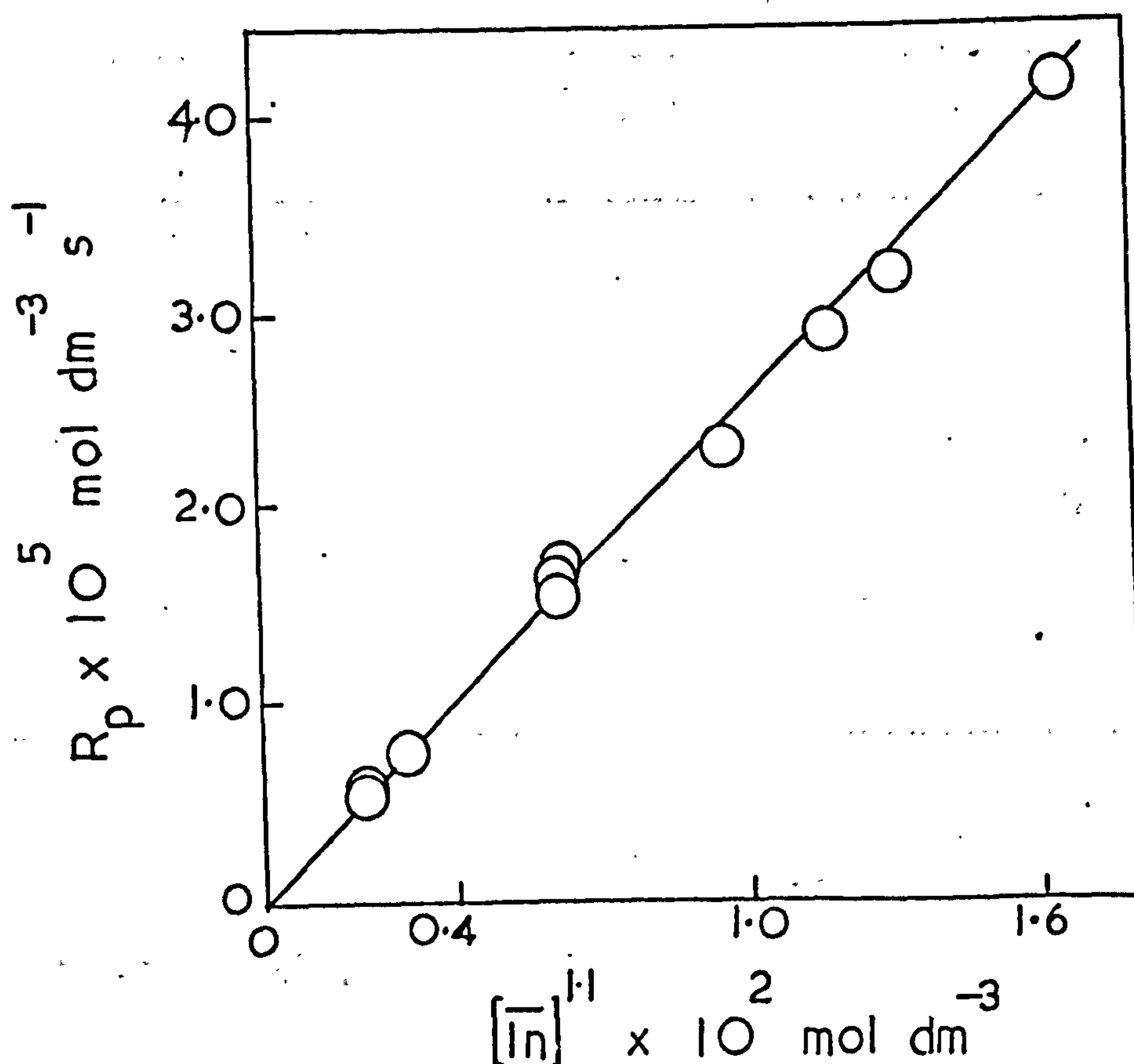


Fig. 2-7 Plot of R_p as a function of $[\text{In}]^{1.1}$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN. $[M]_0 = 4.0 \text{ mol dm}^{-3}$ in all experiments.

polymerization against the monomer concentration at constant initiator concentration and temperature. A mean value of the monomer concentration was used for this plot in accordance with normal practice.¹¹⁹ The mean monomer concentration is given by the following expression:-

$$[\bar{M}] = [M]_0 + [M]_f / 2, \text{ where } [M]_0 = \frac{\text{initial moles of monomer}}{\text{initial volume of solution at } 60^\circ\text{C}}$$

Values of $[\bar{M}]$ are recorded in Table 2-5. A log-log plot of the initial rate of polymerization against the mean monomer concentration is shown in Fig.2-8. The gradient of the straight line obtained using the method of least squares was found to be 1.12 ± 0.056 . Thus $R_p \propto [\bar{M}]^{1.1}$.

Values of $[\bar{M}]^{1.1}$ and R_p are given in Table 2-8 and these are plotted in Fig. 2-9.

Table 2 - 8

Values of R_p and $[\bar{M}]^{1.1}$ for Homopolymerization of Vinylferrocene in Benzene at 60°C . in the presence of AIBN. Constant $[\text{In}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

reaction number	$[\bar{M}]^{1.1} \text{ mol dm}^{-3}$	$R_p \times 10^5 \text{ mol dm}^{-3} \text{ s}^{-1}$
45	0.99	0.42
49	0.99	0.38
24	2.13	0.78
25	3.31	1.34
13	4.55	1.91
14	4.55	1.62
22	4.55	1.71

Thus, R_p is proportional to $[\bar{M}]^{1.1}$ for monomer concentrations between 1.0 and 4.0 mol dm^{-3} .

Therefore, the rate expression for the polymerization of vinylferrocene in benzene at 60°C initiated by AIBN has the following form

$$R_p = k' [\text{In}]^{1.1} [\bar{M}]^{1.1}$$

where k' is a constant

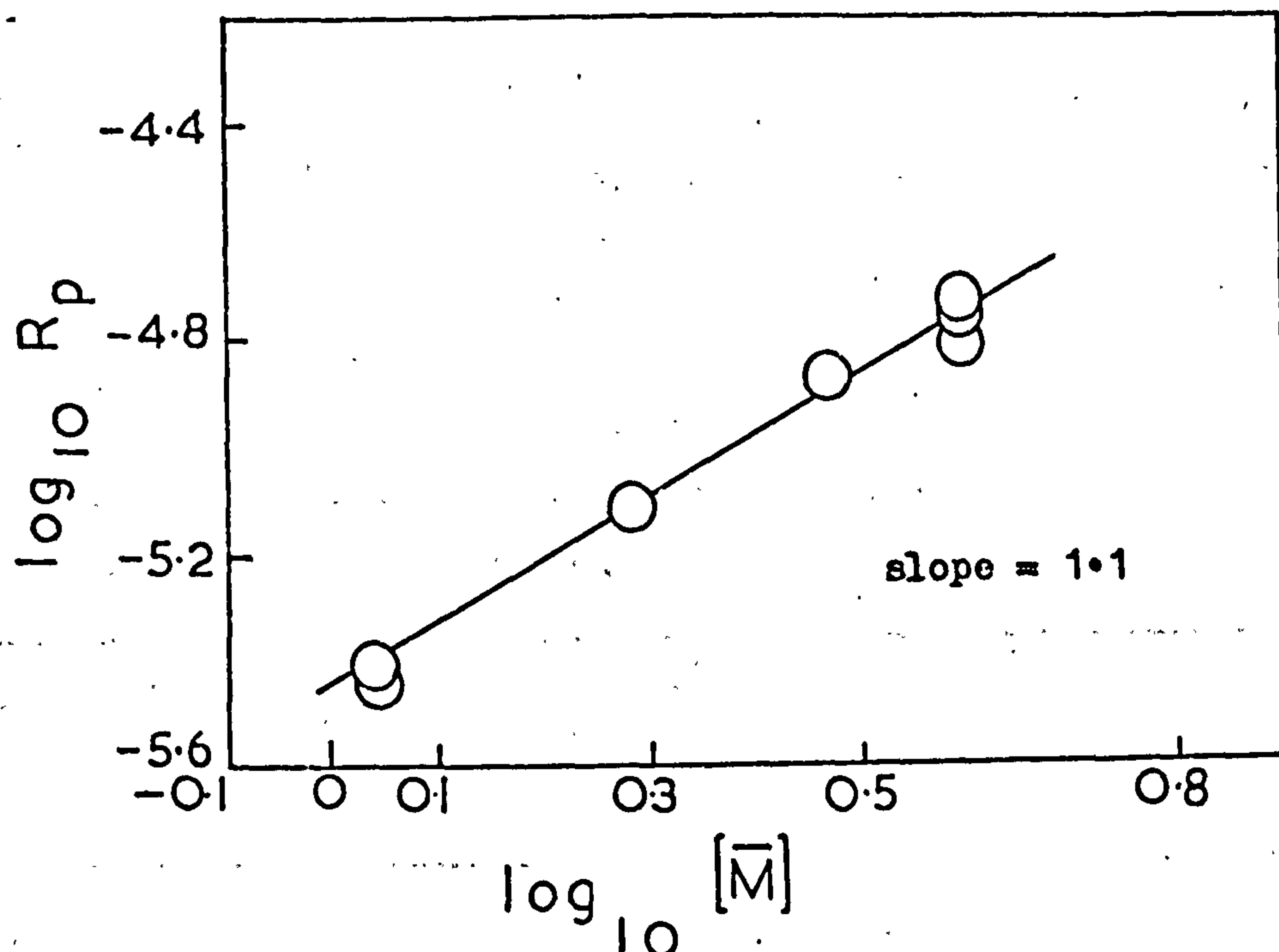


Fig. 2-8 Plot of $\log R_p$ as a function of $\log [M]$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN. $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ in all experiments.

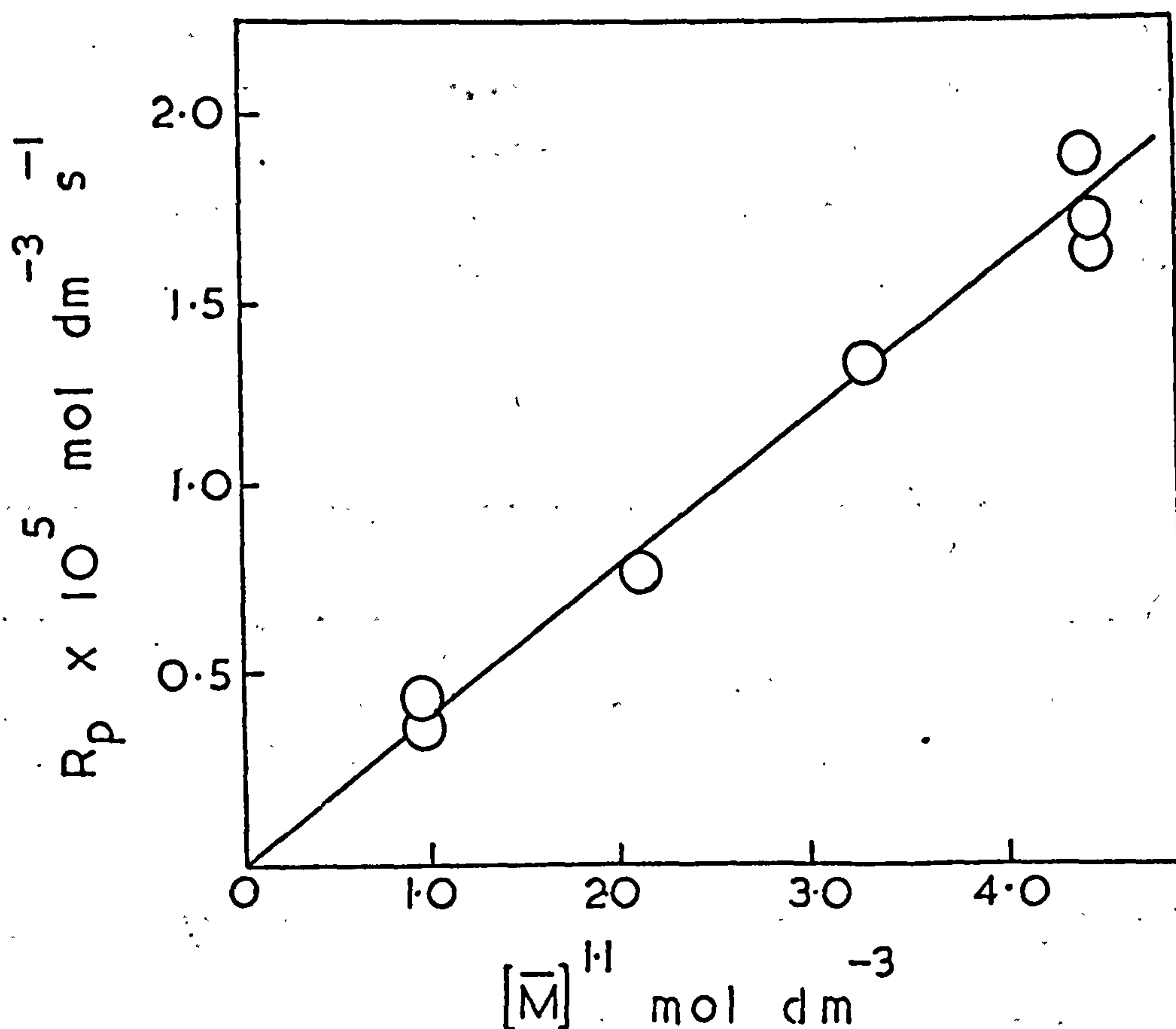


Fig. 2-9 Plot of R_p as a function of $[M]^{1.1}$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN. $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ in all experiments.

The value of the polymerization constant is given by

$k' = R_p / [\overline{\text{In}}]^{1.1} [\overline{\text{M}}]^{1.1}$. Table 2-9 records typical values of this constant.

Table 2 - 9

Values of the Polymerization Constant for Homopolymerization of Vinylferrocene in Benzene at 60°C in the presence of AIBN.

reaction number	$[\overline{\text{M}}]^{1.1}$ mol dm ⁻³	$[\overline{\text{In}}]^{1.1}$ mol dm ⁻³ 10^{-2}	$R_p \times 10^5$ mol dm ⁻³ s ⁻¹	$R_p \times 10^4$ $[\overline{\text{M}}]^{1.1} [\overline{\text{In}}]^{1.1}$
4	4.58	0.22	0.51	5.00
18	4.58	0.22	0.54	5.28
16	4.57	0.29	0.79	5.96
10	4.55	0.61	1.51	5.44
14	4.55	0.61	1.62	5.78
15	4.55	0.61	1.61	5.78
22	4.55	0.61	1.71	6.16
30	4.53	0.96	2.30	5.31
11	4.52	1.17	2.90	5.48
17	4.51	1.31	3.20	5.42
7	4.48	1.67	4.24	5.66
49	0.99	0.61	0.38	6.29
24	2.13	0.61	0.78	5.98
25	3.31	0.61	1.34	6.63

Table 2-9 shows that k is reasonably constant within experimental error. The average value is $k' = 5.6 \times 10^{-4}$ when R_p is expressed in mol dm⁻³ s⁻¹ and $[\overline{\text{M}}]$, $[\overline{\text{In}}]$ in mol dm⁻³.

2.5.6. Overall Activation Energy for the Polymerization of Vinylferrocene

The overall activation energy for the polymerization reaction was determined by examining the rates of reaction at different temperatures. The effect of temperature on reaction rates is most satisfactorily expressed by the Arrhenius equation; the integrated form of which,

$\ln k = -E/RT + \text{a constant}$, requires that a plot of the logarithm of the rate of reaction against reciprocal of the temperature is a straight line, when the slope will be equal to $-E/R$.

A plot of $\log_{10} R_p$ against $1/K$ for the polymerization of vinylferrocene is shown in Fig. 2-10. A linear relationship was obtained. The gradient ($-E/2.303 R$) of the line was determined by the method of least squares and the overall activation energy for the polymerization was calculated to be $139.0 \pm 3.0 \text{ kJ mol}^{-1}$. The experiments were conducted at a constant initial monomer concentration and initiator concentration. However, because the conversions of monomer to polymer varied between 0.9 and 5.8 % in these experiments, $[\bar{M}]$ and $[\bar{I}n]$ will vary slightly. The effect of this variation on the rate of polymerization can be neglected in comparison with the large effect of temperature on the rate.

2.5.7 Number Average Molecular Weights of Polyvinylferrocene Isolated at Low Conversions.

The number average molecular weights ($\bar{M}_n$) of the polymer samples isolated at low conversions were determined by vapour pressure osmometry in benzene solution at 37°C . Instead of measuring the difference in vapour pressure between a solution and pure solvent in order to determine the molecular weight, the osmometer employed measured the difference in temperature between a solvent and solution at the same vapour pressure. It is based on the principle advanced by Hill¹²⁰ in which droplets of a solution and pure solvent are placed on matched thermistors contained within a thermostatted chamber saturated with solvent vapour. Since the vapour pressure of the solution is lower than the solvent, the rates of evaporation are not equal, which results in a temperature difference. The temperature difference between the solvent and solution drops is

given by :

$$\Delta T = (RT^2x) / \Delta H$$

where ΔH = heat of vapourization of solvent (J mol^{-1})

R = gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$)

T = temperature (K)

x = mole fraction of solute

The thermistors form part of a conventional bridge circuit and the temperature difference is recorded as a change in resistance (ΔR). Following the normal procedure ¹⁰⁵ $\Delta R/c$ is plotted against concentration c and the number average molecular weight obtained from the following expression :

$$\bar{M}_n = K / (\Delta R/c)_0$$

where K is a calibration constant for the instrument and the solvent used and $(\Delta R/c)_0$ is the limiting value of $\Delta R/c$ at infinite dilution.

The method tends to be sensitive to operator technique, mainly due to the difficulty in placing droplets of solvent and solution of exactly the same size on to the thermistors. The instrument used in this study contains platinum rings which are fitted around the thermistors, acting as cups which retain precise amounts of solution and solvent. Since equal volumes are consistently placed on the thermistors, the precision of the instrument is assured and much of the operator error associated with the method is removed.

The instrument constant, K , was determined by measuring ΔR for solutions of benzil in benzene and plotting ΔR against c . The curve should be linear and pass through the origin when K will be given by the slope. The calibration curve is shown in Fig. 2-11, whilst

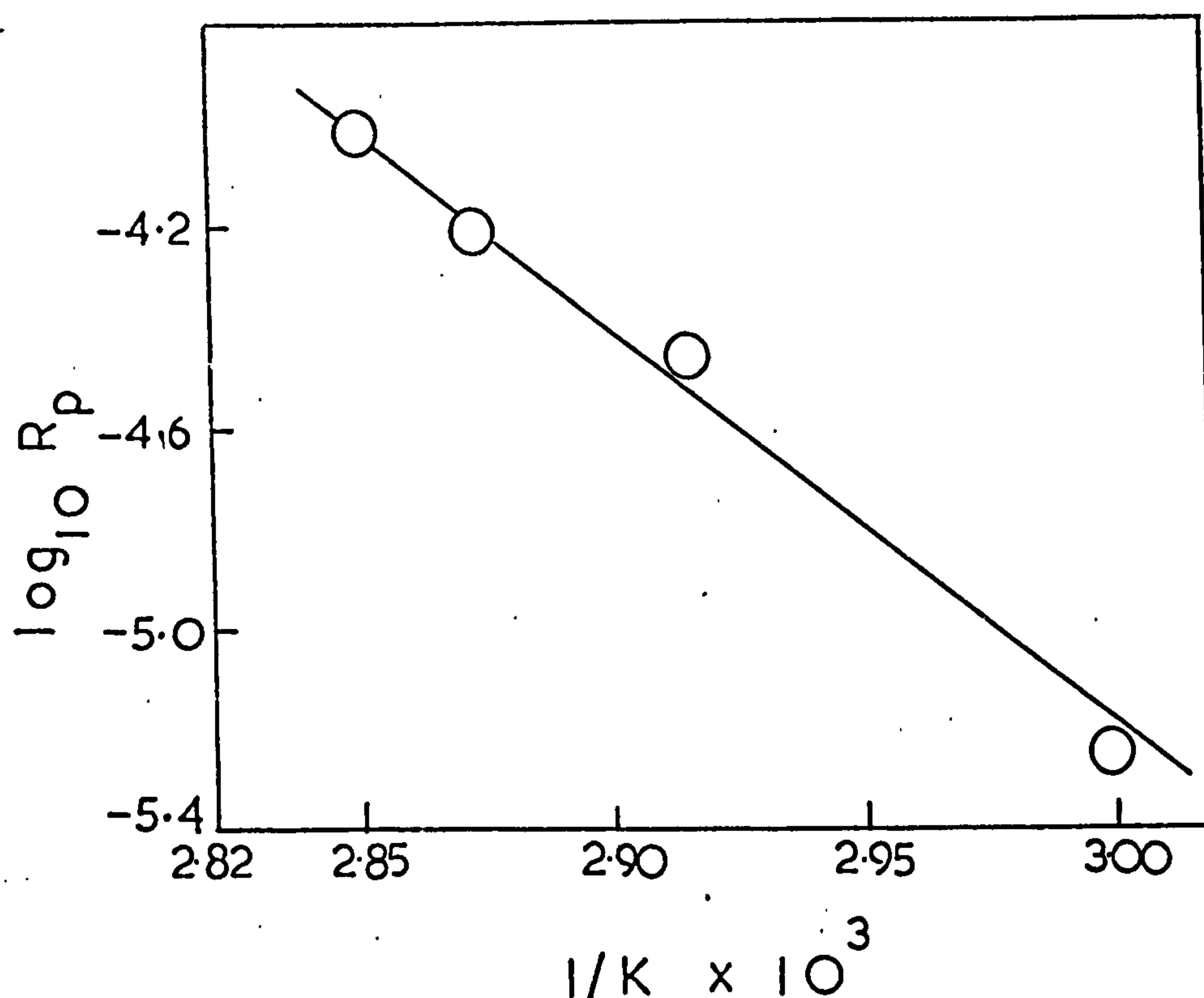


Fig. 2-10 Plot of $\log R_p$ as a function of $\log 1/K$ for the polymerization of vinylferrocene in benzene in the presence of AIBN. $[M]_0 = 4.0 \text{ mol dm}^{-3}$ and $[In]_0 = 0.4 \times 10^{-2} \text{ mol dm}^{-3}$ in all experiments.

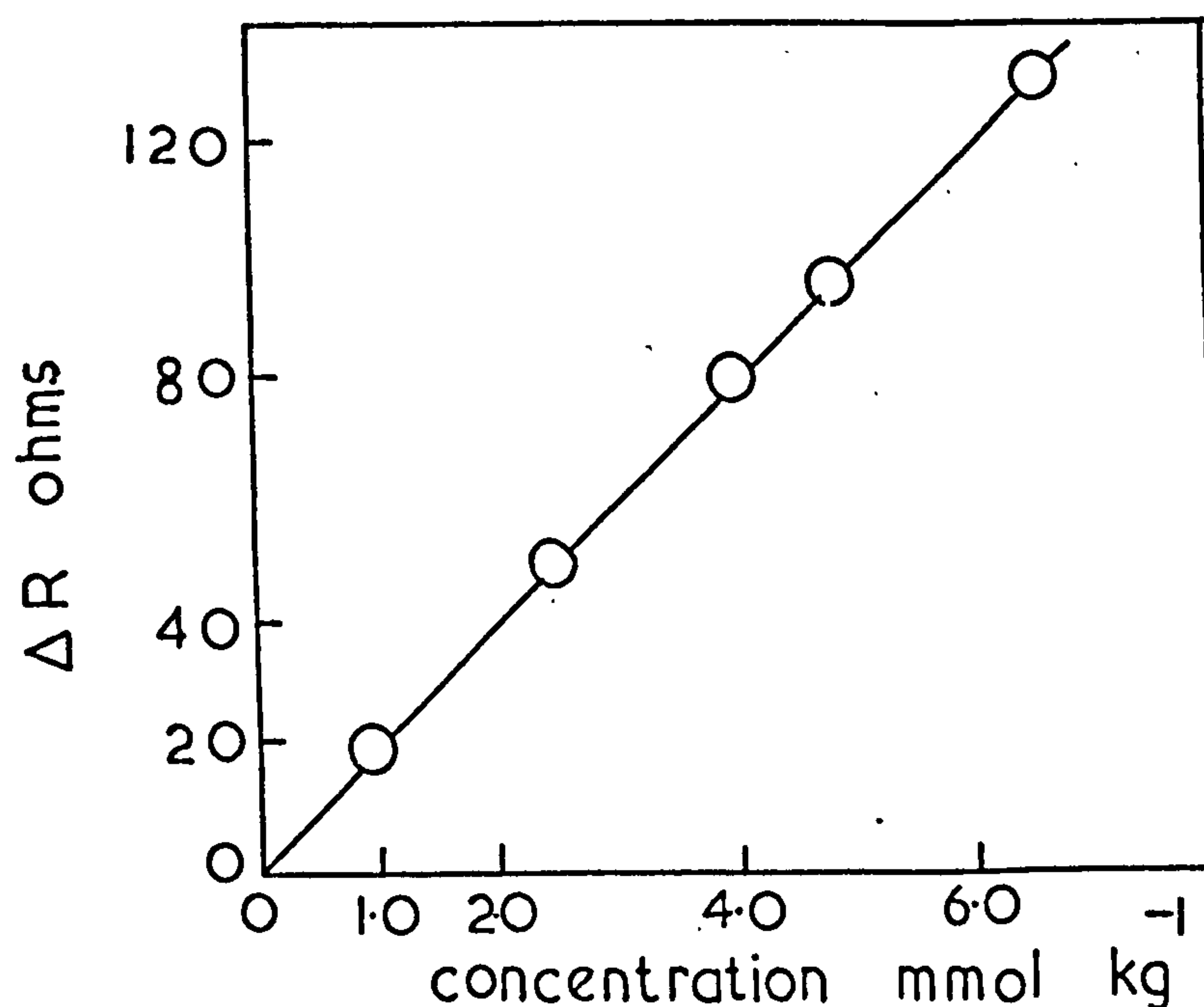


Fig.2-11 Plot of ΔR as a function of concentration for solutions of benzil in benzene at 37°C . Calibration curve for vapour pressure osmometer. Instrument constant, $K = 19,640$

typical plots of $\Delta R/c$ against c for polymer solutions is shown in Fig. 2 - 12. Straight line plots were obtained in all cases. The value of $(\Delta R/c)_0$ was found as the intercept of the line determined by the method of least squares. Fig. 2-12 shows that in some cases a negative slope was obtained. This result was reproducible and will be discussed later.

The accuracy of the number average molecular weights determined for polymers isolated from the dilatometric experiments was limited by the amount of sample available for the determinations. Approximately 4g of vinylferrocene were used in the polymerization experiments and since the conversions were in general below 2 %, most of the experiments produced ca 60 mg of polymer only.

2.6 DISCUSSION OF KINETIC RESULTS OF THE HOMOPOLYMERIZATION OF VINYLFERROCENE

The results reported in Section 2.5 for the kinetic experiments of the homopolymerization of vinylferrocene are unusual for vinyl monomers. The rate dependence on initiator concentration to a power greater than one is particularly unexpected since it suggests a monomolecular termination reaction. Before developing a kinetic scheme to explain the mechanism of the polymerization of vinylferrocene, it is worthwhile considering the kinetic scheme which describes vinyl polymerizations in general.

2.6.1 Simplified Scheme for Radical Polymerization of Vinyl Monomers

The polymerization of vinyl monomers by free radical initiation has been extensively studied and a number of excellent books on the subject are available.^{117,121 - 125} For the simplest kinetic scheme which describes vinyl polymerizations as a radical chain process, three reactions need only be considered; radical formation, radical addition to a double bond and radical destruction.

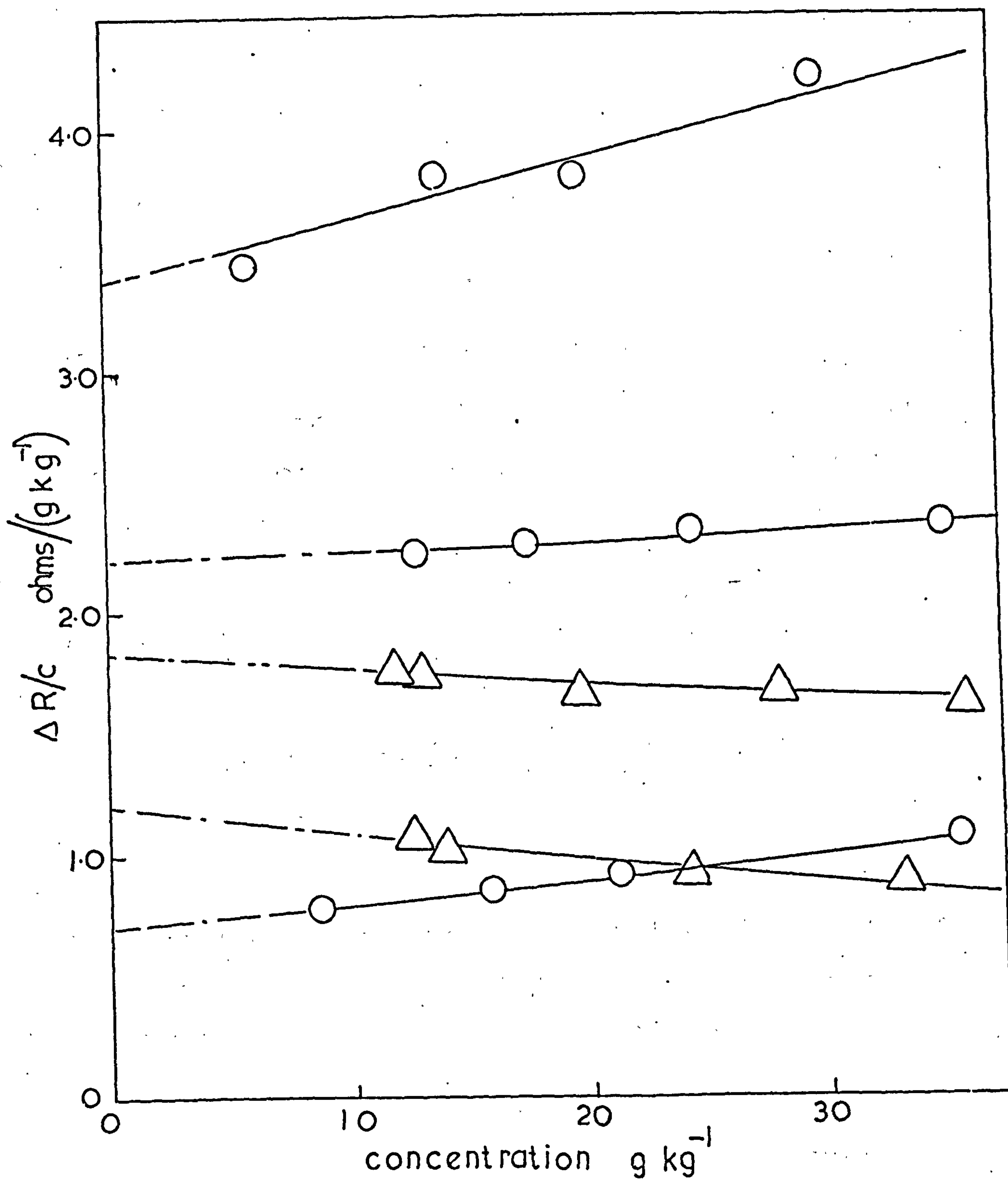
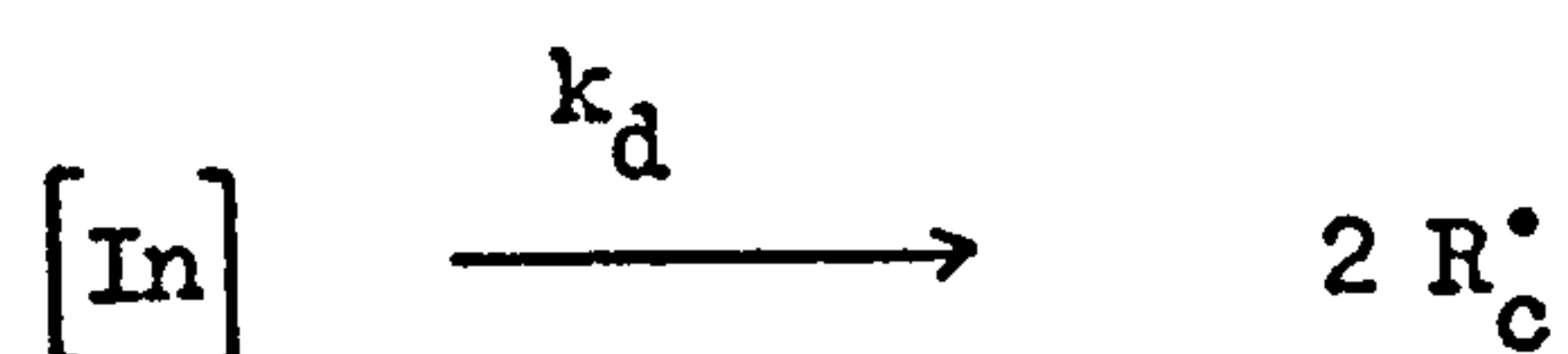
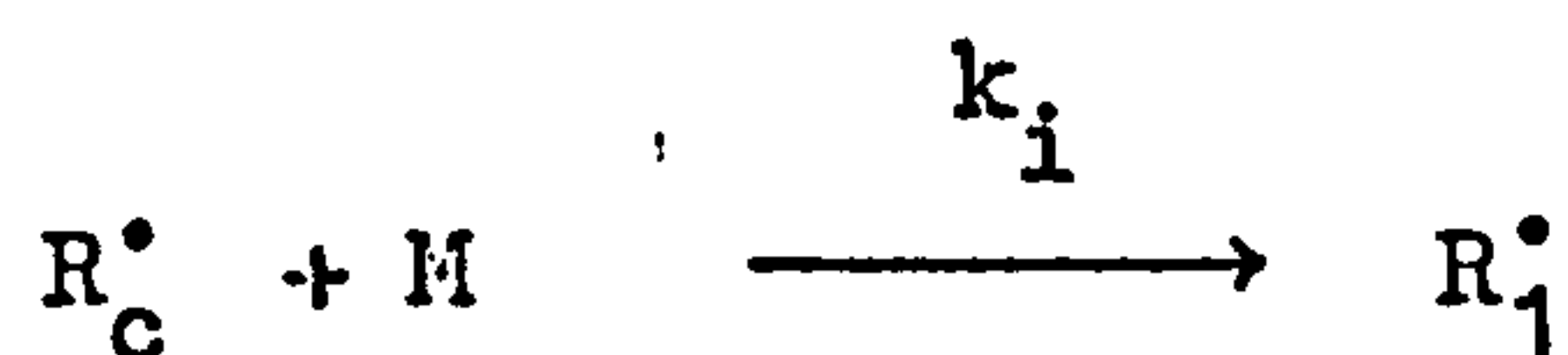


Fig. 2-12 Plots of $\Delta R/c$ as a function of concentration for solutions of polyvinylferrocene in benzene at 37°C showing negative slopes observed for some solutions.

Chain initiation is considered to involve two steps, the first being decomposition of an initiator to yield two primary radicals $R_c^\bullet$



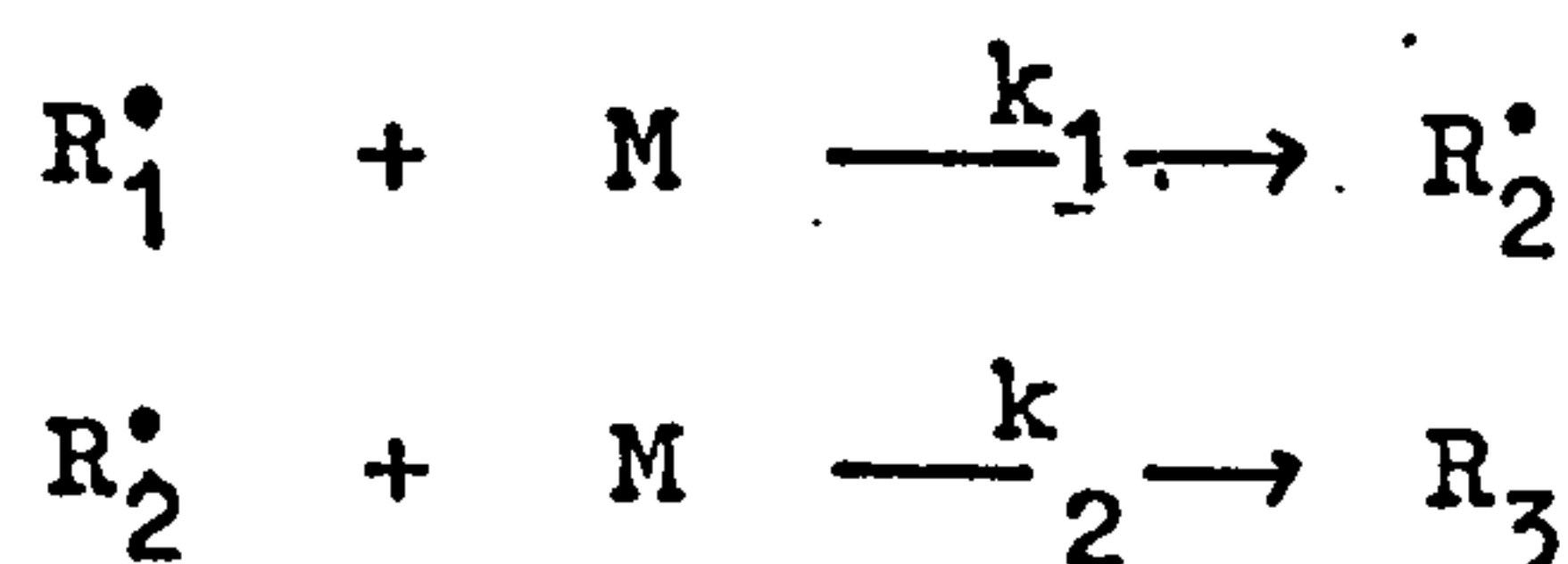
followed by the addition of a monomer molecule M to give a chain radical



The rate of initiation, R_i , is therefore = $2k_d f [In]$ (2.6.1)

where f represents the fraction of initiator fragments which are successful in initiating the polymerization process, $[In]$ is the concentration of initiator and k_d is its velocity constant for decomposition into primary radicals $R_c^\bullet$

The propagation step consists of successive additions of monomer molecules to radicals containing at least one monomer unit



Since the structure of the radical is the same after each propagation step, it can be assumed that only one type of radical is involved. In accordance with this assumption, the radical reactivity is assumed to be independent of the chain length and one velocity constant can be written for all the steps. In general,



The rate of monomer removal in the polymerizing system is given by

$$-d[M]/dt = k_i [R_c^\bullet] [M] + k_p [R^\bullet] [M] \quad (2.6.2)$$

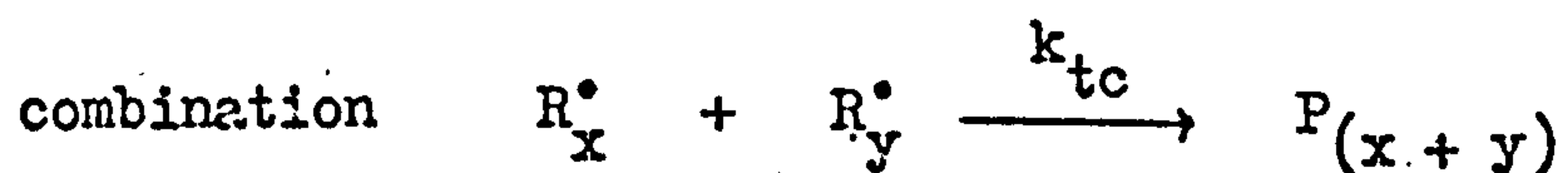
For any long chain process the amount of monomer consumed in the initiation step can be neglected in comparison with the amount used in the

propagation steps and therefore the rate of monomer removal is given by

$$-d[M]/dt = k_p [M] [R^\bullet] \quad (2.6.3)$$

$$\text{where } R^\bullet = \sum_{i=1}^{i=\infty} R_i^\bullet$$

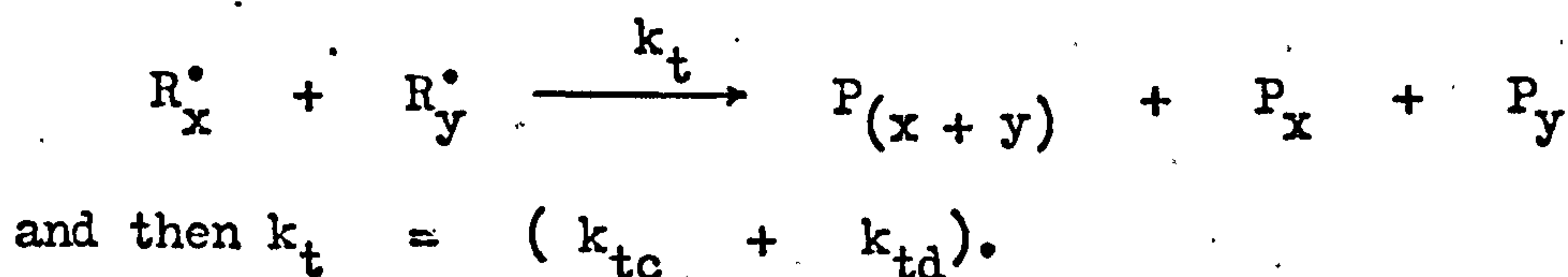
Termination almost always occurs by a bimolecular reaction between two chain radicals and can follow one of two processes.



and/or



The relative importance of termination by combination or disproportionation depends largely on the system. For the purpose of rate analysis the two are equivalent and the bimolecular nature of the reaction alone is important.¹¹⁷ It is usual to combine them as



The rate of termination is therefore $R_t = 2k_t [R^\bullet]^2 \quad (2.6.4)$

The time to form any one polymer molecule, and accordingly the lifetime of any radical, is short compared with the whole polymerization process. Since the initiation reaction is slow an equilibrium situation is attained when the rate of formation of radicals is exactly balanced by their rate of disappearance. Under these conditions the steady state assumption is applicable and therefore from equations (2.6.1) and (2.6.4)

$$[R^\bullet] = (k_d f [In] / k_t)^{0.5} \quad (2.6.5)$$

The rate of polymerization is defined as the rate of disappearance

of monomer, which, neglecting the amount removed in the initiation step, is given by equation (2.6.3). Substitution for $[R^\bullet]$ in this equation gives the rate of polymerization as

$$R_p = k_p [M] (k_d f [In] / k_t)^{0.5} \quad (2.6.6)$$

According to equation (2.6.6) R_p should vary with $[In]^{0.5}$, at constant $[M]$, and if f is effectively a constant, not varying with $[M]$, then the conversion of monomer to polymer will be first order in $[M]$ at constant $[In]$.

The predicted proportionality between R_p and $[In]^{0.5}$ at constant $[M]$ has been abundantly confirmed by experiment and emphasizes the almost universal nature of the termination step in vinyl polymerizations as one involving mutual reaction between two chain radicals.

Deviations from equation (2.6.6), due to various other reactions which have not been discussed here, are considered in detail elsewhere¹²¹⁻¹²⁵ but do not markedly affect the validity of the scheme.

The dependence of R_p on the monomer concentration is not as well defined as its dependence on $[In]^{0.5}$ and is often found to be to an order between 1 and 1.5, except possibly at low monomer concentrations. Reasons for this variation are discussed elsewhere¹²¹⁻¹²⁵.

One notable exception to the above kinetic scheme occurs with allylic monomers, where a first order dependence is found between R_p and $[In]$. This result has been shown^{126,127} to be due to an abstraction reaction which competes with the propagation step. The monomer is involved in both reactions and the abstraction is in effect equivalent to termination by an inhibitor, which in this case is the monomer itself. Since the same reactants are involved in the propagation step and the inhibition step, they are kinetically equivalent and the rate of polymerization is directly proportional to the initiator concentration.¹²³

2.6.2. Simplified Scheme for Radical Polymerization of Vinylferrocene

The experimental results obtained for the homopolymerization of vinylferrocene indicate that the rate of polymerization is expressed by an equation of the following form:-

$$R_p = k' [M]^{1.1} [In]^{1.1} \quad (2.6.7)$$

where k' is a constant

This expression is to be compared with equation (2.6.6) which is obtained for normal polymerizations.

A rate dependence upon both $[M]$ and $[In]$ to a power approximating to 1.0 can be explained by proposing :-

- (i) the termination step involves only one polymer chain radical.

The reaction is therefore monomolecular.

- (ii) the termination step does not involve another molecule such as monomer or solvent, but the chain radical destroys its own activity. The reaction is therefore intramolecular with respect to the chain radical.

- (iii) the products of the termination reaction are inactive and will not reinitiate further polymerization.

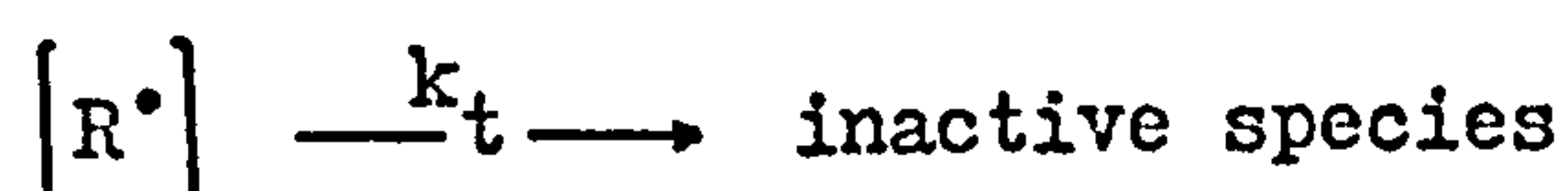
Initiation and propagation can be considered to proceed according to normal vinyl polymerization mechanisms. The rates of initiation and monomer removal are therefore given by equations (2.6.1) and (2.6.3) respectively

$$R_i = 2k_d f [In] \quad (2.6.1)$$

$$-d[M] / dt = k_p [M] [R^\bullet] \quad (2.6.3)$$

The termination reaction for the polymerization of vinylferrocene,

according to the above proposals, may be depicted as



and therefore the rate of termination is given by

$$R_t = k_t [R^\bullet] \quad (2.6.8)$$

Using the steady state approximation

$$R_i = R_t$$

and from equations (2.6.1) and (2.6.8)

$$[R^\bullet] = 2k_d f [In] / k_t \quad (2.6.9)$$

Substituting for $[R^\bullet]$ in equation (2.6.3) gives

$$-d[M] / dt = k_p [M] 2k_d f [In] / k_t \quad (2.6.10)$$

which for long chains is equated with the rate of polymerization, so that

$$R_p = (2k_p k_d f / k_t) [M] [In] \quad (2.6.11)$$

Thus, this kinetic scheme results in a rate expression which is first order in both $[M]$ and $[In]$.

The kinetic scheme implies that the growing polyvinylferrocene radical is deactivated by some reaction with a species in the same chain. Such a reaction does not appear to have been suggested previously for termination in addition polymerizations. Evidence will be discussed in later sections in support of this proposal. However, before proceeding to these discussions it is worthwhile examining some other aspects of the kinetic expressions which seem to apply to vinylferrocene.

2.6.3 Kinetic Scheme for Polymerizations Involving Short Chains.

In deriving the equations for the polymerization of vinylferrocene, it was assumed that the rate of polymerization could be equated with the rate of removal of monomer in the propagation step only.

This is a normal assumption for a long chain process in which the amount of monomer removed in the initiation step can be considered to be negligible compared with the amount consumed in the propagation step.

However, for vinylferrocene this assumption is not completely valid because the chain length is not very long. The number average molecular weights obtained for the polymer samples isolated from the kinetic experiments varied between 2,000 and 6,000. Since the molecular weight of vinylferrocene is 212, the average number of monomer units in the chain falls between 10 and 38.

If the chain length is short, the rate of polymerization cannot be equated with the consumption of monomer in the propagation step alone, and terms must be included to allow for the consumption of monomer in the initiation step and in transfer reactions if present. For the present discussion, transfer reactions will be ignored and the amount of monomer removed in the initiation only, included.

The rates of initiation and termination are given as before by equations (2.6.1) and (2.6.8), $R_i = 2 k_d f [\text{In}]$ and $R_t = k_t [R^\bullet]$ respectively.

The rate of propagation is given by equation (2.6.3) - $d[M] / dt = k_p [M] [R^*]$ and substituting for $[R^*]$ as before gives

$$-d[M] / dt = k_p [M] 2k_d f [In] / k_t \quad (2.6.10)$$

For short chains, the rate of monomer removal is equal to the consumption of monomer in the propagating step and in the initiation step also, and therefore

$$-d[M] / dt = k_p [M] 2k_d f [In] / k_t + R_i \quad (2.6.12)$$

and hence $R_p = -d[M] / dt = k_p [M] 2k_d f [In] / k_t + R_i \quad (2.6.13)$

which by substitution for R_i and rearrangement gives

$$R_p = 2k_d f [In] (1 + k_p [M] / k_t) \quad (2.6.14)$$

which is the rate expression for the polymerization of vinylferrocene allowing for the influence of small chains. However, R_p was found by experiment to be essentially proportional to $[In]$ at constant $[M]$ and $[M]$ at constant $[In]$. Therefore, $k_p [M] / k_t$ must be much larger than one for the values of $[M]$ examined.

Neglecting one in equation (2.6.14) gives equation (2.6.11) from which it is possible to estimate a value of k_t for this kinetic scheme.

Using an average value of k_p in vinyl polymerizations as approximately $200 \text{ mol dm}^3 \text{ s}^{-1}$, $[M]_0 = 4.0 \text{ mol dm}^{-3}$ and, from the data of Blackley and Melville¹¹⁸, $2k_d f [In]$ is approximately equal to $1.6 \times 10^{-7} \text{ mol dm}^{-3}$, suggests that k_t is less than 100 s^{-1} . This is not unreasonable, since in this system k_t is a first order rate constant.

2.6.4 Degree of Polymerization of Polyvinylferrocene

The average degree of polymerization ($\overline{DP}$) of polyvinylferrocene isolated at low conversions was found to be relatively low in comparison to other vinyl polymers. These results are in accord with the work of Baldwin and Johnson ³⁰, Aso et al ³¹ and Pittman et al ^{33,34}. (Pittman ³⁶ has obtained PVF with $\overline{DP} \approx 1,800$ but these were obtained at high conversions and high initiator concentrations. These results will be discussed later).

Since the relationship between R_p and $[In]$ for vinylferrocene polymerization is unusual for vinyl polymers, it might be expected that the equations governing $\overline{DP}$ might also be unusual.

2.6.4.1 $\overline{DP}$ of PVF Allowing for Short Chains but Ignoring Transfer Reactions

The instantaneous degree of polymerization is defined as the rate of monomer disappearance divided by the rate of polymer formation

$$\overline{DP} = (-d[M]/dt) / (d[P]/dt) \quad (2.6.15)$$

To a first approximation the rate of polymer formation in vinylferrocene polymerization is equal to the rate of termination, providing that transfer to monomer and solvent are negligibly small, and therefore from equations (2.6.8) and (2.6.12)

$$\overline{DP} = \left\{ (k_p [M] 2k_d f [In] / k_t) + R_i \right\} / k_t [R^\bullet] \quad (2.6.16)$$

which by substitution for R_i and $[R^\bullet]$ gives

$$\overline{DP} = \frac{2k_d f [In] (1 + k_p [M] / k_t)}{k_t (2k_d f [In] / k_t)} \quad (2.6.17)$$

which re-arranges to $\overline{DP} = 1 + k_p [M] / kt.$ (2.6.17.)

Thus a plot of $\overline{DP}$ against $[M]$ should give a straight line of slope k_p/k_t and an intercept of 1.0 if the assumption that transfer reactions can be neglected is correct.

Values of $\overline{DP}$ are given in Table 2-10. The polymer samples used to obtain these results were isolated from gravimetric experiments. These reactions were taken to higher conversions than the dilatometric experiments. Thus, sufficient sample was obtained for accurate determination of $\overline{M}_n$.

Table 2 - 10

Degree of Polymerization of Polyvinylferrocene Prepared at 60°C in Benzene in the Presence of AIBN. $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$. Samples isolated from gravimetric experiments.

$[M]_0$ mol dm ⁻³	conversion %	$[M]$ mol dm ⁻³	$\overline{DP}$
1.0	15	0.925	23.6
1.0	10	0.95	17.2
2.0	10	1.9	41.5
3.0	7	2.895	52.3
3.0	4	2.94	50.1
3.0	9	2.865	49.4
4.0	7	3.86	60.6
4.0	4	3.92	54.0
5.9 *	20	5.31	57.4

* benzene - insoluble polymer was also obtained.

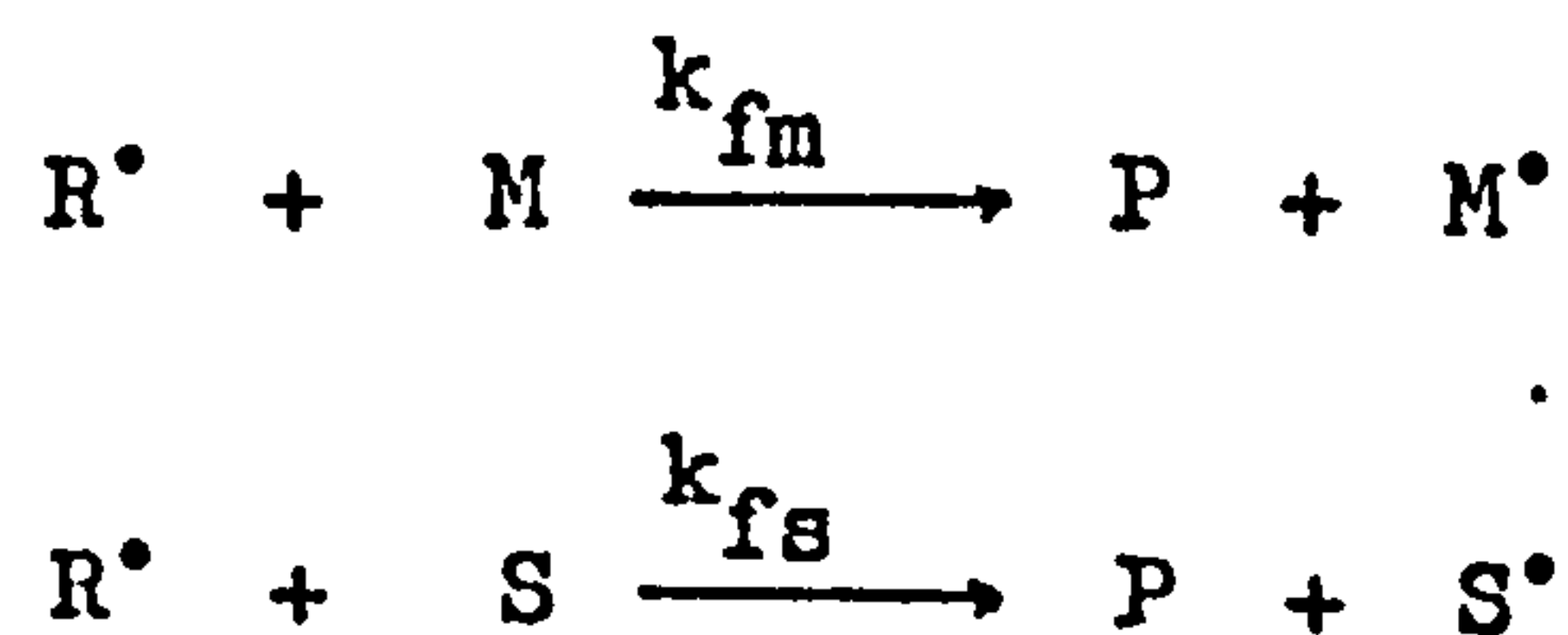
However, when the results in Fig. 2-10 were plotted, a straight line was not obtained. This result suggests that equation(2.6.17) is an oversimplification and that transfer reactions cannot be ignored.

The most notable feature about equation (2.6.17) is that it suggests that the $\overline{DP}$'s obtained in any given experiment are dependent upon the monomer concentration only and independent of the initiator concentration, $[In]$. Such a relationship is not found in normal vinyl polymerizations where $\overline{DP}$ is inversely proportional to $[In]$ at constant $[M]$ and T . The relationship implied in equation (2.6.17) between $\overline{DP}$ and $[M]$ for polyvinylferrocene is supported by the results of Chen and Cassidy²⁷ who polymerized vinylferrocene in bulk and obtained a high $\overline{DP}$ even in the presence of a relatively high AIBN concentration. Pittman et al have also found that the molecular weight of PVF is not increased upon reducing the initiator concentration.³⁶

2.6.4.2 $\overline{DP}$ of PVF Allowing for Short Chains and Transfer Reactions

In the majority of vinyl polymerizations, polymer is obtained in other reactions as well as the termination step. Thus the rate of polymer formation must include polymer formed by transfer to monomer and solvent. Transfer to polymer may be neglected for the present, since at low conversions the amount of polymer present is relatively small.

Using the normal notations



where k_{fm} and k_{fs} are the rate constants for transfer to monomer and solvent respectively and $R^{\bullet}$, M , S and P have the usual significance.

Therefore, from equation (2.6.15), assuming that $M^{\bullet}$ and $S^{\bullet}$ radicals have a reactivity similar to $R^{\bullet}$ and attack monomer molecules M , rather than becoming involved in termination steps

$$\overline{DP} = \frac{k_p [M] [R^\bullet] + R_i}{k_t [R^\bullet] + k_{fm} [M] [R^\bullet] + k_{fs} [S] [R^\bullet]} \quad (2.6.18)$$

which by substitution for $[R^\bullet]$ and R_i gives

$$\overline{DP} = \frac{2k_d f [In] \left\{ 1 + (k_p [M] / k_t) \right\}}{\frac{2k_d f [In]}{k_t} \left\{ k_t + k_{fm} [M] + k_{fs} [S] \right\}}$$

or

$$\overline{DP} = \frac{k_t \left\{ 1 + (k_p [M] / k_t) \right\}}{k_t + k_{fm} [M] + k_{fs} [S]} \quad (2.6.19)$$

Equation (2.6.19) describes the factors governing the average degree of polymerization of PVF allowing for the effects of small chains and transfer to monomer and solvent. It is still evident that $\overline{DP}$ of polyvinylferrocene is independent of the initiator concentration and hence the rate of polymerization. This equation is somewhat intractable in this form. However, if the effect of small chains is neglected, which is reasonable since $k_p [M] / k_t \gg 1$ for $[M]_0 > 1.0 \text{ mol dm}^{-3}$, then the average degree of polymerization can be expressed as

$$\overline{DP} = k_p [M] / \left\{ (k_t + k_{fm} [M] + k_{fs} [S]) \right\} \quad (2.6.20)$$

from which

$$1/\overline{DP} = \left(k_t / k_p [M] \right) + \left(k_{fm} / k_p \right) + \left(k_{fs} [S] / k_p [M] \right) \quad (2.6.21)$$

Equation (2.6.21) can be written in the usual manner as

$$1/\overline{DP} = \left(k_t/k_p [M] \right) + C_m + \left(C_s [S]/[M] \right) \quad (2.6.22)$$

where C_m is the transfer constant to monomer defined as k_{tm}/k_p , and C_s is k_{fs}/k_p .

Rearranging the right hand side of equation (2.6.22) gives

$$1/\overline{DP} = 1/[M] \left\{ (k_t/k_p) + C_s [S] \right\} + C_m \quad (2.6.23)$$

and therefore a plot of the inverse degree of polymerization against the reciprocal of the monomer concentration should give a straight line with slope equal to $\left\{ k_t/k_p + C_s [S] \right\}$. (if $C_s \approx 0$) and intercept equal to C_m , the transfer constant to monomer.

Table 2-11 records values of $\overline{DP}$ for polymers prepared at constant initiator concentration and temperature but with different monomer concentrations. The polymers were isolated from gravimetric experiments to high conversion to give sufficient quantity for molecular weight measurements.

Table 2 - 11

$\overline{DP}$ of Polyvinylferrocene Prepared at 60°C in Benzene in the Presence of AIBN.

$[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$. Samples Isolated from Gravimetric Experiments.

$[M]_0$ mol dm ⁻³	conversion per cent	$[M]$ mol dm ⁻³	$\overline{DP}$	$1/[M]$ dm ³ mol ⁻¹	$1/\overline{DP}$
1.0	15	0.925	23.6	1.08	0.042
2.0	10	1.90	41.5	0.526	0.024
3.0	7	2.895	52.3	0.345	0.019
3.0	9	2.865	49.4	0.349	0.020
4.0	7	3.86	60.6	0.259	0.016
4.0	4	3.92	54.0	0.255	0.0185

$1/\overline{DP}$ is plotted against $1/[\overline{M}]$ in Fig. 2-13. A least-squares fit of the data gave a straight line with slope = $0.031 \text{ mol dm}^{-3}$ and intercept = 8.3×10^{-3} .

A value of $C_m = 8.3 \times 10^{-3}$ suggests that transfer to monomer in the polymerization of vinylferrocene is an important reaction. For comparison C_m for styrene is only 0.06×10^{-3} at 60°C .¹²⁸, whilst C_m for vinyl acetate is 2.0×10^{-3} at 60°C .¹²⁹ Since the amount of transfer to monomer increases with radical reactivity, the high value for vinylferrocene suggests its radical is very reactive. The present study has shown that the polymerization of vinylferrocene is readily inhibited which supports the concept of a highly reactive vinylferrocene radical.

The intercept in Fig. 2-13 is very dependent upon the values of $\overline{DP}$ obtained when $[M]_0 = 1.0 \text{ mol dm}^{-3}$. Therefore errors in these values will have a more marked effect on C_m than errors in $\overline{DP}$ when $[M]_0 = 4.0 \text{ mol dm}^{-3}$. A significant factor which can cause errors in the experimentally determined values of $\overline{DP}$ is loss of soluble low molecular weight polymer during the isolation procedure.^{130,131} Any such loss will result in the recorded value of $\overline{DP}$ being higher than the true value. Obviously, the relative difference between the recorded value and true value will be greater as the degree of polymerization decreases. In the present study loss of low molecular weight polymer cannot be precluded and therefore the value of C_m obtained from the intercept in Fig. 2-13 can only be approximate.

The slope of the plot of $1/\overline{DP}$ against $1/[\overline{M}]$ is equal to $(k_t/k_p + C_s[S])$. If transfer to solvent is negligible then the slope is simply equal to the ratio of the termination constant to propagation constant. An estimate of this ratio may be obtained from the rate results in Table 2-9 where values of $R_p/[M]^{1.1}[In]^{1.1}$ are recorded.

This parameter is equal to the overall polymerization constant k'

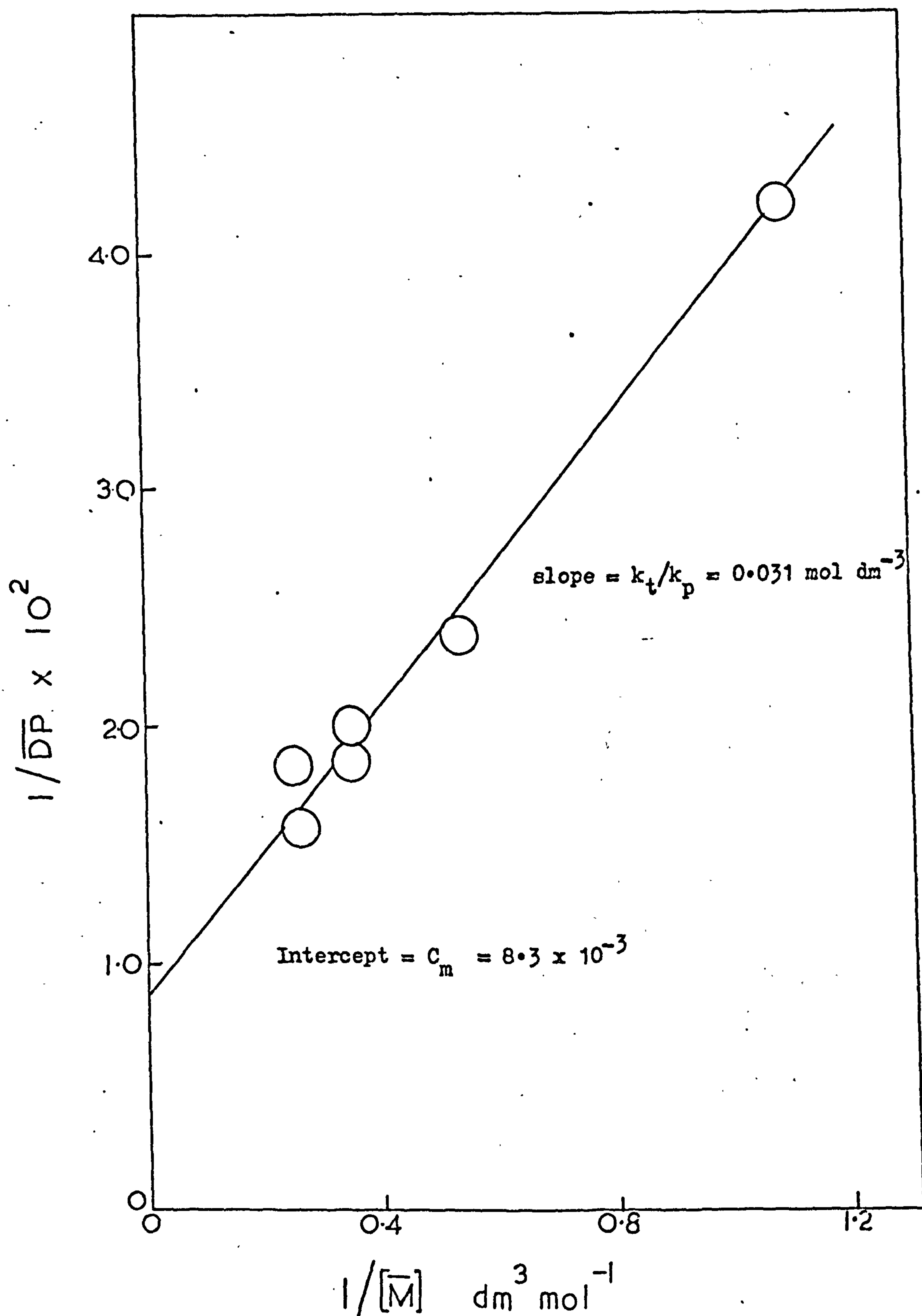


Fig. 2-13 Plot of $1/\overline{DP}$ as a function of $1/[\overline{M}]$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN, $[\text{In}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ in all experiments.

which is a composite constant equal to $2 k_d f k_p / k_t$ for vinylferrocene. The average value for k' was found to be $5.6 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and hence

$$k_p / k_t = 5.6 \times 10^{-4} / 2 k_d f \text{ dm}^3 \text{ mol}^{-1} \quad (2.6.24)$$

$k_d = 1.13 \times 10^{-5}$ and although the efficiency, f , of AIBN with vinylferrocene is not known, a reasonable estimate is 0.75

Therefore from (2.6.24) $k_p / k_t = 33.04 \text{ dm}^3 \text{ mol}^{-1}$

and $k_t / k_p = 0.03 \text{ mol dm}^{-3}$

Thus, this value for k_t / k_p calculated from the rate results is in reasonable agreement with the value obtained from the plot of $1 / \overline{DP}$ against $1 / [\overline{M}]$. The agreement in these results supports the accuracy of the kinetic experiments.

The good correlation between the ratio of the termination constant and the propagation constant found by the plot of $1 / \overline{DP}$ against $1 / [\overline{M}]$ also suggests that $C_s [S] = 0$ and that transfer to solvent is negligibly small.

Equation (2.6.23) can be rearranged by multiplying through by $[M]$ to give

$$[M] / \overline{DP} = k_t / k_p + C_s [S] + C_m [M] \quad (2.6.25)$$

If C_s is negligible then according to equation (2.6.25) a plot of $[M] / \overline{DP}$ against $[M]$ should give a straight line with C_m as the slope and k_t / k_p as the intercept. Values for $[\overline{M}] / \overline{DP}$ and $[\overline{M}]$ were calculated from the data in Table 2-11 and the plot of $[\overline{M}] / \overline{DP}$ is shown in Fig. 2-14

The slope of the straight line obtained by the method of least-squares was found to be 8.2×10^{-3} whilst the intercept was 0.033. Thus the values for C_m and k_t/k_p are in good agreement with those obtained from the previous plot of $1/\overline{DP}$ against $[\overline{M}]^{-1}$.

Both the plots have assumed that $C_s [S]$ is negligible, which appears to be a reasonable conclusion. This assumption can be tested by rearranging equation (2.6.25) to give

$$[\overline{M}] (1/\overline{DP} - C_m) = k_t/k_p + C_s [S] \quad (2.6.26)$$

Therefore, a plot of $[\overline{M}] (1/\overline{DP} - C_m)$ against $[S]$ should give a zero slope if the transfer constant to solvent is negligible. Values for $[\overline{M}]$, $[S]$ and $\overline{DP}$ are recorded in Table 2-12 and the left hand side of equation (2.6.26) is plotted against $[S]$ in Fig. 2-15. Within experimental error a zero slope was obtained.

Table 2 - 12

$\overline{DP}$ of Polyvinylferrocene Prepared at 60°C in Benzene in the Presence of AIEN
 $[\text{In}]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$. $C_m = 8.5 \times 10^{-3}$. Samples Isolated from Gravimetric Experiments.

$[\overline{M}]$ mol dm^{-3}	$[S]$ mol dm^{-3}	$\overline{DP}$	$[\overline{M}] (1/\overline{DP} - C_m)$ mol dm^{-3}
0.925	9.34	23.6	0.031
1.90	7.45	41.5	0.029
2.895	5.56	52.3	0.030
2.94	5.56	50.1	0.031
3.86	1.83	60.6	0.029

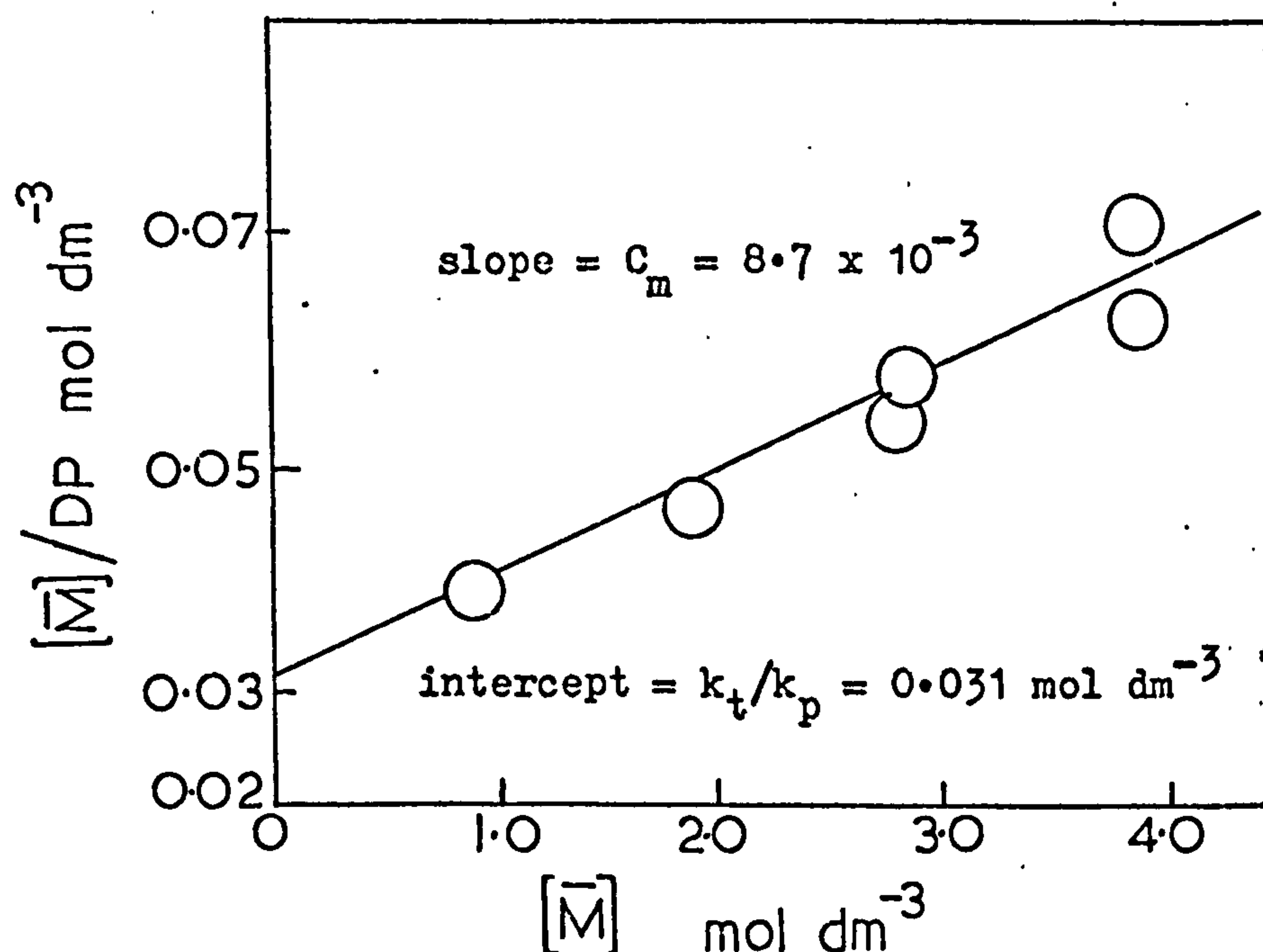


Fig.2-14 Plot of $[M]/\overline{DP}$ as a function of $[M]$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN. $[In]_0 = 1.0 \times 10^{-2}$ mol dm⁻³ in all experiments.

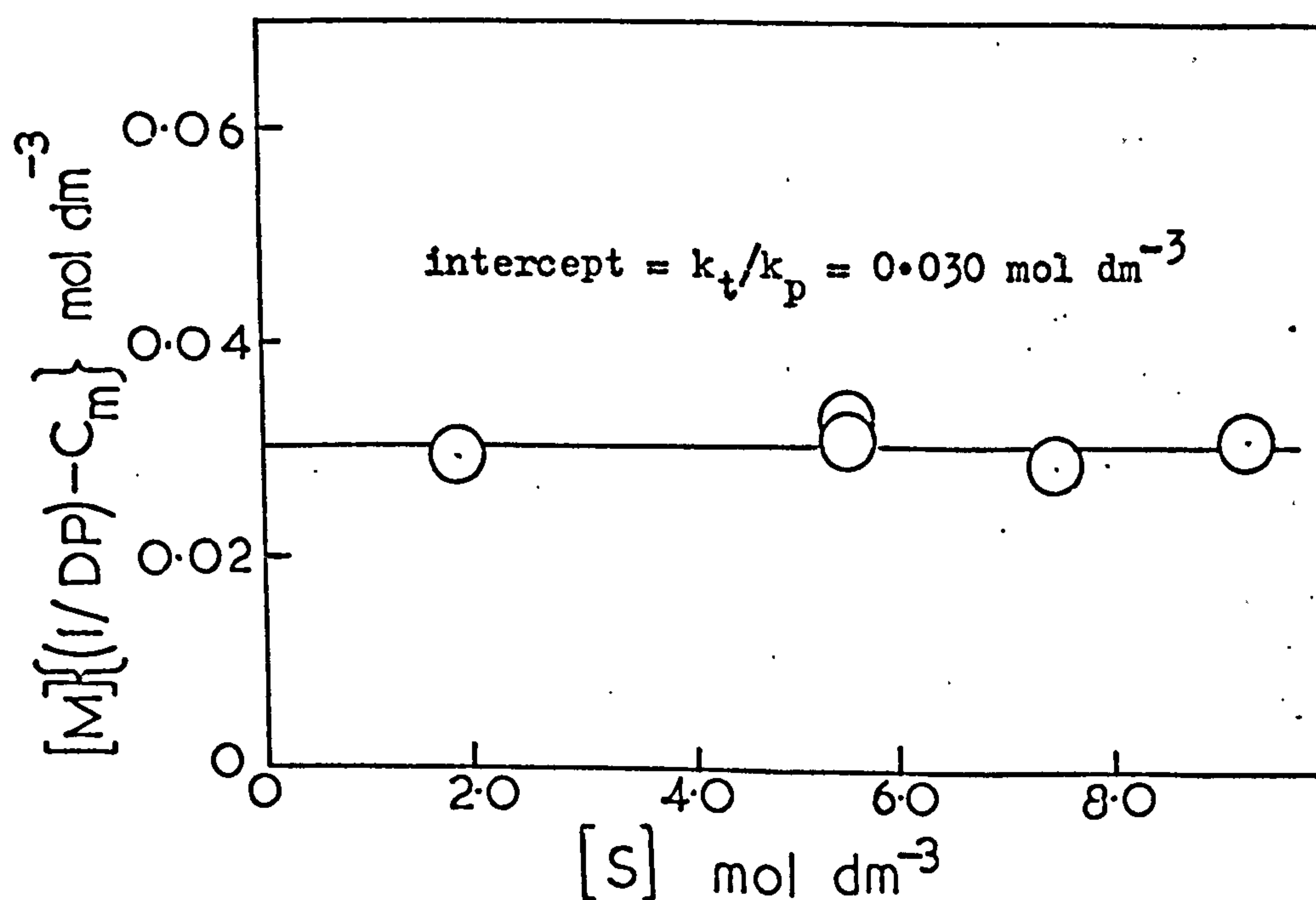


Fig. 2-15 $[M]\{1/\overline{DP} - C_m\}$ as a function of $[S]$ for the polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN $[In]_0 = 1.0 \times 10^{-2}$ mol dm⁻³ in all experiments.

The zero slope supports the assumption that transfer to solvent is negligible. The intercept gives k_t/k_p , in this case equal to 0.030, which is again in good agreement with the result from the previous plots.

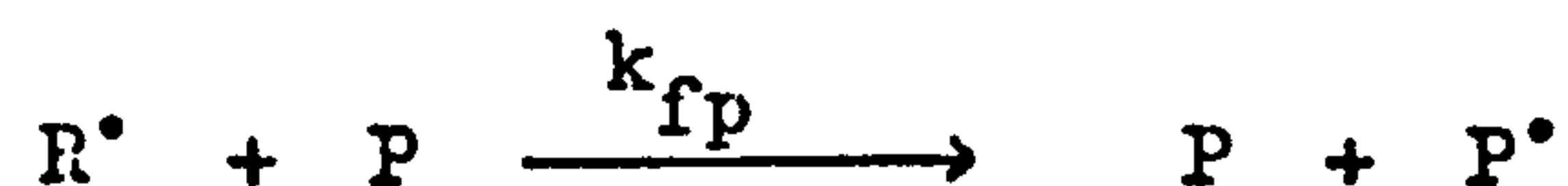
The preceding discussion indicates that the transfer to monomer cannot be ignored in the polymerization of vinylferrocene. The high transfer constant $C_m = 8.5 \times 10^{-3}$ suggests that transfer to monomer determines the polymer molecular weight. Thus, like poly(vinylacetate), the molecular weight of polyvinylferrocene remains practically constant over a wide range of polymerization rates. Analogies with other vinyl monomers can be misleading, however, since equation (2.6.19) indicates that the molecular weight should be independent of the rate of initiation. Chain transfer to monomer will of course explain the low molecular weights which have been obtained previously for polyvinylferrocene.³¹⁻³⁵

The value of the transfer constant determined from the plots of $1/\overline{DP}$ against $[\overline{M}]^{-1}$ and $[\overline{M}] / \overline{DP}$ against $[\overline{M}]$ may be high due to errors in $\overline{DP}$. The experimental values of $\overline{DP}$ have not been corrected to allow for loss of low molecular weight material during the isolation procedure. Thus the experimental values may be high, particularly at low degrees of polymerization. Also, the determination of $\overline{DP}$ for polyvinylferrocene is hindered by the presence of benzene-insoluble polymer in some cases as well as association phenomena in others. However, the good agreement between the plots of $\overline{DP}$ and $[\overline{M}]$ and the rate expressions suggest that the value of C_m is in the order of 5 to 8×10^{-3} . This value is still considerably higher than the majority of vinyl monomers and is only surpassed by allylic monomers where C_m is between 700 - 1,600. Allyl monomers represent a special case in free radical addition polymerizations; vinylferrocene appears to be another monomer which shows anomalous behaviour in free radical polymerizations.

A high transfer constant to monomer suggests that transfer to polymer will also occur quite readily.¹³² Thus, vinyl acetate with $C_m = 2.0 \times 10^{-3}$ also has a high value for C_p , the transfer constant to polymer. As a

consequence, transfer to polymer occurs even at low conversions.¹³³

The high value of C_m for vinylferrocene suggests that transfer to polymer may also occur with this monomer at low conversions. Hence the assumption that transfer to polymer can be neglected at low conversions may not be completely valid and the following reaction must be allowed for



Transfer to solvent has been shown to be negligible and if the effect of short chains is neglected as before, then equation (2.6.20) becomes

$$\overline{DP} = k_p [M] / (k_t + k_{fm} [M] + k_{fp} [P]) \quad (2.6.27)$$

$$\text{from which } 1/\overline{DP} = (k_t/k_p [M]) + C_m + (C_p [P] / [M]) \quad (2.6.28)$$

where

$$C_p = k_{fp} / k_p$$

Equation (2.6.28) shows that as the concentration of polymer increases, the average degree of polymerization decreases, i.e. the polymer is acting as a transfer agent. It is not easy to test equation (2.6.28) since all the above equations, which relate $\overline{DP}$ to other observable quantities, refer to instantaneous values of the average degree of polymerization. In practice therefore, they should only be applied under conditions such that $[M]$, $[S]$, $[P]$ and $[In]$ remain sensibly constant during the time of the experiment.¹²³ However, Pittman et al³⁶ have observed extensive chain branching at high conversions which is in agreement with transfer to polymer.

The effects of transfer to monomer and polymer on the structure of polyvinylferrocene will be discussed later. The resultant radical species formed in the transfer reactions appear to be still effective in continuing the propagation reaction since the rate of polymerization is essentially constant up to 10 % conversions.

2.6.5 Overall Activation Energy for the Polymerization of Vinylferrocene

Before discussing the overall activation energy for the polymerization of vinylferrocene, it is useful to consider the relationship between the overall activation energy and the individual rate constants for normal bimolecular termination.

For normal vinyl polymerizations, the rate of polymerization is expressed by equation (2.66)

$$R_p = k_p [M] (k_d f [In] / k_t)^{0.5}$$

The rate constants for polymerization initiation, propagation and termination are related to the respective activation energies and can be expressed in the Arrhenius form:-

$$\begin{aligned} R_p &= A_o \exp(-E_o/RT) ; & k_p &= A_p \exp(-E_p/RT) ; \\ & & & \\ k_d &= A_d \exp(-E_d/RT) ; & k_t &= A_t \exp(-E_t/RT) ; \end{aligned}$$

where A and E are the pre exponential factors and activation energies for the respective reactions, o,p,d,t indicate overall, propagation, initiation and termination, R is the gas constant and T the absolute temperature.

Substitution for R_p, k_p, k_d and k_t in equation (2.6.6) gives

$$A_o \exp(-E_o/RT) = \left\{ A_p \exp(-E_p/RT) \right\} [M] \left\{ \frac{A_d \exp(-E_d/RT) f [In]}{A_t \exp(-E_t/RT)} \right\}^{0.5}$$

from which

$$A_o \exp(-E_o/RT) = \left\{ \frac{A_p [M] A_d^{0.5} f^{0.5} [In]^{0.5}}{A_t^{0.5}} \right\} \left\{ \frac{\exp(-E_p/RT) \exp(-E_d/2RT)}{\exp(-E_t/2RT)} \right\}$$

$$\text{i.e.} \quad \exp(-E_o/RT) = \text{a constant} \times \exp - \left\{ E_p - \left[(E_d/2) + (E_t/2) \right] / RT \right\}$$

Hence at constant monomer and initiator concentration the relation between the respective activation energies can be expressed by

$$E_o = E_p + (E_d - E_t) / 2 \quad (2.6.30)$$

Thus, if the overall activation energy of a polymerization, E_o , is determined by examining the dependence of overall rate on temperature (at constant initiator and monomer concentrations) and E_d and E_t are known then a value for E_p , the activation energy for the propagation reaction, can be found.

In practice, the activation energy for propagation in radical polymerizations is usually between 16 - 42 kJ mol^{-1} in accord with the concept of a rapid radical addition reaction¹³⁴

The activation energy for the initiation reaction in radical polymerizations is simply that for the decomposition of the initiator, in this case AIBN, and therefore $E_d = 127 \text{ kJ mol}^{-1}$,¹³⁵

The activation energy for the combination of two radicals is very low and for most vinyl polymerizations E_t is often regarded as zero. However, although the combination of radicals in the gas phase show zero activation energy, the combination of polymer chain radicals has a finite value. Some representative values for E_t from Walling¹³⁴ are given in Table 2 - 13. It can be seen that they lie between 5 and 21 kJ mol^{-1} . The activation energy for the termination reaction in vinylferrocene polymerizations is unknown, but for the present discussion, the E_t value for polystyrene can be used i.e. E_t for PVF $\approx 8 \text{ kJ mol}^{-1}$,

Using this value, it is possible to estimate the activation energy for the polymerization of vinylferrocene.

Table 2-13

Activation Energies for Chain Termination in Vinyl Polymerizations from Walling¹³⁴

Monomer	$E_t \text{ kJ mol}^{-1}$
vinyl acetate	13.4
methyl methacrylate	5.0
styrene	7.9
methyl acrylate	ca. 21
vinyl chloride	17.6
methacrylonitrile	20.9

The overall activation energy for the polymerization of vinylferrocene was found to be 139 kJ mol^{-1} (see section 2.5.6). Therefore substitution of values for E_o , E_t and E_d into equation (2.6.30) gives

$$\begin{aligned} E_p &= 139 - (127 - .8) / 2 \\ &= 80 \text{ kJ mol}^{-1} \end{aligned}$$

This value is untenable for a rapid radical reaction and suggests that equation (2.6.30) does not represent the relationship between the respective activation energies for the polymerization of vinylferrocene.

The kinetic results for vinylferrocene have shown that the rate

constants for the polymerization are not related by equation (2.6.6) but by equation (2.6.11) ,

$$R_p = (2k_p k_d f / k_t) [M] [In]$$

Therefore, substitution of the rate constants by Arrhenius expressions as before, and at constant $[In]$, $[M]$, and f , the relationship between the respective activation energies for the polymerization of vinylferrocene is expressed by

$$E_o = E_p + E_d - E_t \quad (2.6.31)$$

Substitution for E_o , E_d and E_t as before gives

$$\begin{aligned} E_p &= 139 - 127 + 8 \\ &= 20 \text{ kJ mol}^{-1} \end{aligned}$$

A value of 20 kJ mol^{-1} for the activation energy for the propagation reaction is within the range expected for rapid radical addition reactions. Table 2 - 14 lists some values of E_o and E_p for various vinyl monomers.

It should be realized that literature values for activation energies can vary quite considerably and Table 2- 14 represents accepted average values. It is apparent however, that the value estimated for the propagation of vinyl ferrocene is in agreement with that for other vinyl polymerizations.

Thus, the overall activation energy for the polymerization of vinylferrocene is consistent with the rate expression given in equation (2.6.11) . Furthermore, the apparently high overall activation energy for the polymerization of vinylferrocene (139 kJ mol^{-1} compared to 80 kJ mol^{-1}

for normal vinyl monomers), supports the monomolecular termination proposed in the kinetic scheme.

Table 2 - 14

Activation Energies for Chain Propagation in Vinyl Polymerizations

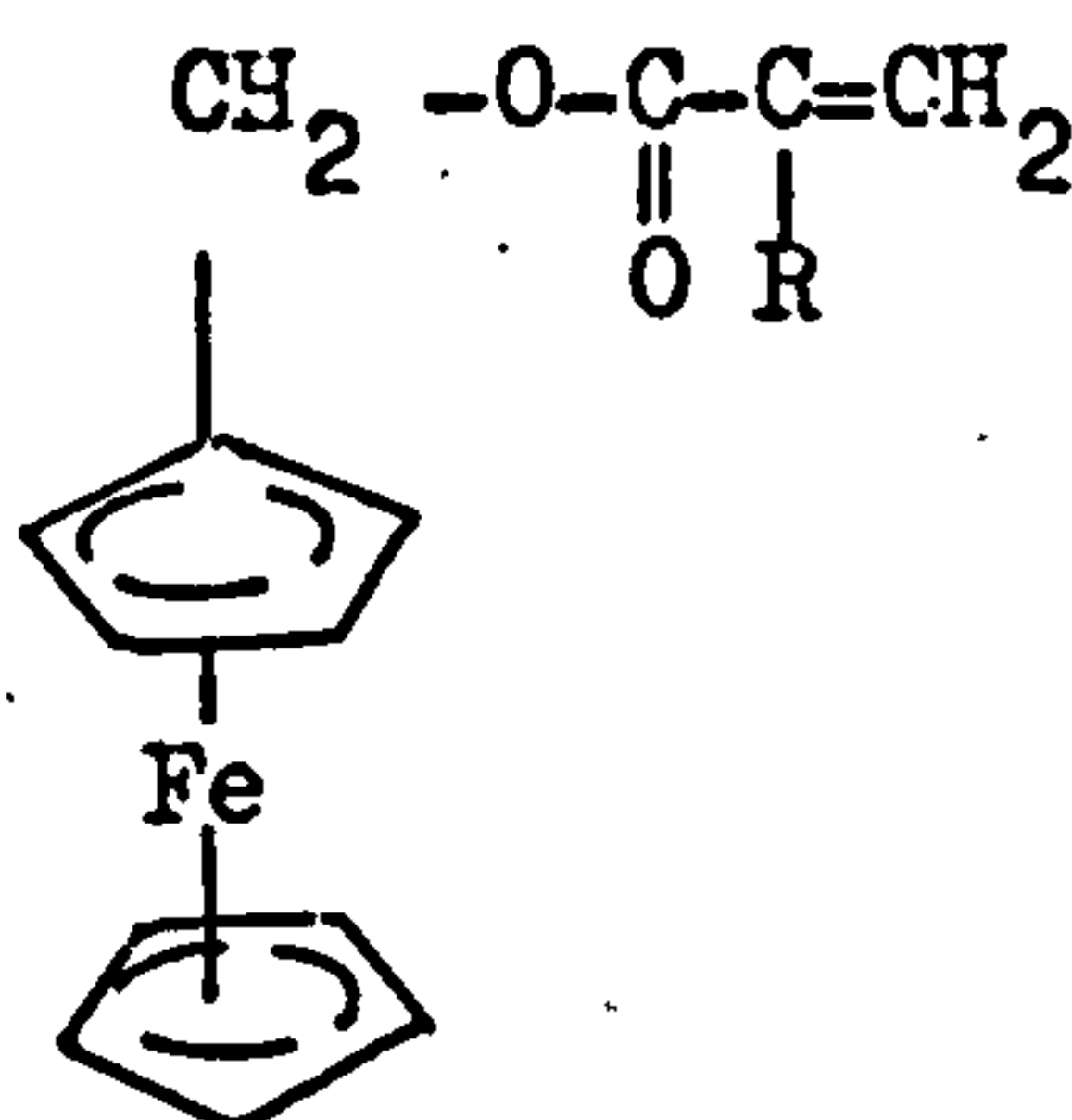
monomer	E_p kJ mol ⁻¹	E_o kJ mol ⁻¹
vinyl acetate	26	82
methyl methacrylate	19	79
styrene	30	87
vinyl chloride	15	69
methyl acrylate	29	81
vinylferrocene ^a	20	139
ferrocenylmethyl acrylate ^b	-	78
ferrocenylmethyl methacrylate ^b	-	137

a estimated with $E_t = 8$ kJ mol⁻¹.

b see Pittman et al refs. 33,136

Table 2-14 also records overall activation energies for two other ferrocene-substituted vinyl monomers. In both cases, the overall activation energies were obtained by kinetic studies in benzene solution initiated by AIBN (identical conditions to those of the present study) Pittman et al ^{33,136} concluded from their studies that both ferrocenylmethyl acrylate (FMA) and ferrocenylmethyl methacrylate (FMMA) obey normal vinyl kinetics with the rate being proportional to the square root of the initiator concentration. If this is correct, then the

relationship between the overall activation energy and the activation energies for initiation, propagation and termination will be given by equation (2.6.30), $E_o = E_p + (E_d - E_t)/2$.



ferrocenylmethyl methacrylate (FMMA) $R = CH_3$

" acrylate (FMA) $R = H$

The high value for the overall activation of FMMA is not consistent with a bimolecular termination reaction however. For, as shown previously with vinylferrocene, substitution into equation (2.6.30) for $E_o = 137$ and using the lowest possible value for E_t , i.e. zero, the activation energy for the propagation reaction of ferrocenylmethyl methacrylate is 74 kJ mol^{-1} .

However, such a high activation energy is not acceptable for a propagation reaction in vinyl polymerizations.¹³⁴ Therefore, the high overall activation energy for the polymerization of FMMA suggests that this monomer does not obey normal vinyl kinetics. In fact, the overall activation energy for the polymerization of ferrocenylmethyl methacrylate is more consistent with a monomolecular termination reaction.

Whether or not the polymerization of FMMA follows normal vinyl kinetics with a bimolecular termination reaction can only be decided by further studies.

2.6.6 Ratio of Rate Constants for Propagation and Termination

For normal bimolecular termination in free radical polymerizations, the rate of polymerization is expressed by equation (2.6.6)

$R_p = k_p [M] (k_d f [In] / k_t)^{0.5}$ and hence $R_p \propto (k_p / k_t)^{0.5}$. At equal initiation rates, the rates of polymerization of different monomers are proportional to this value and can therefore be compared. The average chain length of the polymer is also mainly determined by this parameter.

For vinylferrocene, because of the first order dependence between the rate of polymerization and the initiator concentration, the rate of polymerization is given by equation (2.6.11), $R_p = (2k_p k_d f / k_t) [M] [In]$ and hence $R_p \propto k_p / k_t$. Thus, it is not possible to make direct comparisons between vinylferrocene and other vinyl monomers on the basis of these ratios. The determination of the absolute values of the rate constants is also outside the scope of this thesis. However, it is possible to make some semi-quantitative estimates from this ratio.

An estimated value of k_p / k_t can be obtained from the rate expression $R_p = (2k_d f k_p / k_t) [\bar{M}]^{1.1} [\bar{In}]^{1.1}$, since the composite constant k' is equal to $2k_d f k_p / k_t$ which has been shown to be equal to 5.6×10^{-4} . With $k_d = 1.13 \times 10^{-5}$ and f approximately 0.75 then $k_p / k_t = 33 \text{ dm}^3 \text{ mol}^{-1}$.

Similarly, estimates of k_p / k_t can be found from graphical plots of equations (2.6.23) $1 / \overline{DP} = 1 / [\bar{M}] \left\{ (k_t / k_p) + C_s [S] \right\} + C_m$ and equation (2.6.25), $[M] / \overline{DP} = (k_t / k_p) + C_s [S] + C_m [M]$

The estimates of the ratio of k_p / k_t obtained from these plots will be low, because the transfer constants to solvent and polymer are not known and have been essentially neglected in these equations. Even so, the estimate of k_p / k_t from these plots was 32.3 and 30.3 $\text{dm}^3 \text{ mol}^{-1}$ respectively, which is in good agreement with the estimate obtained from

the rate equation. Therefore, taking an average value

$$k_p/k_t = 33 \text{ dm}^3 \text{ mol}^{-1} \cdot \quad (2.6.32)$$

From equation (2.6.32) it is possible to estimate the rate constant for the termination reaction. The propagation reaction for the polymerization of vinylferrocene can be expected to be similar to other vinyl monomers and therefore, will probably have a comparable rate constant. Some representative values are shown in Table 2-15. It can be seen that the rate propagation constants for most vinyl monomers fall between 10^2 and $2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$

Table 2 - 15

Rate Constants for the Propagation Reaction of Vinyl Monomers at 60°C ¹³⁴

monomer	$k_p \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
vinyl acetate	3700
methyl acrylate	720
styrene	176
isoprene	50
methyl methacrylate	734

Therefore, to a first approximation, if k_p for vinylferrocene is also in this range, it can be seen from equation (2.6.32) that, the rate constant for the termination reaction of vinylferrocene, must be between 3.0 and 60.0 s^{-1} .

2.6.7 Stationary State Radical Concentration

In the stationary state, the rate of initiation is exactly balanced by the rate of termination. For normal vinyl polymerizations, the rate of initiation is given by $R_i = 2k_d f [\text{In}]$ (equation 2.6.1) whilst the rate of termination is $R_t = 2k_t [R^\bullet]^2$ (equation 2.6.4). Hence the radical concentration in the steady state is given by equation (2.6.5)

$$[R^\bullet] = (k_d f [\text{In}] / k_t)^{0.5}$$

The termination constant for a bimolecular coupling reaction in vinyl polymerization is in the order of $10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, 121-125 and if $[\text{In}] = 1.0 \times 10^{-2} \text{ mol} \cdot \text{dm}^{-3}$, $k_d = 1.13 \times 10^{-5} \text{ s}^{-1}$ and $f \sim 0.75$, then it follows from equation (2.6.5) that $[R^\bullet]$ is about 10^{-8} molar.

With vinylferrocene the rate of initiation is $R_i = 2k_d f [\text{In}]$ as above. However, because of the monomolecular termination step, the rate of termination is $R_t = k_t [R^\bullet]$ (equation 2.6.8). Therefore, the stationary state radical concentration is

$$[R^\bullet] = 2k_d f [\text{In}] / k_t \quad (\text{equation 2.6.9})$$

The termination constant for vinylferrocene has been estimated to be between 3.0 and 60.0 s^{-1} and therefore, from equation (2.6.9), $[R^\bullet]$ in the polymerization of vinyl ferrocene is approximately $10^{-8} \text{ mol dm}^{-3}$.

Hence, the stationary state radical concentration in the vinylferrocene system is approximately the same as that expected for free radical polymerizations.

$R^\bullet$ is a low concentration intermediate and the usual assumptions which simplify the kinetic description of vinyl polymerizations are equally applicable to vinylferrocene, notwithstanding its monomolecular termination.

2.6.8 Rate of Reaction for the Termination Step.

The rate at which the termination reaction proceeds is equal to the rate constant for the reaction multiplied by the concentration of the reacting species. For normal bimolecular termination the rate is, $R_t = k_t [R^\bullet]^2$ and using the quantities from the previous section, $k_t = 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, $[R^\bullet] = 10^{-8} \text{ mol dm}^{-3}$

$$R_t \approx 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$$

which is the value expected for normal vinyl polymerizations ¹²¹⁻¹²⁵

For vinylferrocene, $R_t = k_t [R^\bullet]$ and hence with k_t between 3 and 60 s^{-1} and $[R^\bullet] \approx 10^{-8} \text{ molar}$

$$R_t \approx 0.3 \text{ to } 6.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$$

It can be seen that the rate of the monomolecular termination for vinylferrocene proceeds at a faster rate than the normal bimolecular radical coupling reaction. Thus, the ferrocene substituent appears to exert a profound effect which alters the classical mechanism of the termination reaction in vinyl polymerizations to one even more favourable than bimolecular radical coupling.

2.7. CONCLUSIONS FROM KINETIC RESULTS OF HOMOPOLYMERIZATION OF VINYLFERROCENE

The prime conclusion from the kinetic study of the homopolymerization of vinylferrocene is that this monomer is unique in comparison with other vinyl monomers. It is definitely not simply a ferrocene analogue of its benzene counterpart, styrene. Thus the published reports^{30,83} which claim a strong resemblance between vinylferrocene and styrene are not supported by experimental facts.

The literature review in Chapter 1 indicated that the presence of a ferrocene nucleus might exert a profound influence on the polymerization reactions of the vinyl group. Intuitively, perhaps the novel features which have been observed in this study, may not have been completely unexpected.

The radical-initiated polymerization of vinylferrocene in benzene was found to obey a rate expression of the following form :-

$$R_p = (2k_p k_d f / k_t) [M]^{1.1} [In]^{1.1}$$

This rate expression is contrary to the results of Baldwin and Johnson³⁰ who found that radical-initiated polymerization of vinylferrocene in benzene obeyed normal vinyl polymerization mechanisms i.e.

$$R_p = k_p [M] (k_d f [In] / k_t)^{0.5}$$

However, a log-log plot of R_p against $[In]$ from Baldwin and Johnson's result gives a straight line whose slope is equal to 1.15. This suggests that the square root dependence between R_p and $[In]$ which they claim for vinylferrocene is incorrect. The reasons why

they reported that $R_p \propto [\text{In}]^{0.5}$ are not clear. Although their paper contains only three kinetic experiments, their results are, in fact, in agreement with those obtained in this present study.

It is unlikely that adventitious impurities in the system could have influenced the results of the kinetic experiments, in view of the agreement between the results of Baldwin and Johnson and those in this thesis. Also all the materials used in the present study were rigorously purified and the reproducibility of the kinetic results is evidence of the purity of the system. Furthermore, the experimental results have been supported by theoretical predictions developed from the rate expressions.

Finally, the elucidation of mechanisms of the polymerization, which is the basic justification for the kinetic study, has been supported and verified by NMR, ESR and Mössbauer spectroscopy. These results will be discussed in Chapter 3.

A kinetic scheme has been proposed for the polymerization of vinylferrocene to explain the rate expression. This scheme is the same as that used to describe normal vinyl polymerizations for the initiation and propagation steps. However, an entirely different mechanism has been proposed for the termination step.

Normally, a bimolecular radical coupling reaction is predominant in the termination of radical-initiated polymerizations of vinyl monomers.¹²¹⁻¹²⁵ For radical-initiated polymerization of vinylferrocene, the scheme proposes that termination occurs by a monomolecular radical reaction. Moreover, the termination step is intramolecular with respect to the polymer chain radical. Hence, termination does not involve reaction with another molecule, such as monomer, as in the case of allylic polymerizations. Lastly,

the scheme proposes that the products of this reaction, are inactive in further radical polymerization reactions.

Basically, then the growing polyvinylferrocene radical terminates itself by a reaction with some species on the same polymer chain and the product of this reaction is inactive.

This scheme has been shown to be in accord with the experimental results. It has also been shown that such a scheme explains the first order dependence of the initial rate of polymerization on both the monomer and initiator concentration. Expansion of the scheme to include the effects of short chains on the kinetic parameter is also in accord with the rate dependence between R_p , $[M]$ and $[In]$.

The relationship between the average degree of polymerization and the kinetic parameters has also been shown to be in accord with the predictions from the proposed scheme. Thus, to a first approximation, the average degree of polymerization is dependent upon the monomer concentration only and independent of the initiator concentration. This conclusion is supported by the results of Pittman et al.³⁶ Such a relationship is not found in normal vinyl polymerizations. Normally¹²¹⁻¹²³, $\overline{DP}$ is inversely proportional to $[In]^{0.5}$.

Modification of the expressions which govern $\overline{DP}$, to include the effects of short chains and transfer reactions, have also been shown to be in agreement with the experimental results. Thus, the degree of polymerization of vinylferrocene was found to be expressed by the following:-

$$\overline{DP} = \frac{k_t \left\{ 1 + (k_p [M] / k_t) \right\}}{k_t + k_{fm} [M] + k_{fs} [S]}$$

From a series of plots of the relationship between the average

degree of polymerization and the monomer concentration, an estimate of C_m , the transfer constant to monomer, has been obtained. The transfer constant to monomer has been shown to be in the order of 8.0×10^{-3} . Such a high value suggests that transfer to monomer is a facile reaction with vinylferrocene. A high transfer constant to monomer partially explains the low molecular weights which have been obtained for PVF by other workers.³¹⁻³⁵

Concomitant with a high transfer constant to monomer, a high transfer constant to polymer is expected.¹³² This conclusion is supported, again by Pittman et al, who observed extensive branching of PVF at high conversions.³⁶

An attempt has been made to estimate C_s , the transfer constant to solvent, in this case benzene. The results suggest that C_s is negligible in this system.

The overall activation energy for the polymerization of vinylferrocene was found to be $139 \pm 3.0 \text{ kJ mol}^{-1}$. This value is considerably higher than that obtained for normal vinyl polymerizations.¹³⁴ It has been shown that such a high value is not consistent with a bimolecular termination reaction. However, it is in accord with a monomolecular termination reaction and further supports the rate expression for the polymerization of vinylferrocene and the proposed kinetic scheme.

Pittman et al.¹³⁶ have found that the polymerization of ferrocenylmethyl methacrylate also exhibits an unusually high overall activation energy, (137 kJ mol^{-1}), which suggests that this monomer may also show unusual kinetics.

The ratio of the propagation constant to the termination constant has been estimated to be $33 \text{ dm}^3 \text{ mol}^{-1}$. The ratio k_p/k_t calculated from the rate expression, $R_p = 2 k_p k_d f / k_t [\bar{M}]^{1.1} [\bar{In}]^{1.1}$, has been shown to be in

close agreement with the ratio obtained from experimental plots of $1/\overline{DP}$ against $1/[\overline{M}]$. This good correlation supports the validity of the rate expression and the relationships between the instantaneous degree of polymerization and the kinetic parameters. It also suggests that the estimate of the ratio is reasonably accurate.

From this ratio, an estimate of the termination constant, k_t , has been made by assuming that k_p for vinylferrocene will be of the same order as for other vinyl monomers. Allowing for a variation in k_p from 100 to 2000 gives k_t for vinylferrocene in the range $3 - 60 \text{ s}^{-1}$.

Using this value to calculate the stationary state radical concentration which for the monomolecular termination of the polyvinylferrocene radical is given by R_i/k_t , shows that $[R^\bullet] \approx 10^{-8} \text{ mol dm}^{-3}$. This value is in agreement with that expected for radical-initiated polymerizations of vinyl monomers.

The rate of the termination step for vinylferrocene is given by $R_t = k_t [R^\bullet]$ and not by $k_t [R^\bullet]^2$ as for normal vinyl polymerizations. Hence, for vinylferrocene the rate of the termination reaction is approximately $0.3 \text{ to } 6.0 \times 10^{-7} \text{ mol dm}^{-3} \text{ s}^{-1}$. Thus, the monomolecular termination proceeds at a faster rate than a bimolecular radical coupling reaction ($R_t \approx 10^{-9} \text{ mol dm}^{-3} \text{ s}^{-1}$).

An analysis of the kinetic results suggests that the proposed reaction scheme for the polymerization of vinylferrocene is in agreement with the experimental results. The essential difference between this scheme and the scheme for normal vinyl polymerizations is in the termination step. It is of interest to consider the termination step in more detail.

2.7.1 Proposed Scheme for the Termination Reaction.

The proposed scheme for the termination step in the polymerization of vinylferrocene can be depicted by the following reaction.



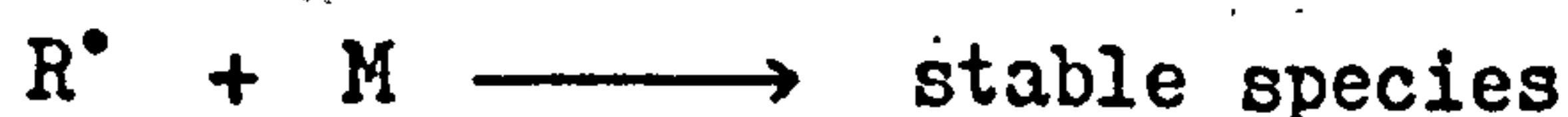
Thus, it is suggested that the growing polyvinylferrocene radical reacts with itself to terminate the chain and produce an inactive species. The reaction is therefore, first order in $[R^{\bullet}]$ and also intramolecular with respect to $[R^{\bullet}]$.

The most common termination mechanism in normal vinyl polymerizations involves mutual reaction of two chain radicals.



It is relatively unimportant whether termination occurs by combination or disproportionation for the present discussion. The important feature is that the termination reaction for normal vinyl polymerizations is second order in $[R^{\bullet}]$.

It is also possible to have a termination reaction involving transfer between a chain radical and another molecule to produce a stabilized radical which does not propagate further



Such a reaction is, of course, first order in $[R^{\bullet}]$ but not intramolecular with respect to $[R^{\bullet}]$.

Similarly, any other transfer reaction will involve an intermolecular reaction between $R^\bullet$ and some other species.

Bamford et al.¹²³ point out that it is possible to visualize termination by interaction of two electrons of unpaired spin on the same diradical. This reaction would be first order in $[R^\bullet]$ and intramolecular with respect to $[R^\bullet]$. They remark that there is no evidence to suggest that such a reaction is important in practice.

A termination mechanism involving a chain radical and some species in the same chain has not been considered or proposed, hitherto, in vinyl polymerizations. This is understandable, since a reaction of this type would be considered energetically unfavourable in comparison to mutual reaction of two radicals. Obviously, with vinylferrocene some other influence must be present, which makes a monomolecular and intramolecular termination of the chain radical more favourable.

Buel, McKewen and Kleinberg⁵³, have demonstrated some of the unusual reactions of vinylferrocene which make it unique amongst other monosubstituted ethylenes. The enhanced reactivity of vinylferrocene, and other ferrocene compounds in general, has been explained by direct participation of the ferrocene nucleus in their reactions^{53,56-60}. The influence of the metal atom on the chemistry of metallocenes is, of course one of the main characteristics which distinguishes these compounds from their benzene analogues^{1-6,56-60}.

It seems obvious therefore, that with vinylferrocene, the presence of the ferrocene substituent must alter, a priori, the normal course of the termination reaction in the radical polymerization of this monomer. If this logic is correct, then it should be relatively easy to confirm or refute the proposed kinetic scheme.

The proposed termination mechanism for the polymerization of vinylferrocene can be considered to involve only one growing chain

radical and to result in an inactive species



The following observations can be deduced from this scheme.

- (i) A monomolecular termination reaction should produce a unit which differs from interchain units. Furthermore, if the iron atom is involved, Mössbauer spectroscopy should detect iron in an environment other than the ferrocene nucleus.
- (ii) An intramolecular reaction between a chain radical and a neutral species from the same chain must produce an odd electron species. Moreover, if this species is inactive, as proposed, and does not disappear by bimolecular coupling, the polymer molecule should contain a paramagnetic component.
- (iii) The kinetics derived from this scheme suggest that there should be a quantitative relationship between the degree of polymerization and the concentration of the species formed in the termination reaction.

It will be shown in the next Chapter that these observations have been supported by spectral analysis of the polymer isolated from the kinetic experiments.

3. SPECTROSCOPIC AND PHYSICAL PROPERTIES OF POLYVINYLFERROCENE

3.1 RESULTS AND DISCUSSION OF SPECTROSCOPIC EXAMINATION

3.1.1 Infrared Spectroscopy

The infrared spectrum of polyvinylferrocene was examined in solutions of benzene, chloroform and carbon disulphide, as films cast from these solvents and in KBr discs.

The polymer can easily be cast on to NaCl discs, but the film tenaciously retains traces of solvent. Even heating the films at 40°C for 7 days at 0.1 mm Hg did not remove all traces of solvent in some cases. The presence of solvent was shown by their characteristic bands which were reduced by heating in vacuo and eliminated completely in KBr discs. Thus the band at 670 cm^{-1} reported by Pittman et al¹³⁶ in the spectrum of PVF cast from benzene is due to residual solvent.

A more accurate method of examining the spectrum was in solution. Using the above solvents the whole spectrum can conveniently be scanned. A variable path length cell containing the respective solvent was used in the reference beam to eliminate solvent absorptions. A typical spectrum is shown in Fig.3-1 and the main absorptions are listed in Table 3-1. The spectrum is identical to that reported by Aso et al³²

The spectrum shows the characteristic absorptions of the ferrocene substituent as described by Lippincott and Nelson⁴⁵, together with those typical of a vinyl polymer.

Thus the main ferrocene absorptions appear at 3090 cm^{-1} , 1411 cm^{-1} , 1108 cm^{-1} , 1002 cm^{-1} and 815 cm^{-1} . The high frequency band is due to the ferrocene ring C-H stretch in accord with the aromatic nature of the ring. The ring antisymmetric C-C stretching occurs at 1411 cm^{-1} and the ring C-H bend perpendicular to the plane of the ring appears

at 815 cm^{-1} .

Table 3 - 1

Characteristic Infrared Absorption Frequencies of Polyvinylferrocene. Samples Examined as Films Cast from Benzene.

frequency cm ⁻¹	intensity	assignment
3090	s	ferrocene ring ν CH
2930	s	chain ν CH ₂ antisymmetric
2850	w	chain ν CH ₂ symmetric
1480	w	chain CH ₂ scissor
1411	w	ring ν C-C
1240	w	chain CH
1108	s	ring breathing antisymmetric
1002	s	ring CH bend
920	m	ν CH ₂ =C out-of-plane
885	m	ν CH ₂ =C /1,3 homoanular substitution/ferricenium ion

The most important bands from a structural point of view are those which appear at 1108 cm^{-1} and 1002 cm^{-1} . These are the ring anti-symmetric breathing and the ring C-H bend parallel to the plane of the ring. These bands form the basis of Rosenblum's "9-10 rule" ; ⁶⁸ namely ferrocene derivatives which have both rings substituted do not exhibit absorptions at 9μ and 10μ (1100 and 1000 cm^{-1})

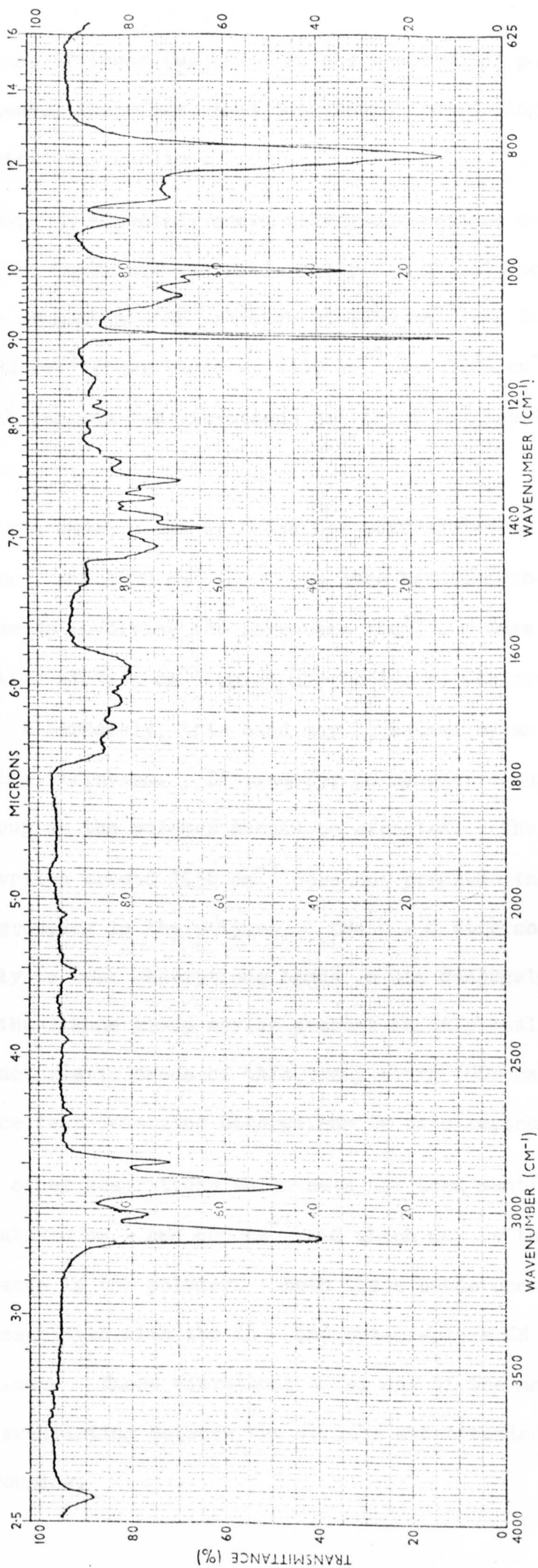


Fig 3-1. Infrared absorption spectrum of polyvinylferrocene. Polymer prepared by polymerization of vinylferrocene in benzene at 60°C in the presence of AIBN. $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$. Spectrum examined as film cast from benzene.

The presence of these two bands in the spectrum of polyvinylferrocene suggests, therefore, that the unsubstituted ring is unaffected by the polymerization reaction.

The polymer, as expected, shows alkane absorptions not present in the monomer. These are the antisymmetric $-CH_2$ stretch at 2930 cm^{-1} ; the symmetric $-CH_2$ stretch at 2850 cm^{-1} and the $-CH_2$ scissor at 1480 cm^{-1} other bands at 1300 cm^{-1} and 1280 cm^{-1} are associated with various C-H vibrations but their diagnostic value is limited.

The spectrum shows a rather broad and weak series of absorptions between 1750 cm^{-1} and 1600 cm^{-1} . These have been ascribed to combination and overtone bands involving the ferrocene ring⁴⁵. Some spectra show a weak absorption at 1635 cm^{-1} which may be due to ferrocene ring absorptions. Alternately, this band may be caused by an aliphatic $C = C$ stretching vibration. If transfer to monomer occurs the presence of a $C = C$ group in the polymer should be expected. The absence of a strong absorption around 1630 cm^{-1} does not preclude the presence of an alkene grouping in the polymer. The $C = C$ stretching vibration gives rise only to weak absorptions bands in non conjugated compounds.¹³⁷ Furthermore, the alkene group may be present in only small quantities. Also any characteristic bands of this group above 3000 cm^{-1} may be obscured by the ferrocene ring absorptions in this region.

The only other absorptions which have not been mentioned are two which appear at 920 cm^{-1} and 885 cm^{-1} and which may be the most significant bands in the polymer. Both these bands occur in the frequencies associated with the in - and out-of-plane CH bending modes of olefines. These vibrations offer one of the most important means of differentiating between the various substitution patterns of the alkene grouping.

Their presence in the spectrum of polyvinylferrocene suggests that the polymer does in fact contain unsaturation.

An absorption band near 900 cm^{-1} is characteristic of the $\text{CH}_2 = \text{C} \angle$ out-of-plane deformation in vinyl and vinylidene groups. The band is caused by the two hydrogens wagging together, above and below the plane of the $\text{C} = \text{C}$ bond¹³⁷. A substantial change in dipole moment is involved and therefore the band is intense. Hence, small amounts of unsaturation may be detected by this band even though the $\text{C} = \text{C}$ stretch may not be apparent at ca. 1630 cm^{-1} . It is reasonable to suggest that the band at 920 cm^{-1} in polyvinylferrocene may be due to a $\text{CH}_2 = \text{C}$ wagging mode, its position being displaced slightly by the inductive effect of the ferrocene substituent.

It is also possible, that the band at 920 cm^{-1} is due to an out-of-plane twisting mode in a trans disubstituted ethylene. Although this band normally occurs around 965 cm^{-1} its position is very dependent upon substituent effects¹³⁷.

Since vinyl ($\text{CH}_2 = \text{CHR}$) or vinylidene ($\text{CH}_2 = \text{CR}_1\text{R}_2$) or trans disubstituted ethylene ($\text{CHR} = \text{CHR}$) groups can all be introduced into the polymer by transfer reactions¹²³ an exact assignment is difficult.

However, the absorption at 885 cm^{-1} suggests that the presence of a $\text{CH}_2 = \text{CR}_1\text{CR}_2$ grouping is more likely. This band is caused by an out-of-plane twisting deformation of the hydrogen atoms and is a characteristic feature of the presence of the vinylidene grouping in vinyl polymers.¹³⁸

The presence of a vinyl group is unlikely since there is no absorption near 1000 cm^{-1} , which can be ascribed to the C-H deformation in $\text{CH}_2 = \text{CHR}$. Although ferrocene has a strong absorption at

1002 cm^{-1} , this does not interfere with the above C-H deformation, since in vinylferrocene it appears at 983 cm^{-1} . The spectra of the polymer and monomer between 1000 cm^{-1} and 800 cm^{-1} are shown in Fig. 3-2 which illustrates this point. There is also no obvious mechanism by which a vinyl group can be introduced into the polymer.

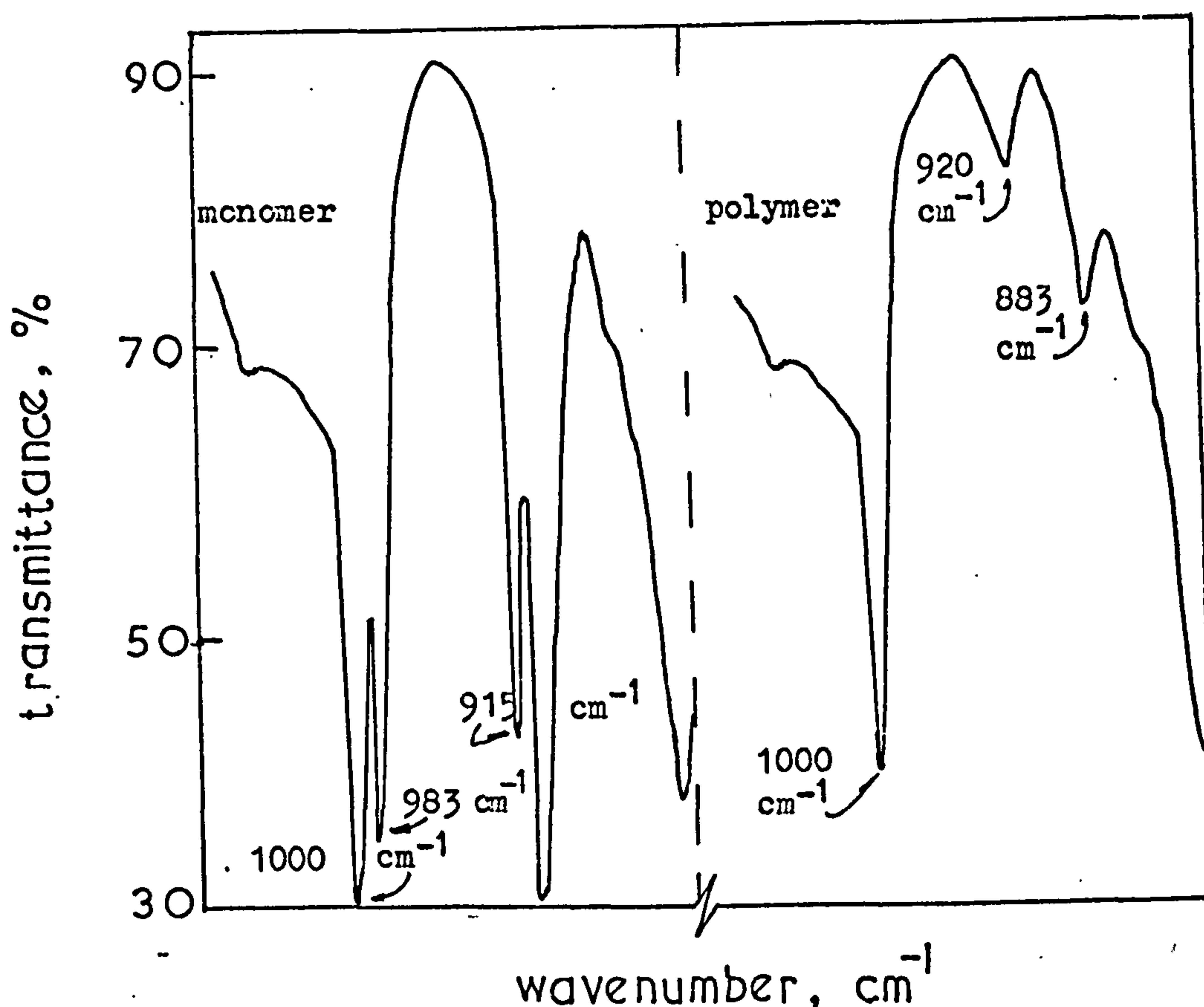


Fig. 3-2. Infrared spectra of polyvinylferrocene and vinylferrocene between $1000\text{--}800\text{ cm}^{-1}$. Solutions in benzene with benzene reference. Bands at 983 cm^{-1} and 915 cm^{-1} in the monomer are due to the C-H deformation in $\text{CH}_2 = \text{CHR}$.

Thus, both bands at 920 cm^{-1} and 885 cm^{-1} can be assigned to out-of-plane deformations of the vinylidene grouping, $\text{CH}_2 = \text{CR}_1\text{R}_2$, although the presence of a trans disubstituted ethylene group cannot be precluded. The presence of unsaturation in polyvinylferrocene is in accord with the high transfer constant of the monomer.

The previous discussion has tacitly assumed that there are no absorptions between 1000 cm^{-1} and 850 cm^{-1} which are due to the ferrocene nucleus. This is true for ferrocene and vinylferrocene but may not be

correct for polyvinylferrocene. Rosenblum¹³⁹ has shown that homoanular disubstitution of the ferrocene ring produces characteristic absorptions around 900 cm^{-1} . In particular, 1,3 substituted derivatives show two bands, which for aryl substituents occur at 920 cm^{-1} and 885 cm^{-1} .

Therefore, it is possible that these two bands reflect a substitution pattern in the ferrocene ring and not the presence of unsaturation in the aliphatic backbone polymer.

Furthermore, Spilners¹⁴⁰ has reported a shift in the strong ferrocene absorption between 810 cm^{-1} and 830 cm^{-1} to higher frequencies in ferricenium chloroferrates. Therefore, the band at 885 cm^{-1} could be caused by some charge transfer effect.

These possibilities will be discussed in detail in a subsequent section on the structure of polyvinylferrocene.

3.1.2 Ultraviolet and Visible Spectroscopy

The electronic spectrum above 300 nm was obtained in benzene and chloroform using matched quartz cells containing the polymer solution and solvent respectively. Spectra were also examined below 300 nm using chloroform and matched synthetic sapphire cells. As expected, the polymer shows very strong absorptions between 200 nm and 300 nm characteristic of the ferrocene substituent. However, the usefulness of these bands is limited as their assignments are uncertain.¹

Above 300 nm, polyvinylferrocene is characterized by two absorptions which can be assigned with some degree of certainty to (d-d) transitions of the ferrocene nucleus within the ligand field formalism.

A typical spectrum of polyvinylferrocene is shown in Fig.3-3 as a plot of absorbance against wavelength. The two absorptions around

330 nm and 445 nm appear on the edge of an intense UV absorption which is centred near 256 nm. In order to obtain an accurate measure of the true absorbance, a tangent base line was drawn as shown in Fig.3-3. This was used to give an approximate measure of the background or absorption continuum and the absorbance was measured from this line.

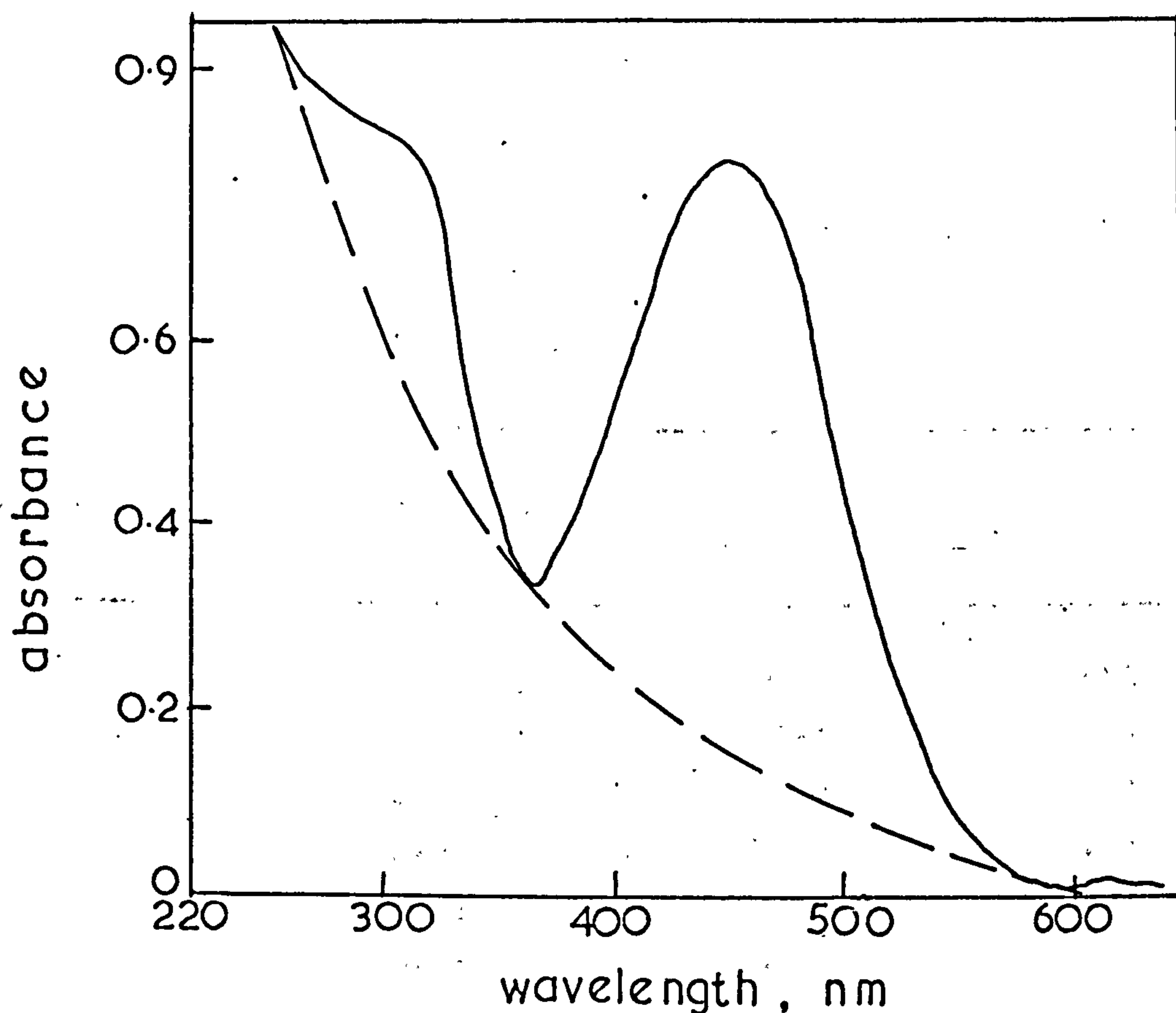


Fig. 3-3 Plot of Absorbance as a function of wavelength for polyvinylferroce in benzene (1.8 g dm^{-3}). Polymer prepared in benzene in presence of AIBN. Dashed line indicates absorption continuum.

The fraction of incident light absorbed by a species in solution is proportional to the number of absorbing molecules in the light path. This is normally expressed by the Beer-Lambert Law as

$$A = cd \times (\text{a factor})$$

where A is the absorbance, c is the concentration of the absorbing species

and d is the path length. The most commonly used proportionality factor is ϵ , the molar absorptivity with the concentration expressed in mol dm^{-3} . For addition polymers it is usual to use the molecular weight of the repeat unit to calculate the molar absorptivity of the polymer. Some typical values of the molar absorptivity of PVF are shown in Table 3-2.

Table 3 - 2

Molar Absorptivities of Polyvinylferrocene in Benzene Solution (1.22 g dm^{-3})

Wavelength nm	absorbance	ϵ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$	$\log_{10} \epsilon$
320	0.15	26.1	1.41
326	0.26	45.1	1.65
328	0.28	48.7	1.69
330	0.29	50.4	1.70
340	0.24	40.8	1.61
350	0.11	17.37	1.24
360	0.02	3.47	0.54
380	0.05	9.51	0.98
400	0.28	48.1	1.68
420	0.51	88.6	1.95
440	0.63	109	2.04
450	0.62	107	2.03
470	0.55	95	1.98
500	0.25	42.6	1.63
530	0.03	5.2	0.73

The ultraviolet and visible spectrum of PVF is shown in Fig. 3-4 as a plot of $\log_{10} \epsilon$ against wavelength. The spectra of different samples of PVF are essentially the same as that shown in Fig. 3-4, although some slight changes are apparent especially in the long wave absorption. Table 3-3 lists $\lambda_{\max}$ and ϵ for PVF samples as well as monomer and ferrocene for comparison.

Table 3 - 3

Absorption Maxima and Molar Absorptivities of Polyvinylferrocene ^a, Vinylferrocene and Ferrocene

	$[M]_0$ mol dm ⁻³	conversion per cent	$\lambda_{\max}$ nm	ϵ dm ³ mol ⁻¹ cm ⁻¹	solvent
PVF	1.0	15	330 ^b ; 444	53; 100	benzene
"	2.0	10	" ; 442	51; 112	"
"	3.0	9	" ; 448	44; 103	"
"	4.0	7	" ; 445	53; 110	"
"	4.0	1.8	" ; 442	53; 91	"
"	1.0	15	" ; 446	88; 99	CHCl ₃
"	2.0	10	" ; 446	85; 96	"
"	5.0	2	" ; 446	92; 95	"
vinylferrocene	-	-	328 ^b ; 452	203	benzene
ferrocene	-	-	325 ; 440	51; 91	95% ethanol

a polymer samples prepared at 60^oC in benzene with
 $[In]_0 = 1.0 \times 10^{-2}$ mol dm⁻³

b shoulder

Table 3 - 3 shows that the absorptions in the monomer are enhanced compared with ferrocene and polyvinylferrocene. This is due to the effect of the olefinic group conjugated with the ferrocene ring.¹⁴¹ The band at 440 nm also undergoes a bathochromic shift as expected because of the electron acceptor properties of the vinyl group.

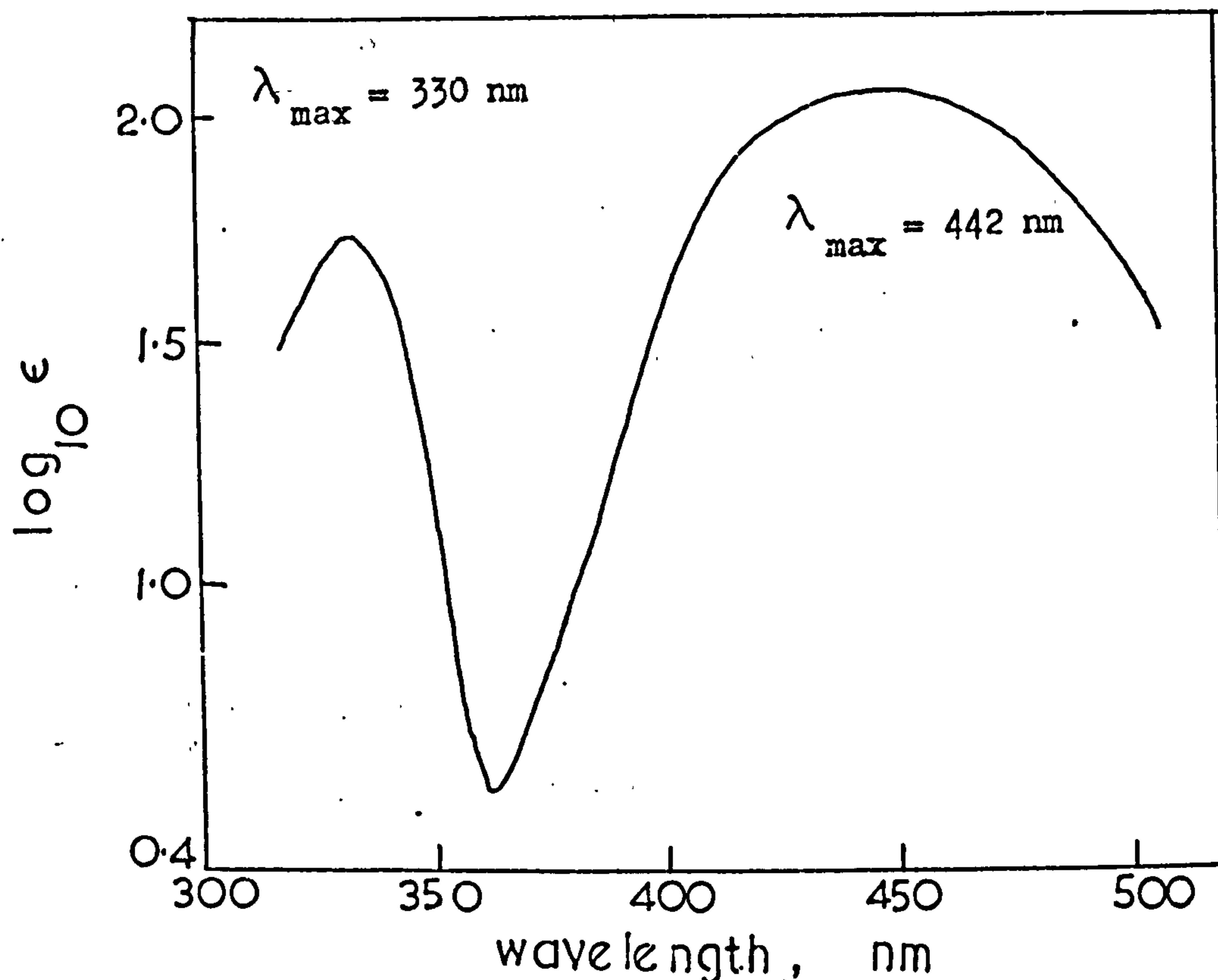


Fig.3-4 Plot of $\log_{10} \epsilon$ as a function of wavelength for polyvinylferrocene. Solution in benzene 1.22 g dm^{-3} .
 $[M]_0 = 4.0 \text{ mol dm}^{-3}$ $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

The spectra of the polymer samples are very similar to that of ferrocene itself. This is to be expected since alkyl substituents do not have a marked effect on the characteristic ferrocene absorptions.¹⁴²

Thus, the band at 325 nm in ferrocene appears at a slightly longer wavelength but ϵ is virtually constant. Accurate assessment of the position and intensity of this band is difficult because of its overlap with the intense band at 256 nm. However, the longer wavelength band seems to be subject to some variation.

Thus, λ_{max} increases from 442 nm to 445 nm, and the respective molar extinction coefficients from $91 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ to $110 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, as the percentage conversion of monomer to polymer increases from 1.7 to 7.0.

Alkenyl substituents on the ring produce an increase in intensity and position of the 440 nm in ferrocene band. Also at high conversions of monomer to polymer some unsaturation is expected because of the high transfer activity of vinylferrocene. Therefore, the enhancement and bathochromic shift of this band at higher conversions can be explained by the presence of unsaturation in polyvinylferrocene.

The variation in the band can also be explained by the presence of different amounts of unsaturation in the polymer samples. Hence, when $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $\epsilon = 110 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$, whilst when $[M]_0 = 1.0$, $\epsilon = 100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. At high monomer concentrations, more transfer is possible and hence more unsaturation can be introduced into the polymer which is reflected by the higher value of ϵ .

Thus, the ultraviolet and visible spectra of the polymer samples suggest the presence of unsaturation which is in accord with the kinetic results and supports the infrared spectroscopy of PVF. There appears to be no significant information from the uv and visible spectra which might suggest the presence of a charge transfer complex. However, any bands due to this species may be hidden by the massive ferrocene absorptions.

There are no bands near 635 nm in any of the polymer spectra. The absence of such bands suggests that the ferricenium species is not present. Thus, oxidation of polyvinylferrocene to the cationic species has not occurred in the experimental conditions of this study.

3.1.3 Nuclear Magnetic Resonance Spectroscopy

The NMR spectra of vinylferrocene and polyvinylferrocene were examined in carbon disulphide and deuterated benzene using tetramethylsilane as an internal standard. The spectrum of the polymer was also examined at variable temperatures up to 150 °C in o - dichlorobenzene.

The spectrum of the monomer was identical with that reported by Horspool and Sutherland⁶⁸. Thus, the vinyl protons appear as a doublet of doublets in an AXY pattern; $H_A = 3.40$ ppm $H_X = 4.81$ ppm and $H_Y = 5.10$ ppm (reference Si (CH₃)₃ $\tau = 10.0$ ppm) The substituted ferrocene ring protons appear as a multiplet at 4.94 ppm and 5.78 ppm, whilst the five unsubstituted ring protons resonate as a singlet at 6.03 ppm.

It was not possible to analyse the NMR spectrum of polyvinylferrocene due to excessive line broadening. A typical spectrum is shown in Fig.3-5. It can be seen that the spectrum consists of a single broad absorption centred around 5.8 ppm. In carbon disulphide the absorption appeared between 5.6 ppm to 6.4 ppm, whilst in D-benzene it shifted to slightly lower field between 5.2 ppm and 6.2 ppm.

It is well known that polymers seldom give resonance linewidths as narrow as those of less complex organic molecules.¹⁴³ To obtain a single, sharp resonance line from environmentally equivalent nuclei along a polymer chain, each must experience a similar magnetic field. This is only achieved when there is complete freedom of rotation, which in turn depends upon rapid segmental motion of the polymer chain.

It is possible, therefore, that the line broadening observed in the spectrum of FVF may be indicative of an extremely rigid polymer molecule.

The deleterious influence of rigidity on the NMR spectrum of polymers can be alleviated by increasing the temperature of the solution. This will result in increased segmental motion and a progressive narrowing of the linewidth, usually to a constant value.

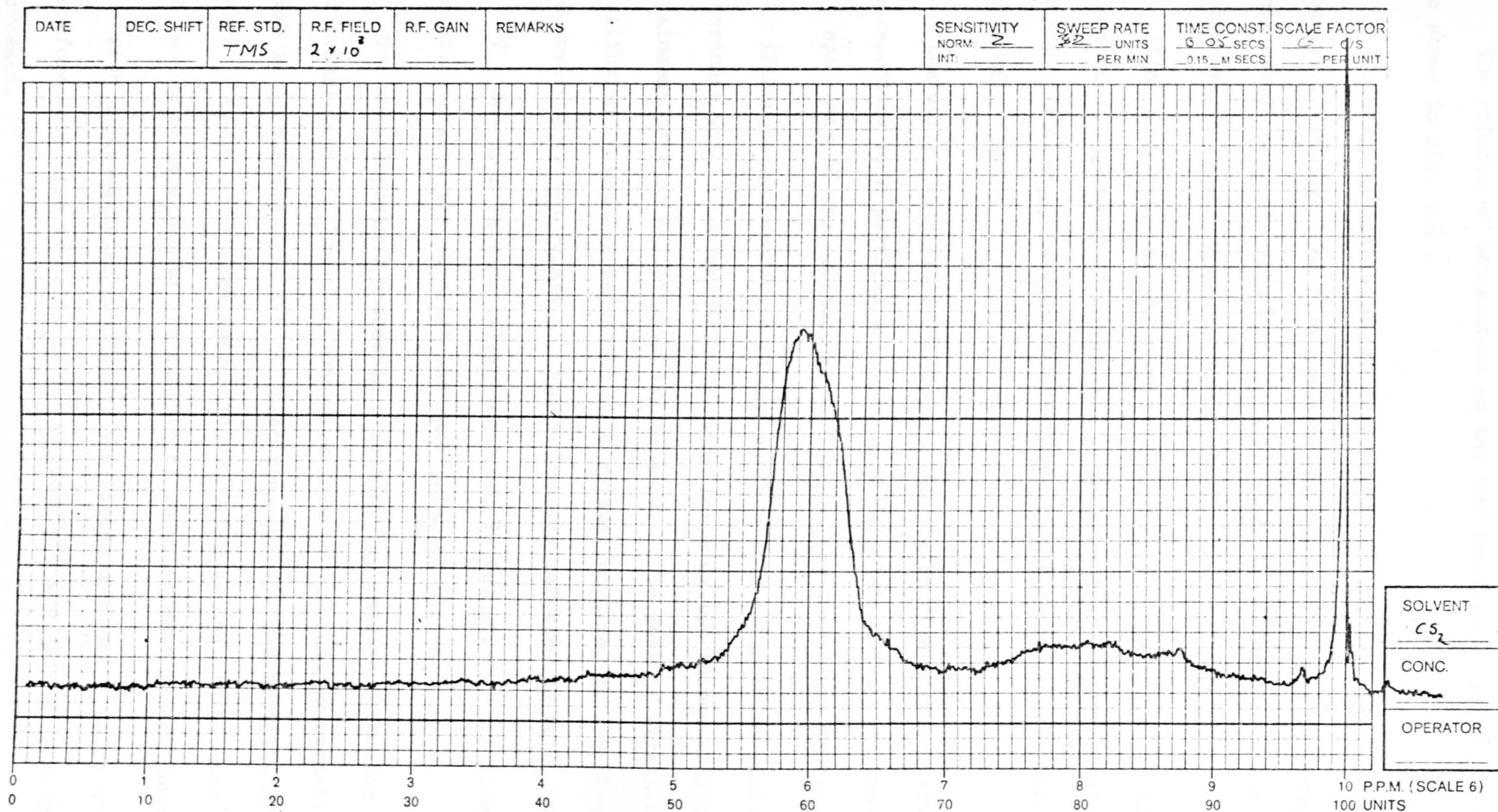


Fig 3-5. Typical nuclear magnetic resonance spectrum of polyvinylferrocene prepared by radical-initiated polymerization in benzene at 60°C. Spectrum examined as solution in carbon disulphide.

The effects of temperature on the NMR spectrum of polyvinylferrocene is shown in Fig. 3-6 .

Virtually no alteration in line width of the resonance absorptions occurred, although some fine structure is apparent at higher temperatures. This result suggests that some factor, other than rigidity in the polymer molecule, is causing the line broadening.

Line broadening of NMR spectra always occurs, of course in the presence of a paramagnetic species. The effect of a paramagnetic species in NMR spectroscopy is best measured by its influence on the spin lattice relaxation time, T_1 .

Basically for a proton there are two states of nuclear orientation representing spin parallel and spin anti parallel states with respect to the spin axis of the nucleus, or to the applied field in a NMR experiment.

Although the population of the nuclear spin orientation states is in accordance with a Boltzmann distribution for a system in equilibrium, the attainment of such equilibrium may be slow. The rate of attainment of equilibrium is usually expressed by a relaxation time, T . Nuclear processes are governed by two relaxation times, usually referred to as T_1 and T_2 .

T_1 , the spin lattice relaxation time, is essentially the rate of spin transfer between the parallel and anti parallel states.

The most important processes affecting T_1 , involve molecular rotations and translations. These motions give rise to fluctuating magnetic fields which in a molecule with all its electrons spin-paired are relatively small. However, they are radio frequency fields and, like those used in the resonance experiments are capable of inducing spin transitions.

With a paramagnetic substance, the fields are much greater and therefore more spin transitions are induced and the rate of spin transfer is increased.

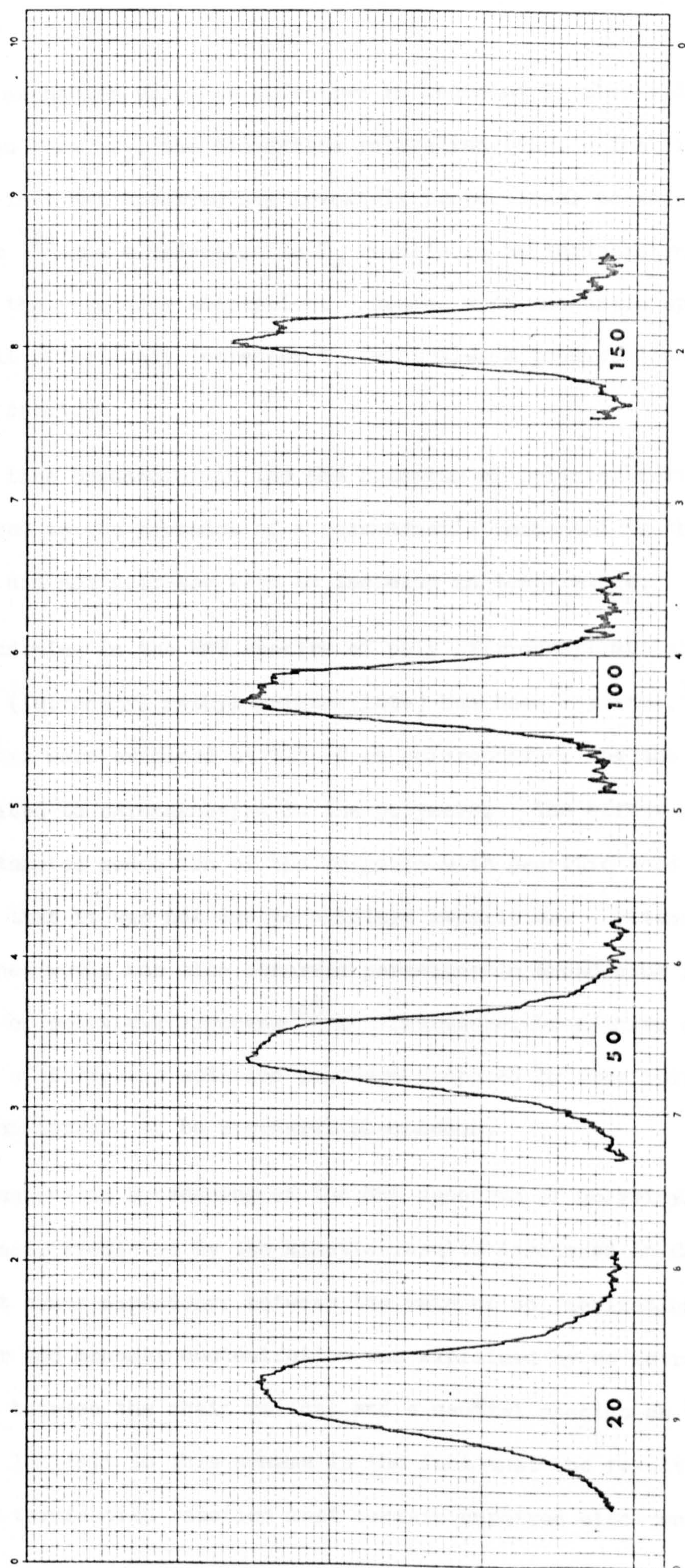


Fig 3-6. Effect of temperature on the proton absorptions at 5.8 ppm in the spectrum of polyvinylferrocene. Polymer samples examined in o-dichlorobenzene.

Thus, a paramagnetic species reduces the spin lattice relaxation time, T_1 .

Any mechanism which is effective in reducing T_1 also reduces the other relaxation time, T_2 , the transverse relaxation time. The linewidths obtained in a NMR spectrum are inversely proportional to this latter parameter¹⁴⁴ and a reduction in T_2 results in an increase in the linewidth of the resonance absorption. Hence, a paramagnetic species, because it effectively increases T_2 , will always produce line broadening of a NMR spectrum.

The line broadening in the NMR spectrum of polyvinylferrocene can be ascribed to the presence of a paramagnetic component in the polymer since it did not decrease with an increase in temperature.

Broadening in the NMR spectra of poly (ferrocenyl methyl acrylate) and poly (ferrocenyl methyl methacrylate) has been reported.^{33,136} The spectra were examined at 125 °C in chlorobenzene and the broadening was ascribed to paramagnetism in the polymers. The effect persisted after attempted reduction of the polymers with ascorbic acid which suggests that it was not due to oxidized impurities. Pittman, in unpublished work, has also observed paramagnetic broadening in the NMR spectrum of polyvinylferrocene¹⁴⁵. Therefore, broadening of the NMR spectrum of ferrocene addition polymers prepared by free radical initiation appears to be a general phenomenon.

Paramagnetic broadening of the NMR spectrum of polyvinylferrocene, was in fact, predicted by the kinetic results discussed in Chapter 2. The first order dependence between the rate of polymerization and the initiator and monomer concentration was explained by an intramolecular reaction between the chain radical and a neutral species on the same chain. Implicit in this scheme is the fact that the resulting product from the termination reaction must contain unpaired electrons.

Thus, the observed paramagnetic broadening of the NMR spectrum of PVF is in accord with, and supports the kinetic analysis of the free radical polymerization of vinylferrocene. The presence of a paramagnetic species in PVF also suggests that the odd-electron species does not disappear through a bimolecular coupling reaction.

It is unlikely that the paramagnetic species has been introduced into the polymer because of some reaction during storage, since the area of the absorption peak remains constant with time. Finally, the effect varies dependent upon the molecular weight of the polymer. This is in accord with Pittman's work in which he did not observe paramagnetic broadening in the spectra of samples with high molecular weights.¹⁴⁵

3.1.4 Electron Spin Resonance Spectroscopy

Polyvinylferrocene was examined by electron spin resonance spectroscopy (ESR) in order to confirm or refute the suggestion that the polymer contains unpaired electrons, since by definition ESR will only respond to paramagnetism.

Polymer samples were examined as powders and as solutions in benzene both at room temperature and at liquid nitrogen temperature. The monomer was also examined to check for the possible, if unlikely, presence of a paramagnetic impurity in the starting material.

As predicted by the kinetic study, ESR signals were observed with all the polyvinylferrocene samples. Moreover, signals were observed under every experimental condition. As expected, no signals was observed from the monomer.

Some typical ESR spectra obtained from polyvinylferrocenes are shown in Fig. 3-7 . A scan of the monomer and cavity background

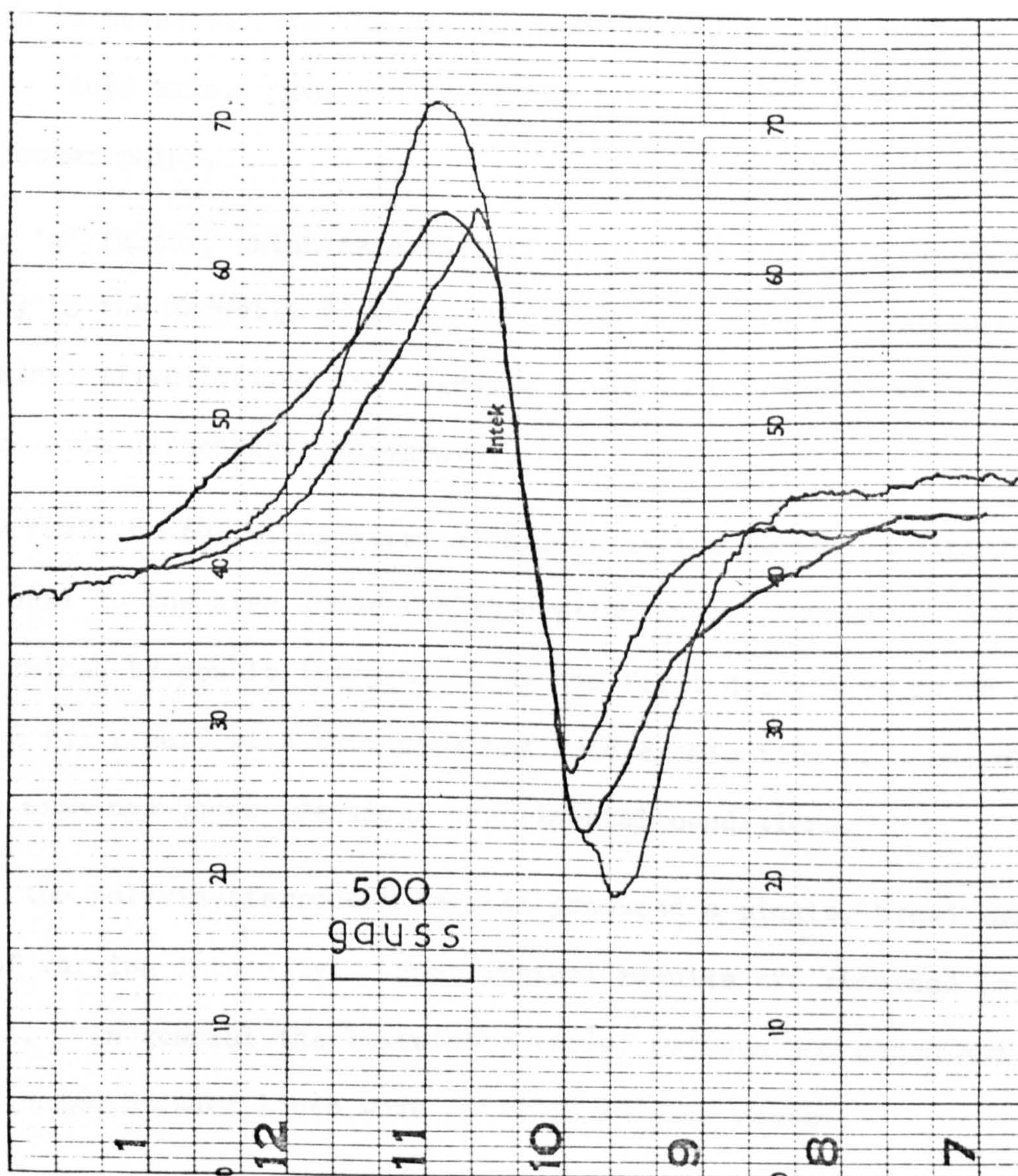


Fig 3-7. Typical electron spin resonance spectra obtained from powdered samples of polyvinylferrocene at room temperature. Polymers prepared by radical initiation in benzene at 60°C and isolated below 5% conversion. Field modulation 1000 Hg; Gain 100.

examined under identical operating conditions produced no signal.

The ESR spectra of the polymer samples are presented as the first derivative curves of the absorption peaks in the normal manner. The linewidth is measured from the displacement of maximum and minimum points along the field axis. The centre of the peak is sharply defined by the crossover point.

The 'g' factor, which is a variable parameter relating the observing frequency to the magnetic field at which the resonance absorption occurs, was obtained directly from the magnetic field by comparison with the resonance from diphenylpicrylhydrazyl.

The total number of unpaired electrons in the sample is directly proportional to the area under the absorption curve. Thus the concentration was determined by double integration of the first derivative curve and comparing the result with that obtained from examination of a suitable standard examined under identical experimental conditions.

All the polyvinylferrocene samples produced a single, broad ESR signal of varying intensity. Some typical results are recorded in Table 3-4. In general the linewidths varied between 300 gauss and 600 gauss although broader lines were obtained in some cases.

Thus, a typical sample examined in benzene solution at room temperature produced a strong resonance signal of width 425 gauss. The same sample examined as a powder produced a linewidth of 600 gauss at room temperature which broadened to 850 gauss at 77K.

The 'g' value obtained for the centre of the peaks in all the samples was found to be 2.06 ± 0.01 . Therefore, it is apparent that the same paramagnetic species is responsible for the ESR signal in all the polymer samples.

The observation of an ESR spectrum from polyvinylferrocene provides unequivocal evidence for the presence of a paramagnetic species in the polymer, in accord with predictions from the kinetic analysis. Furthermore, the similarity in the spectra of all the polymer samples is in excellent agreement with the kinetic results.

Thus, the paramagnetic species is produced in polyvinylferrocene as a result of the monomolecular termination reaction which will obviously occur by the same mechanisms in all the polymerizations.

Table 3-4

ESR Data for Polyvinylferrocene. Polymers Prepared by Radical-Initiated Polymerizations of Vinylferrocene in Benzene at 60°C. Modulation 1000 Hz; Gain 250

sample conditions	'g' factor	line width gauss
solution in benzene 298K	2.06	425
solid powder 298K	2.06	600
" " 77K	"	825
" " 298K *	"	325

* gain 100

The variation in the signal intensity also supports the kinetic analysis of the polymerization reaction. Thus, as the degree of polymerization of polyvinylferrocene increases, the mole percent of the paramagnetic terminal unit must decrease, within the limitation of a linear polymer structure. Table 3-5 shows some values for the intensities of the ESR signals for PVF of different degrees of polymerization. The

conversions were all below 4 % and therefore branching in the polymer may be reasonably disregarded for the present discussion.

Table 3 - 5

Relative Intensities of the ESR Signals from Polyvinylferrocenes of Different Degrees of Polymerization. Field Modulation 1000 Hz; Gain 100

sample	$\overline{DP}$	conversion(%)	relative intensity	linewidth (gauss)
1	12.7	1.8	210	400
2	26.4	2.9	170	325
3	33.0	1.6	80	555
4	54.0	3.2	11	300

The relative intensities were obtained by comparison of the peak heights obtained under identical conditions from similar amounts of solid polymer. Although some inaccuracies are inevitable, Table 3-5 shows that the relationship between $\overline{DP}$ and the concentration of the paramagnetic species, predicted by the kinetic analysis is observed within reasonable error.

Further proof for the validity of the kinetic analysis of vinylferrocene polymerization is given by the measured 'spin' concentration of the paramagnetic species in the polymer. The spin concentration of a polymer sample of $\overline{M}_n = 6,800$ was 10^{19} spins g^{-1} . The measured spin concentration was somewhat imprecise because it was obtained by comparison of the broad ESR absorption obtained from the polymer with the narrow line

from the standard (chromium in magnesium oxide). However, the recorded spin concentration is in good agreement with the concept of one paramagnetic species per polymer molecule. A recorded value of 8.5×10^{18} spins g^{-1} would correspond to one spin per molecule for a molecular weight of $\bar{M}_n \approx 7,000$.

Thus, the electron spin resonance spectroscopy of polyvinylferrocene confirms the presence of a paramagnetic species in the polymer.

ESR is an extremely sensitive technique for detecting unpaired electrons and erroneous results can easily be obtained because of paramagnetic impurities in the atmosphere.

It is obvious however, that the ESR signal from polyvinylferrocene is not due to adventitious impurities since the intensity of the signal was found to vary systematically with the $\bar{DP}$ of the polymer. The presence of paramagnetic impurities in the monomer can also be precluded.

Thus, the ESR signal is a characteristic of the polymer and not due either to adventitious impurities or other extraneous effects.

The 'g' value obtained from the ESR signal in PVF was close to that of the free electron ($g_e = 2.00232$). Such values are often associated with organic free radicals. However, the broad linewidth is not consistent with an organic radical.¹⁴⁶

The 'g' values and linewidths are more consistent with unpaired electrons in an iron atom on the polymer chain, in particular Fe(III) in a high spin configuration ($3d^5$)¹⁴⁷

The signal cannot be caused by the ferricenium cation since the ground state of this ion is orbitally degenerate and therefore an electron spin resonance absorption is not observed.¹⁴⁷

The presence of an Fe(III) high spin complex is supported by the ease with which the spectra can be observed, even at room temperatures. In

a $3d^5$ configuration the electron shell is half full, with the spins aligned and the orbital angular momenta of the electrons cancelled out. Therefore, the ion has no orbital angular momentum to be quenched, and there is no mechanism for spin-lattice relaxation.¹⁴⁸ Hence the spin-lattice relaxation times are very long and the linewidths correspondingly narrower. Transition metal ions with short relaxation times (e.g. the ferricenium cation) give an ESR signal too broad to be observed. This can only be improved by reducing the temperature which increases the relaxation time. However, even at temperatures below 4K the relaxation time is often still too short to give a reasonable linewidth¹⁴⁹

Although 5 unpaired electrons are present in Fe (III) in a high spin state, only one transition is observed between the doublet $S = \pm \frac{1}{2}$ since the zero-field splitting is very large in this ion¹⁵⁰. Thus, a 'g' value near 2.0 is observed along the axis of the crystalline field. However, the 'g' value will vary with respect to the axis. This anisotropy in the 'g' values explains the variable linewidths obtained from the powdered samples.

The significance of a high spin Fe (III) complex in polyvinylferrocene will be considered subsequently in the discussion of the possible mechanisms of the polymerization reactions of vinylferrocene.

However, paramagnetism in PVF was predicted by the kinetic study of the polymerization. Therefore, the observation of an ESR signal from the polymer is conclusive evidence that the kinetic analysis of the polymerization reaction is reasonable. Thus, the polyvinylferrocene chain radical is terminated by a reaction with a neutral species on the same chain and this reaction results in a polymer molecule which contains a paramagnetic component.

3.1.5 Mössbauer Spectroscopy

The previous results from ESR spectroscopy confirmed the presence of paramagnetism in PVF and indicated that it was due to unpaired electrons in an iron atom. To confirm this conclusion and identify the species, the polymer was examined by Mössbauer spectroscopy.

Mössbauer spectroscopy is a type of nuclear resonance spectroscopy which depends upon the phenomenon of recoil-less resonance absorption and emission of gamma-quanta, known as the Mössbauer effect.¹⁵¹

The Mössbauer effect with iron depends on the fact the the nuclide ⁵⁷Fe which is formed in the decay of ⁵⁷Co has an excited state 14.4 keV above the ground state which can lead to a very sharp resonance absorption peak. Thus, γ radiation from a ⁵⁷Co source will undergo a resonance absorption with an absorber where the iron nuclei are in an identical environment with that of the source atoms.

If the Fe nuclei are in a different environment no absorption occurs and the radiation is transmitted and can be measured. In order to observe resonance absorption it is necessary to impart a velocity to the source relative to the absorber. This motion changes the energy of the incident quanta (due to the Doppler effect) so that at certain velocities there is a correspondence between the excitation energy of the nuclei in the absorber. The shifts in the absorption position, relative to an arbitrary zero, are then customarily expressed in velocities (mm s^{-1}) rather than in energies.

The shift in the resonance absorption depends upon the chemical environment of the nuclei and on the temperature. Even when all nuclei in the absorber are in identical environment, splitting of the resonance absorption peaks can occur, due to interaction of an electric field gradient at the nucleus with the nuclear quadrupole. The field gradient is dependent upon the asymmetry of the electronic charge distribution and hence quadrupole splitting is only evident from ions with an asymmetric charge distribution.

Thus, the two basic parameters from Mössbauer spectroscopy, the isomer shift and the quadrupole splitting provide a 'fingerprint' of the iron compound and a means of distinguishing oxidation states and electronic configurations.

The Mössbauer spectra of polyvinylferrocene and vinylferrocene were examined in the Mössbauer Unit of the Harwell Scientific Services, AERE, Harwell, Berks. Spectra were obtained at 77K, 300K and 400K using normal procedures.¹⁰⁷

The spectrum of the monomer is shown in Fig.3-8 together with a typical spectrum of polyvinylferrocene, isolated at low conversions.

The positions of the absorption peaks and their areas were obtained from a computer fit of the Mössbauer data.

The isomer shifts (IS) were measured relative to iron metal as zero, and the quadrupole splitting (QS) obtained as the difference between the peaks.

Table 3-6 shows some typical Mössbauer data for monomer and polymer obtained from a computer fit.

The Mössbauer spectrum of vinylferrocene is essentially the same as that of ferrocene. Thus, the monomer contains two peaks with $IS = + 0.43 \pm 0.01 \text{ mm s}^{-1}$ and $QS = 2.30 \pm 0.02 \text{ mm s}^{-1}$. These values are in good agreement with those from Collins and Pettit⁷³ for ferrocene, $(IS = + 0.475 \pm 0.01 \text{ mm s}^{-1}, QS = 2.40 \pm 0.02 \text{ mm s}^{-1})$. The slight variance is due to the effect of temperature. The spectra should, of course be the same, since substitution in the ferrocene rings has very little effect on the Mössbauer parameters because the σ -bonding in the rings is essentially independent of the iron-ligand bonding.¹⁵²

The Mössbauer spectrum of polyvinylferrocene is more complex. Three peaks are observed in samples of polymer isolated at low conversions. The two outer peaks are characteristic of iron in the ferrocene nucleus.

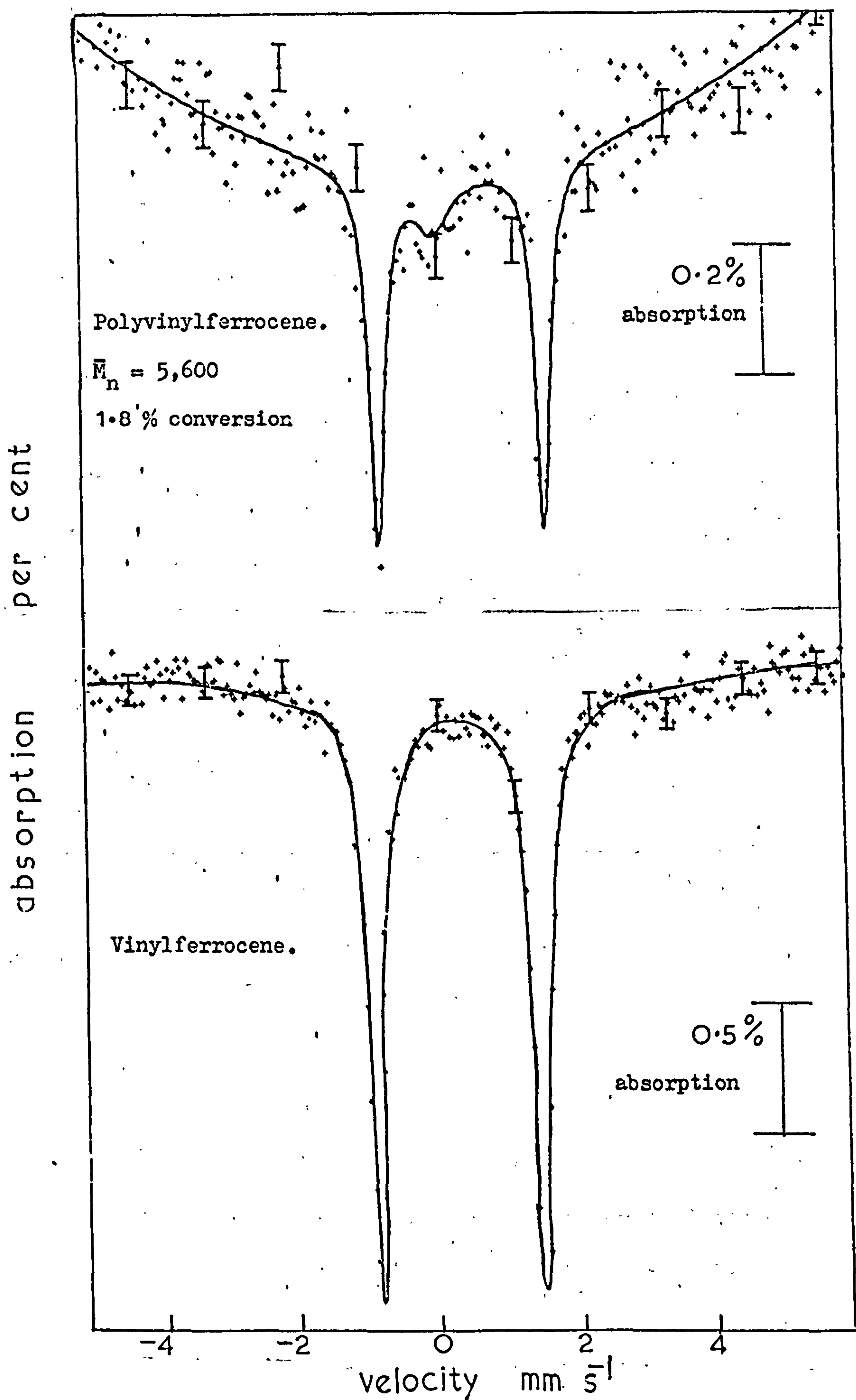


Fig 3-8. Mössbauer spectra of polyvinylferrocene and vinylferrocene. The extra peak in the polymer is due to iron as Fe(III) . Samples examined in powder form at 300K. Velocities expressed relative to iron metal.

Table 3 - 6

Computer Fit of Mössbauer Data for Polyvinylferrocene and Vinylferrocene
at 300K. Precision $\pm 0.01 \text{ mm s}^{-1}$

Sample	peak 1 mm s^{-1}	peak 2 mm s^{-1}	peak 3 mm s^{-1}
PVF ^a	-0.75	0.13	1.64
"	-0.73	0.17	1.63
"	-0.75	0.11	1.64
"	-0.73	0.07	1.58
"	-0.75	0.20	1.62
"	-0.73	0.12	1.62
"	-0.76	0.17	1.65
monomer	-0.72	-	1.58
ferrocene ^b	-0.76	-	1.68

a polymer samples prepared with different values for $[M]_0$ and $[In]_0$

b determined at 77K⁷³

The average value for the isomer shift is $+ 0.44 \pm 0.01 \text{ mm s}^{-1}$
whilst the quadrupole splitting is $2.37 \pm 0.02 \text{ mm s}^{-1}$.

The position of the third peak is more difficult to determine because the peak is small and appears as a shoulder on the negative absorption. An average value for its position is $IS = 0.14 \pm 0.01 \text{ mm s}^{-1}$. However, it is clear that the polymers contain an absorption which is not present in the monomer. Since Mössbauer spectroscopy is so specific, this peak can only be ascribed to iron in an environment which is different from that of the ferrocene nucleus.

The third absorption peak in the polymer is not due to the ferricenium cation since this species produces isomer shifts near $+ 0.5 \text{ mm s}^{-1}$ relative to iron metal.⁷³ The position of the peak corresponds to that expected for Fe (III) in a high spin configuration although Fe (II) low spin is also possible. However, since the ESR data suggested the presence of Fe (III) high spin, this species seems more likely.

When the polymer was examined at 77K the third peak tended to become obliterated because of the enhancement of the two outer peaks. This suggests that the third peak is associated with iron in an ionic complex, since peaks due to these complexes tend to decrease at low temperatures. Peaks ascribed to covalently-bonded iron increase with decreasing temperature. Thus, the Mössbauer data shows that polyvinylferrocene as well as containing iron as Fe (II) in the ferrocene nucleus as expected, also contains iron, ionically-bound, as Fe (III).

This result is, of course in accord with the kinetic results and suggests that the termination reaction must involve an electron transfer from an iron atom in the polymer chain to the chain radical.

As with the ESR data, it is unlikely that the Mössbauer results are caused by an impurity, since the relative intensity of the third peak varies with the sample examined. This effect is shown in Table 3-7 where the relative percentage areas of the peaks have been listed for some representative polymer samples.

The Mössbauer results for polyvinylferrocene isolated from the kinetic experiments suggested that there was a quantitative relationship between the intensity of the third peak and the kinetic parameters. To examine this effect in more detail, a second series of polymerizations were carried out and isolated after 10 % conversion. The Mössbauer data for this series is recorded in Table 3-8 together with the average degrees of polymerization determined by VPO.

Table 3 - 7

Relative Percentage Areas of the Mössbauer Absorptions for Polyvinylferrocene^a and Vinylferrocene at 300K

sample	peak 1 (Fe II) area %	peak 2 (Fe III) area %	peak 3 (Fe II) area %
PVF	46.7	3.9	49.3
"	39.8	14.3	45.9
"	44.2	9.5	46.3
"	46.2	3.1	50.6
"	45.0	8.9	46.1
"	46.0	6.3	47.6
monomer	48.0	-	52.0

^a polymers prepared with different values of $[M]_0$ and $[In]_0$

It can be seen in Table 3-8 below that as the average degree of polymerization increases, the relative area of the peak due to Fe (III) decreases.

Table 3 - 8

Relationship between Percentage Area of Fe (III) Absorption and Average Degree of Polymerization for Polyvinylferrocene, 10-12 % conversion.

$[M]_0$ mol dm ⁻³	$\overline{DP}$	position mm s ⁻¹	Peak 2 (Fe III) area %
1.0	27.0	0.06	1.4
1.0	26	0.11	8.9
2.0	41.5	0.17	5.3
3.0	52.4	0.27	3.5
4.0	73.6	0.02	0.2

^a prepared at 60°C, $[I_n]_0 = 1.0 \times 10^{-2} [M]_0 = 4.0 \text{ mol dm}^{-3}$

This result is in accord with the predictions from the kinetic experiments. Thus, each polymer chain should contain one terminal unit which differs from interchain units. Hence, the mole per cent of this species will decrease with increasing length of the chain.

Obviously, this suggestion is somewhat oversimplified because transfer reactions have been ignored. However, the results obtained from examination of the Mössbauer spectra of PVF are in good agreement with the other results in the present study.

Implicit in the above results is the fact that at high degrees of polymerization the mole percent of the terminal unit will be very small. In general, at least 5 % of an absorbing species is required before a Mössbauer spectrum is observed. Therefore, at high degrees of polymerization when the mole percent of the terminal unit is relatively low, the Mössbauer spectrum of PVF will not show an extra absorption. This conclusion is in accord with the results of Pittman et al.¹³⁶ Thus, these workers examined the Mössbauer spectrum of PVF of high molecular weight and only observed the two peaks characteristic of iron in the ferrocene nucleus.

It is evident from the ESR results discussed previously and those obtained from the Mössbauer study that the kinetic analysis of the polymerization of vinylferrocene is reasonable. Thus, the growing polymer chain radical is terminated by an intra-molecular reaction which is monomolecular with respect to the chain radical. Most probably termination occurs by electron transfer from an iron atom. This reaction terminates the growing polymer chain and produces a terminal paramagnetic species which is inactive in further polymerization reactions. The precise mechanism of this reaction will be discussed in detail in a later section. (3.3.1. p146.)

3.2. RESULTS AND DISCUSSION OF PHYSICAL PROPERTIES OF PVF

3.2.1 Magnetic Susceptibility

Since ESR spectroscopy demonstrated the presence of unpaired electrons in PVF, it should be possible to measure the magnetic susceptibility of the polymer and hence calculate the magnetic moment of the odd-electron species.

A sample of polyvinylferrocene which gave a strong ESR signal was therefore examined on a susceptibility balance by the Faraday method.¹⁰⁸ The sample was examined at ten temperatures from 77K to 291K. Force measurements were made at four settings of the applied magnetic field at each temperature, to ensure that there were no ferromagnetic impurities present, and then corrected for the force exerted on the empty sample bucket. Values of the net force were combined with the sample weight to give the mass susceptibility, χ_g .

Normal paramagnetism is inversely proportional to the absolute temperature and this relationship can be expressed by the Curie - Weiss Law, $\chi_m = C/(T + \theta)$, where χ_m is the molar susceptibility T is the absolute temperature and C and θ are the Curie and Weiss constants respectively. Hence a plot of $1/\chi_m$ against T should give a straight line of slope C from which the magnetic moment μ can be obtained since $C = N \mu^2 / 3k$, where N is Avagadro's number and K is the Boltzmann constant.

For accurate work the molar susceptibility must be corrected for diamagnetism and temperature independent paramagnetism. The magnetic moment of the species responsible for the paramagnetism may also be conveniently calculated from the expression, $\mu = 2.84 (\chi_m T)^{1/2}$ ¹⁵³ at any given temperature.

The spin of a single electron is given by $\mu_s = 2 S(S + 1)^{1/2}$.

ESR and Mössbauer spectroscopy indicate that the paramagnetism is caused by an Fe(III) species in a high spin d^5 configuration. Thus, the ground state of this ion is an S state and there is no orbital angular momentum to contribute to the magnetic moment. Hence, the 'spin only' expression is applicable and the calculated magnetic moment should be 5.92 Bohr magnetons (BM).

Unfortunately, the results obtained from the sample of polyvinylferrocene examined, show an extremely small susceptibility effect. The value of χ_g obtained was around $1.0 \times 10^{-6} \text{ cm}^3 \text{ g}^{-1}$ which is just about comparable with the uncertainty of the data. The precision was also too low to permit any accurate plots of susceptibility against temperature. Undoubtedly, the relatively high molecular weight of the polymer must inevitably lead to a fairly low mass susceptibility. Limitations in the amount of sample which could be handled also hampered more accurate measurements.

The number average molecular weight of the polymer examined was 8,000 and hence χ_m is 8×10^{-3} from which $\mu = 4.3 \text{ BM}$. The probable errors involved in the respective measurements mean that this value is unreliable and it is not realistic to compare it with the calculated value of 5.92 BM. However, the sample does show paramagnetic behaviour in accord with the ESR results.

A more important conclusion from the study of the magnetic susceptibility of PVF is that the paramagnetic behaviour of the polymer is definitely not caused by oxidized impurities.

Paramagnetism is dependent upon temperature but is independent of field strength. The force measurements of PVF at a fixed temperature but different applied magnetic fields were essentially constant. Thus, the results are in accord with paramagnetism.

Ferromagnetism, has a complex dependence upon both temperature and field strength.¹⁵³

Hence, measurements at constant temperature but varying field strength will immediately show the presence of ferromagnetic impurities in any paramagnetic sample under investigation.

The above results, therefore, afford further confirmation that the polymer contains a paramagnetic species. Furthermore, they show that there are no ferromagnetic impurities, such as ferric oxides, in the polymer.

3.2.2 Electrical Properties of Polyvinylferrocene

Since PVF demonstrates magnetic properties, it was examined for electrical conduction. It was found to be a good insulator, its resistivity being in the order of $10^{16} \Omega \text{ m}$. This result is in accord with the polymer structure, since its backbone is saturated and the paramagnetic species are well separated.

Neuse and Rosenblum have concluded from their recent review of metallocene polymers, that pure ferrocene polymers, regardless of structural features, will have no conduction properties.¹⁵⁴ Only in the presence of oxidized impurities, e.g. ferricenium units do these polymers exhibit conductivity.

Thus, the high resistivity of PVF is further evidence of the purity of the polymer. The paramagnetism, therefore, appears to be an intrinsic property of polyvinylferrocene prepared by free radical mechanisms.

3.2.3 Glass Transition Temperature

The glass transition temperature, T_g , was determined by differential scanning calorimetry (DSC). Samples were examined at four different heating rates. Some typical plots of differential heat capacity versus temperature are shown in Fig. 3-9. The glass transition temperature was taken as the point of inflection from these curves, and are recorded in Table 3-9.

The T_g temperature is not an equilibrium phenomenon, but rather a rate effect. It depends upon the time scale of the experiment; shorter scanning times resulting in higher values of T_g .

Table 3 - 9

T_g of Polyvinylferrocene ($\bar{M}_n = 28,000$) at Different Scanning Rates.
Samples Examined in Sealed Pans.

scanning rate deg. min ⁻¹	T_g °C
8	226; 225
16	227; 231
32	238; 236
64	258; 262

In extremely long tests, a transition may not be observed at all. Fig.3-9 shows this effect with the inflection of the base line becoming less apparent at the lower scanning rates.

The T_g observed by DSC is usually considerably higher than that obtained by dilatometry with a slow heating rate (0.06 deg.min⁻¹). However, the ease with which small samples (10-20 mg) can be examined by DSC is an important factor in its use.

It is possible to relate the experimental scanning rate to the observed T_g ¹⁵⁵, but for comparative purposes, the T_g from DSC is usually recorded at a scanning rate of 1-deg.min⁻¹. Fig.3-10 shows a typical plot of T_g against scanning rate. The T_g at 1 deg. min⁻¹ obtained from this graph was 222 ± 2 °C. Although the T_g occurs on the edge of a

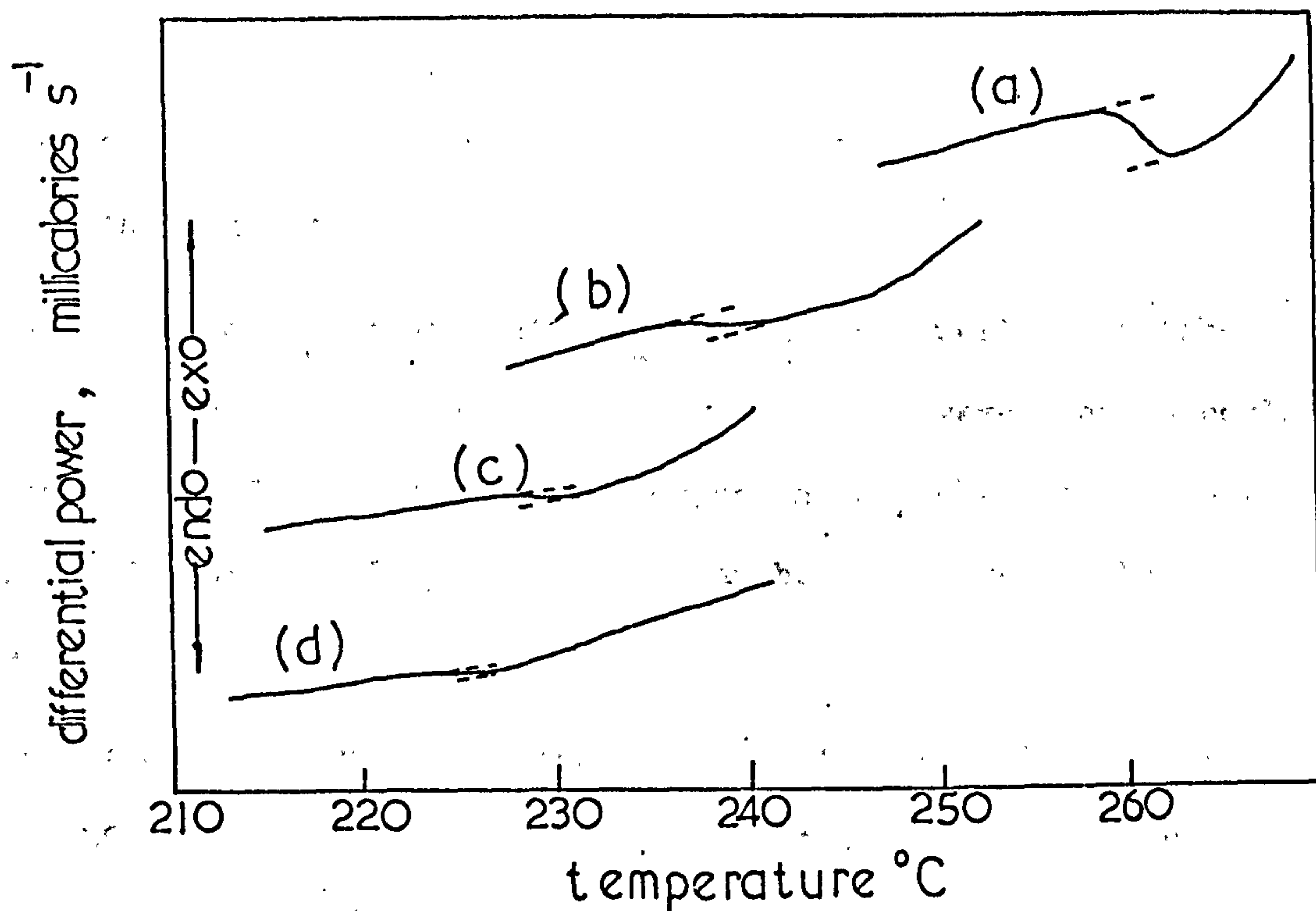


Fig 3-9. Effect of scanning rate on the DSC traces of polyvinylferrocene, $\bar{M}_n = 28,000$. (a) 64 deg.min.⁻¹, (b) 32 deg.min.⁻¹, (c) 16 deg.min.⁻¹, (d) 8 deg.min.⁻¹.

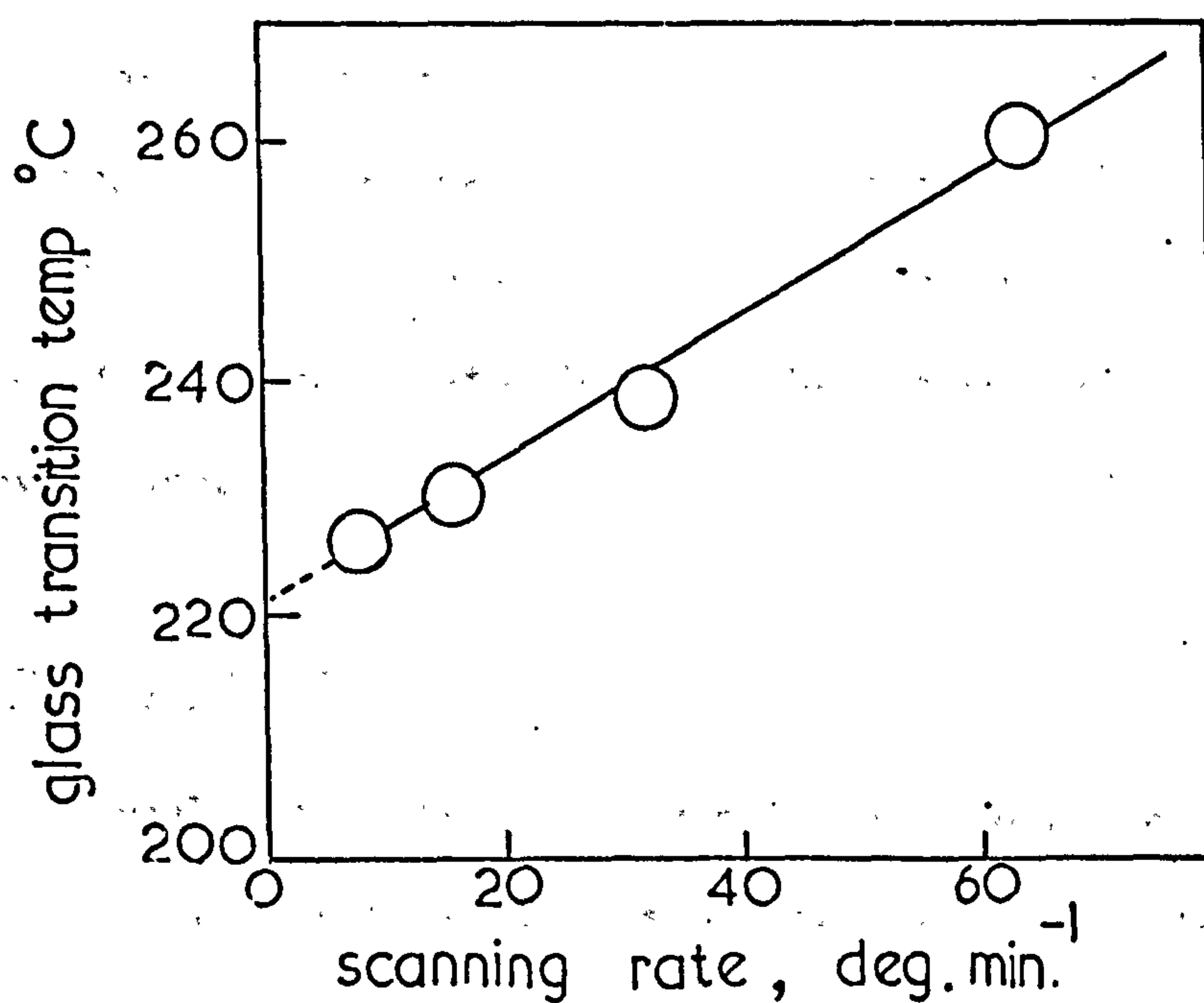


Fig 3-10. Plot of glass transition temperature observed by DSC as a function of scanning rate for polyvinylferrocene, $\bar{M}_n = 28,000$. T_g at 1 deg.min.⁻¹ = $222 \pm 2^\circ\text{C}$.

decomposition curve, the straight line suggests a reasonable degree of confidence in the results.

The dependence of T_g on molecular weight has been well established.¹⁵⁶ In general the T_g decreases with molecular weight. However, at molecular weights above 25,000 T_g is practically independent of molecular weight.¹⁵⁶ Therefore, the T_g for PVF of $\bar{M}_n = 28,000$ can be considered to be a true value.

Pittman et al³⁴ have briefly reported the T_g of polyvinylferrocene obtained by DSC as 184 - 194 °C. They point out that these values are only approximate as the DSC curves were not always sharp and easily interpreted. No experimental details were recorded which might suggest a reason for the ten degree range. However, the values of $\bar{M}_n$ recorded in the same paper are all below 13,000 which might explain their lower values in comparison with the present study.

The effects of the nature of the chain repeat units on T_g are closely related to intermolecular forces, chain stiffness and symmetry. Probably the most important factor among these is steric hindrance to free rotation along the polymer chain due to the presence of stiff bonds or bulky side groups. Therefore, the high T_g of PVF relative to polystyrene ($T_g \approx 80$ °C) is in accord with the greater bulk of the ferrocene group compared with the phenyl group.

3.2.4 Thermal Stability of PVF

The thermal stability of polyvinylferrocene was examined by thermogravimetry. Essentially, some measure of the thermal stability of a polymer is readily obtained by examining the weight loss and the rate of weight loss versus temperature. The temperature at which a weight loss is first detected, is also an important parameter for comparing thermal

stability of different polymers.

A sample of PVF was heated at 64 deg. min^{-1} in an atmosphere of nitrogen and the cumulative weight change with temperature recorded. Some typical values are given in Table 3-10. These results are plotted as per cent residual weight loss versus temperature in the normal manner.

Table 3 - 10

Cumulative Weight Loss of PVF Between 200°C and 650°C heating rate $64 \text{ deg. min.}^{-1}$, powdered sample under nitrogen.

temperature $^{\circ}\text{C}$	weight loss per cent
200	-
240	0.9
300	1.5
350	2.0
400	2.5
450	20.0
470	56.0
500	83.0
600	85.0

A characteristic thermogram of polyvinylferrocene is given in Fig. 3-11. The thermogram shows that the degradation of PVF occurs essentially in one step. The first weight loss is recorded at 240°C indicating that the polymer is stable to this temperature. The degradation of the polymer proceeds at a slow rate up to 400°C

and has still only lost 2.5 % of its weight at this temperature. Rapid weight loss occurs between 400°C and 500°C when 83 % of the polymer is volatilized. From 500°C to 700°C the residual weight remains virtually constant, indicating that the polymer has been degraded to a stable form.

The initial weight loss can be associated with scission reactions of the aliphatic backbone of PVF. The massive degradation between 400°C and 500°C is due to degradation of the ferrocene nucleus, probably to complex nitrides of iron which are stable to above 700°C.

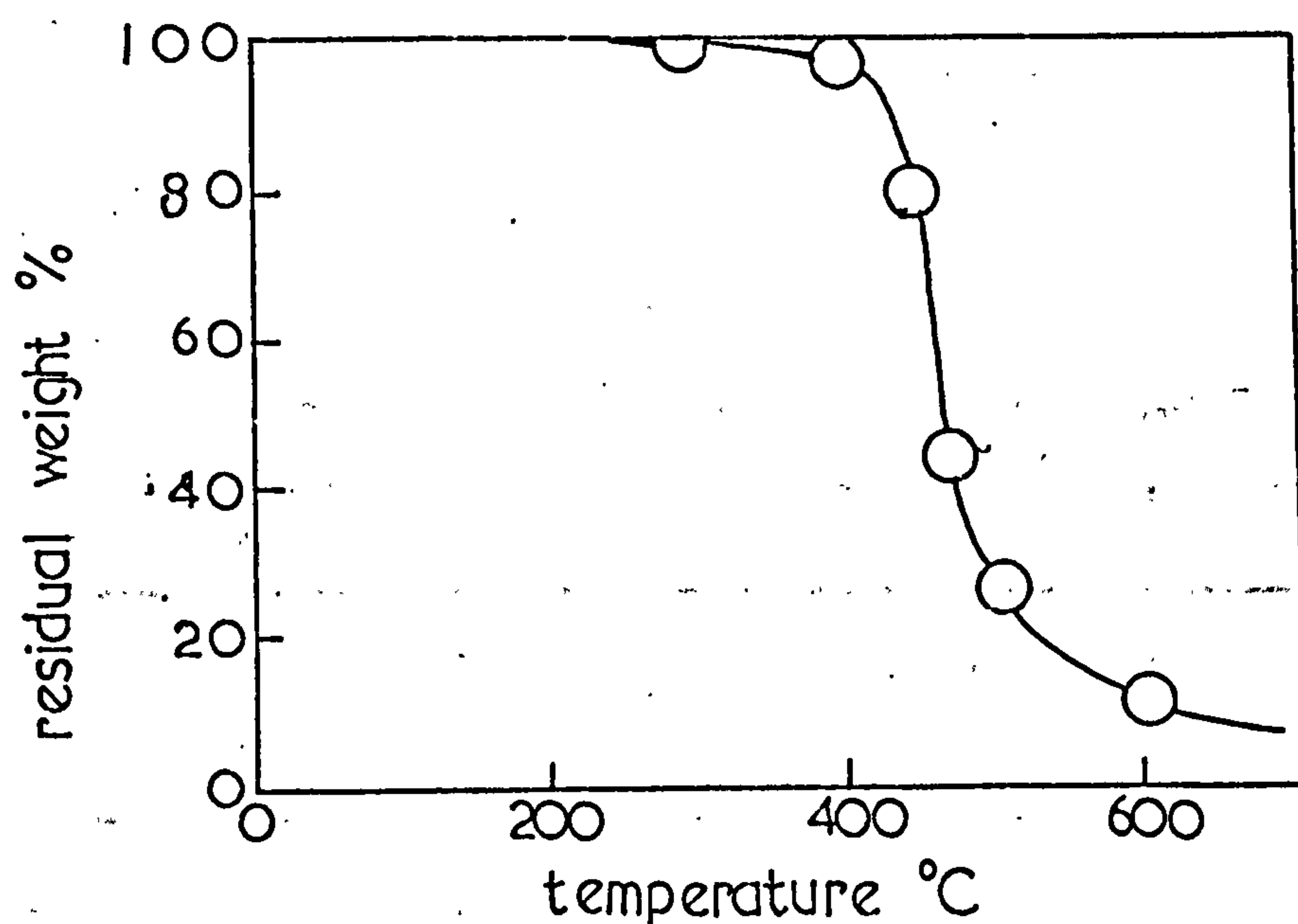


Fig 3-11. Plot of weight loss as a function of temperature for polyvinylferrocene heated at 64 deg.min.⁻¹ under nitrogen. $\bar{M}_n = 23,000$.

The thermogravimetric analysis of PVF is in good agreement with the results of Simonescu et al.³⁵ They report 52 % weight loss between 230 °C and 420 °C for PVF prepared by free radical mechanism. The lower apparent stability in comparison with this study can be ascribed to different experimental parameters particularly heating rate.¹⁵⁷

The activation energy for the decomposition of PVF between 270°C and 430°C was determined by differential scanning calorimetry using the method of Rogers and Morris.¹⁵⁸ The data were obtained from the distances measured between the reaction curve and the scanning base line at associated absolute temperatures. This distance is proportional to the rate of heat evolution at that temperature which in turn is proportional to the rate constant. Thus, from a plot of log. distance versus reciprocal temperature, the activation energy is obtained from the slope of the straight line in the usual manner. Values of d and K obtained from the DSC curve are shown in Table 3-11 whilst a plot of $\log d$ against $1/K$ is given in Fig. 3-12.

Table 3-11

Kinetic Data from Thermal Decomposition Curve of Polyvinylferrocene.^a
Sample Scanned at 64 deg. min⁻¹ in hermetically sealed sample pans.

temperature K	$1/K$ $\times 10^3$	distance, d mm	$\log_{10} d$
585	1.709	2.0	0.301
602	1.661	3.8	0.579
620	1.613	5.5	0.742
635	1.575	8.0	0.903
652	1.534	11.0	1.041
668	1.497	13.9	1.143
690	1.449	21.2	1.326

^a $\bar{M}_n = 28,000$

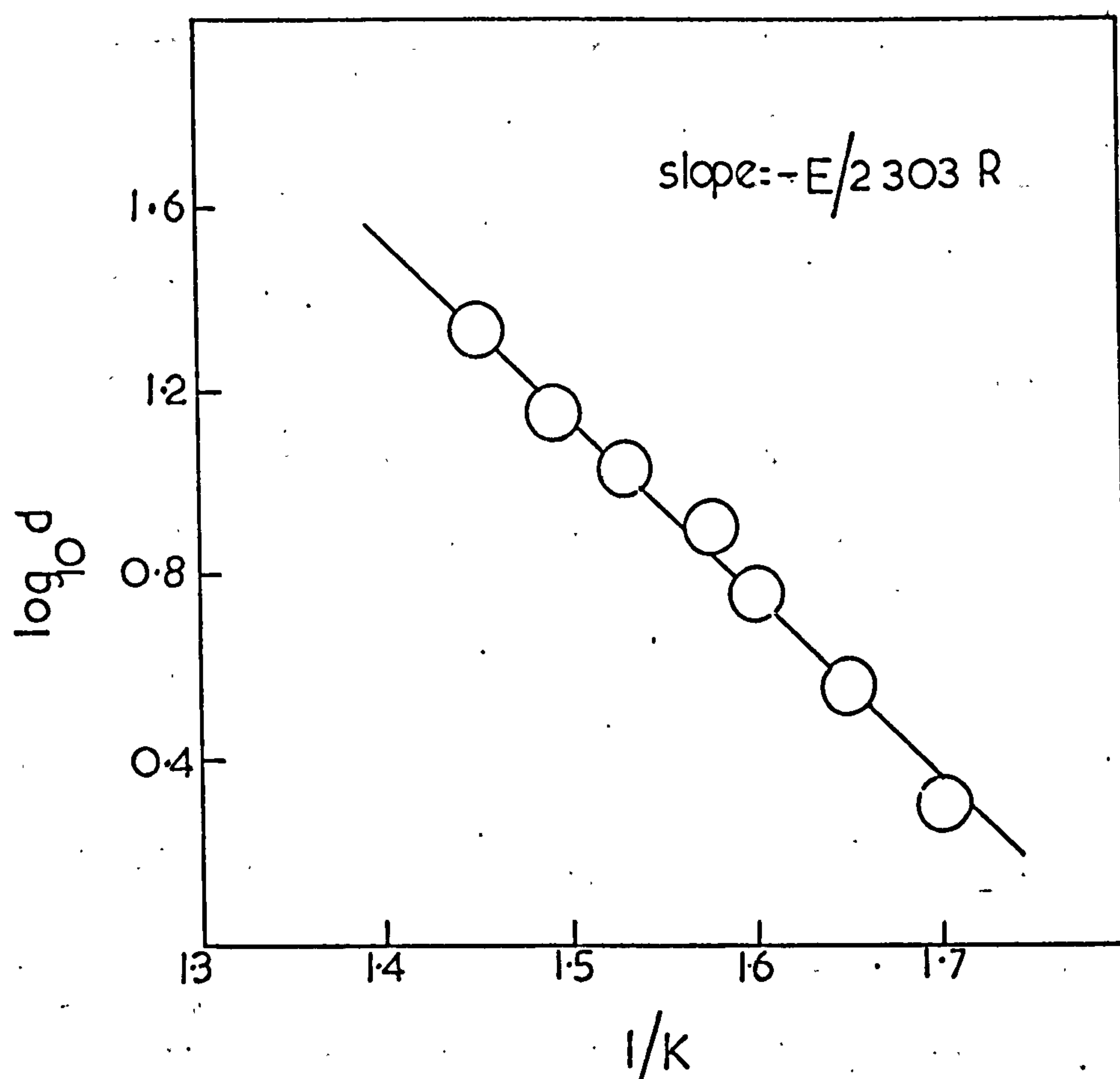


Fig 3-12. Plot of $\log_{10} d$ as a function of $1/K$ for the decomposition of polyvinylferrocene.

$\bar{M}_n = 28,000$. Sample heated at 64 deg.min.^{-1} in hermetically sealed pans.

From the gradient of the straight line in Fig. 3-12 the activation energy for the decomposition of polyvinylferrocene between 270°C and 430°C was found to be : $E_A = 73 \pm 5 \text{ kJ mol}^{-1}$. This value is more than double that reported by Simonescu et al.³⁵ They found E_A for the decomposition of PVF between $230\text{--}420^\circ\text{C}$ to be 35 kJ mol^{-1} . For comparison, the activation energy for the decomposition of polystyrene is 138 kJ mol^{-1} between $240\text{--}270^\circ\text{C}$.¹⁵⁹

From a structural point of view, it might be expected that the activation energy for the degradation of PVF should be higher than polystyrene. The low values might, in part, be explained by the relatively low molecular weights of the polymers examined ($\bar{M}_n = 28,000$ in the present study).

As expected, the activation energy for the thermal degradation of polyferrocene (a polymer which contains the ferrocene rings in its backbone) is considerably higher than that for PVF which only contains pendent ferrocene groups. Thus, $E_A = 172 \text{ kJ mol}^{-1}$ for polyferrocene decomposed between $200 - 400^\circ\text{C}$ ³⁵.

3.2.5 Molecular Weight Distribution

The molecular weight distribution of polyvinylferrocene was examined by gel permeation chromatography (GPC). Initial chromatograms obtained by GPC were recorded as a plot of concentration against elution volume. Some typical chromatograms of PVF isolated at $\sim 3\%$ conversion are shown in Fig. 3-13.

The mechanism of separation by GPC results in the higher molecular weight fractions being eluted first and therefore the molecular weight decreases from left to right in Fig. 3-13. The concentration of the species eluted was detected by a differential refractometer and is recorded as differential refractive index on the ordinate scale. The elution volume is shown for every 5 cm^3 eluted as a pulse on the chart record.

The molecules are separated by GPC according to their size in solution. Thus, Fig. 3-13 shows that the polymer samples isolated from the kinetic experiments have virtually identical size. This result is in agreement with the small variation in the number average molecular weights of these polymers when examined by VPO, (see tables 2-4, 2-5 and 2-6).

Fig. 3-13 also shows that the molecular weight distributions of the PVF samples are similar. All are relatively broad as expected for polymers prepared by free radical mechanisms. The curves are relatively symmetrical, suggesting that all the polymer has been fractionated. However, there is some indication of a small shoulder at the high molecular weight end.

Such a shoulder could be indicative of branching in the polymer since the size of a branched homopolymer molecule in solution is greater than its linear counterpart.¹⁶⁰ Branching does not normally occur at low conversions.¹²³ However, the high transfer constant of vinylferrocene (see section 2.6.4.2) suggests that branching could also be in the polymer even at low conversions.

Fig. 3-14 shows gel permeation chromatograms of two samples of PVF. Both polymers were prepared with $[M]_0 = 4.0 \text{ mol dm}^{-3}$ and $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$, under identical experimental conditions, except that they were isolated at different per cent conversions. The GPC data shows that the sample isolated at the higher conversion has a definite peak at the high molecular weight end of its distribution curve. The bimodal curve suggests that the polymer contains branched material. Since the conversion is still relatively low, ($\sim 5\%$), the presence of branching is in accord with the high transfer activity of vinylferrocene.

At higher conversions the bimodal nature of the GPC curve becomes much more pronounced. This result is shown in Fig. 3-15. Similar results have been obtained by Pittman et al^{36,84,136} who report that polyvinylferrocene becomes increasingly branched at high conversions of monomer to polymer.

As well as the qualitative examination of the GPC data, some attempt was made to obtain quantitative information.

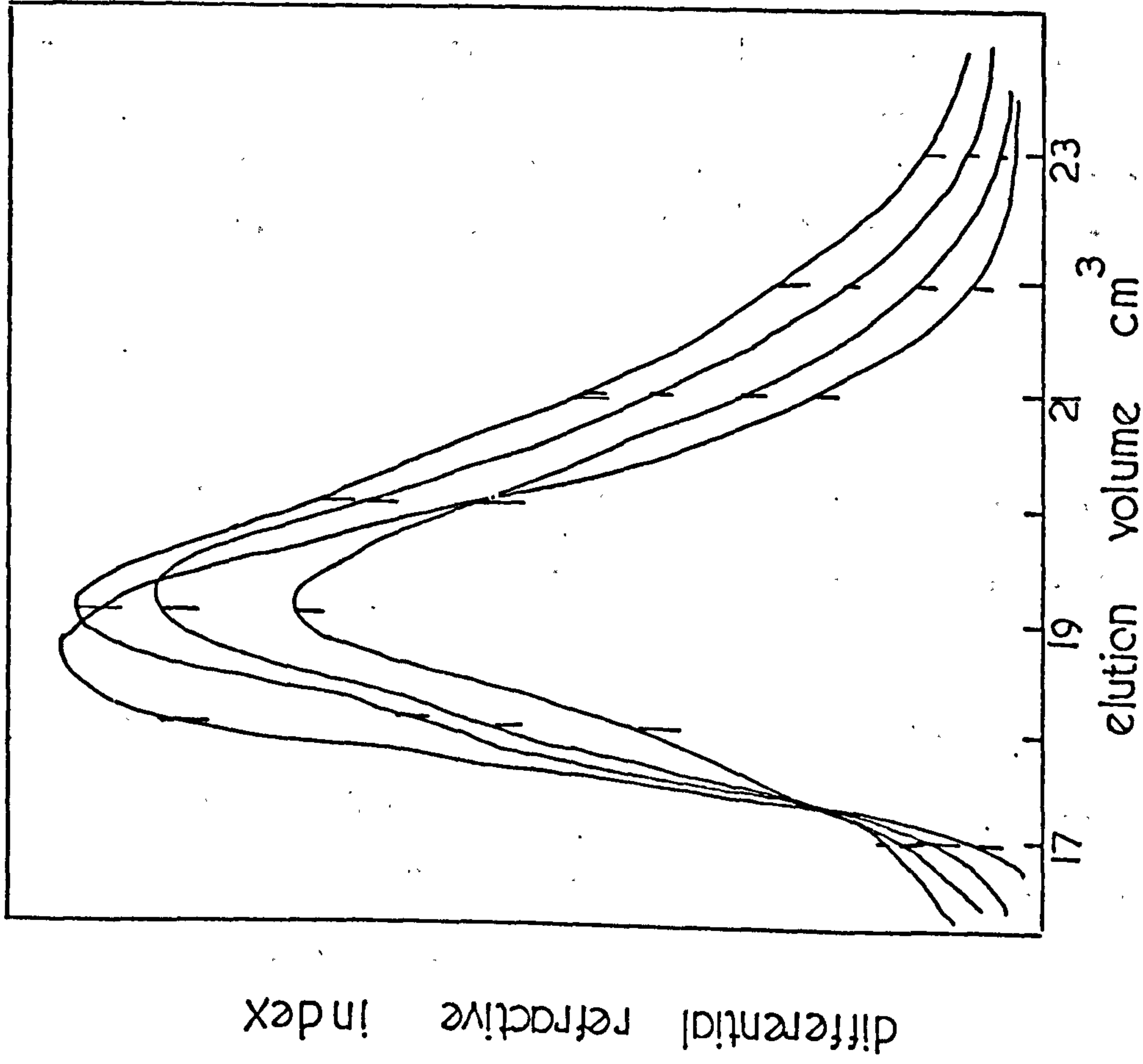


Fig 3-13. Typical GPC curves for polyvinylferrocene prepared by radical initiation in benzene at 60°C. Polymers isolated at 3% conversion. $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

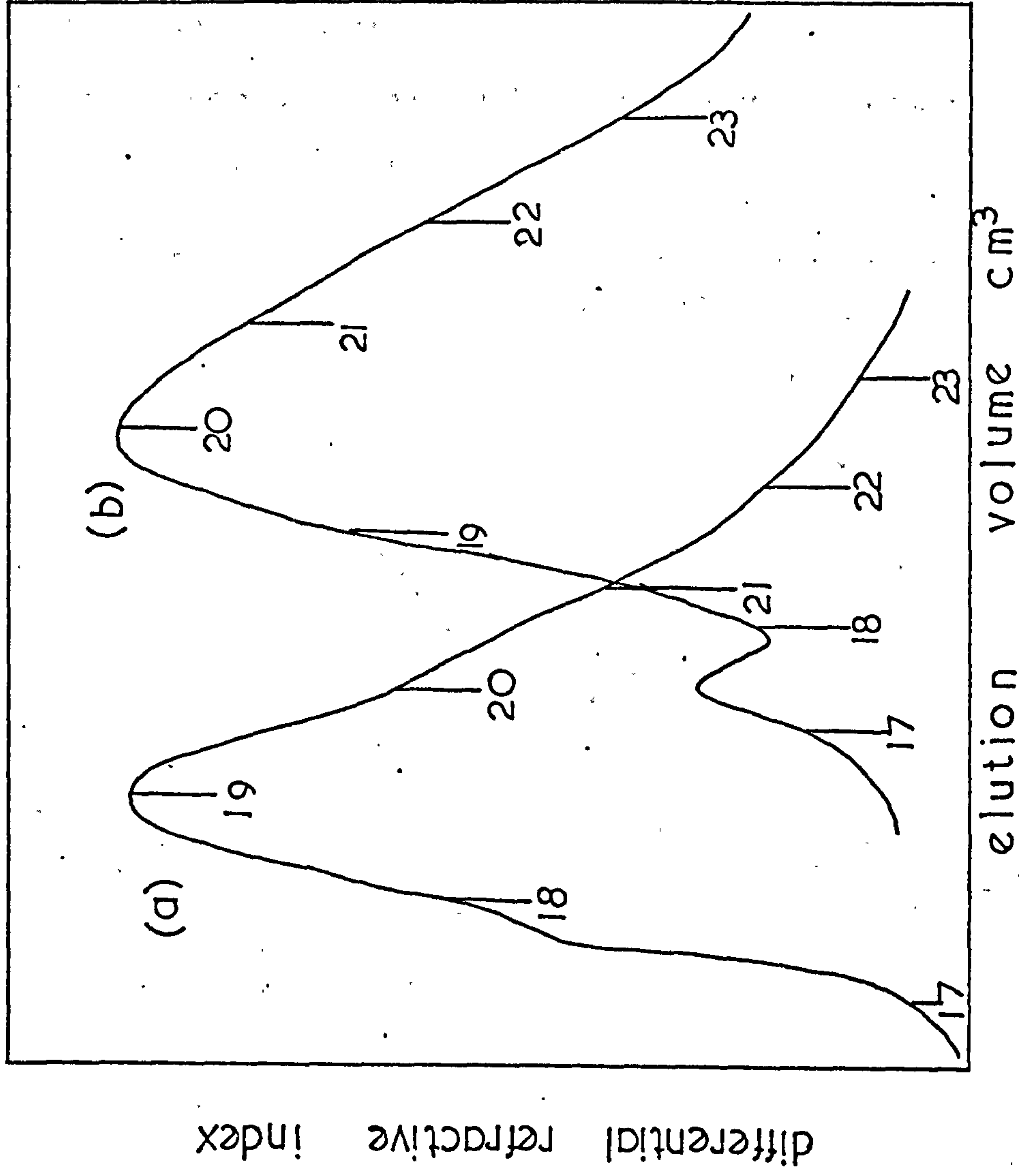


Fig 3-14. GPC curves for polyvinylferrocene showing appearance of second peak even at low percentage conversions (a) 1.8% conversion, (b) 5.4% conversion. $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ in both cases.

Specific molecular weights can only be determined by GPC from a calibration curve. The elution volume gives a measure of the size of the dissolved molecule.

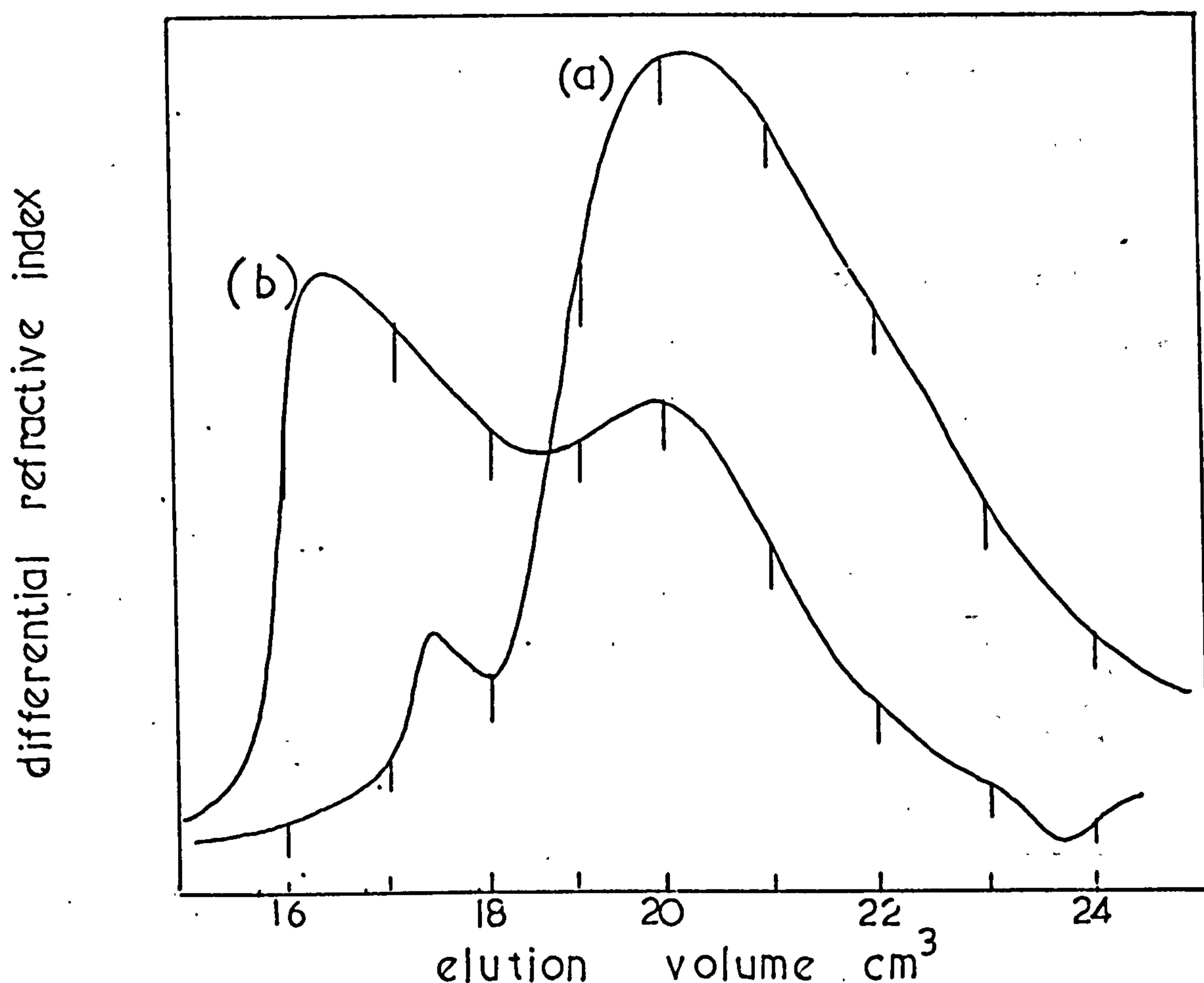


Fig 3-15. Gel permeation chromatograms of polyvinylferrocene showing effect of conversion on the bimodal nature of the curves. (a) 5.4% conversion; (b) 22% conversion. $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ for both samples.

Calibration is achieved by measurement of the peak elution volume of a standard fractionated polymer of narrow molecular weight distribution and known molecular weight. To date, the only calibration standard is polystyrene and a method of indirect calibration is used to convert from the polystyrene calibration to one applicable to the measured polymer. The interpretation of GPC data by this method is discussed in detail by Evans.¹⁶¹ The net result of this method is a true differential

molecular weight distribution curve from which the molecular weight parameters and the polydispersity indices can be calculated. The distribution curve is obtained as a plot of weight fraction per log molecular weight increment, $dw/d \log M$, against $\log M$.

This procedure was used to examine the polymers isolated above 10 % conversions. The molecular weight distribution curves are often bimodal and broad in agreement with branching in the polymers. The computer fit of the data from the chromatograms is given in Table 3-12 together with the number average molecular weights determined by an absolute method.

Table 3 - 12

Molecular Weights of Polyvinylferrcene. GPC at Ambient Temperature in THF. Data obtained by Universal Calibration with Polystyrene.

Mark-Houwink Constants for PVF³⁶. $K = 0.72 \times 10^{-4} \text{ } 100 \text{ cm}^{-3} \text{ g}^{-1}$, $\alpha = 0.72$ VPO at 37 °C in benzene.

$[M]_0$ mol dm ⁻³	$[In]_0 \times 10^2$ mol dm ⁻³	GPC $\bar{M}_n$ $\bar{M}_w$ $\bar{M}_w / \bar{M}_n$	VPO $\bar{M}_n$		
1.0	1.0	8,238	11,783	1.43	5,000
2.0	1.0	1,751	2,855	1.63	8,800
3.0	1.0	2,198	3,781	1.72	10,600
4.0	1.0	6,178	17,314	2.80	12,800
4.0	1.0	21,495	73,344	3.41	11,400
4.0	2.0	7,020	11,279	1.61	28,000
4.0 ^a	2.0	4,342	6,978	1.61	-
4.0 ^a	2.0	8,112	17,332	2.13	-
4.0 ^b	2.0	13,208	24,464	1.8	-
5.9 ^a	1.0	1,400	1,668	1.2	11,400
5.9 ^a	4.0	24,972	53,871	2.16	-

a benzene-insoluble fractions obtained in these polymerizations; only the benzene-soluble portion examined.

b partially insoluble in Tetrahydrofuran(THF).

Table 3-12 shows that the number average molecular weights obtained from GPC do not agree with those determined by VPO. In general, the values obtained from GPC are lower, although in some instances, this is reversed.

Pittman et al³⁶ have shown that the universal calibration method cannot be applied to the GPC data of polyvinylferrocene. Therefore, the GPC values in Table 3-12 must be error. However, there does appear to be similar trends in the GPC and VPO data insofar as $\bar{M}_n$ increases with $[M]_0$ and $[In]_0$ in the majority of cases.

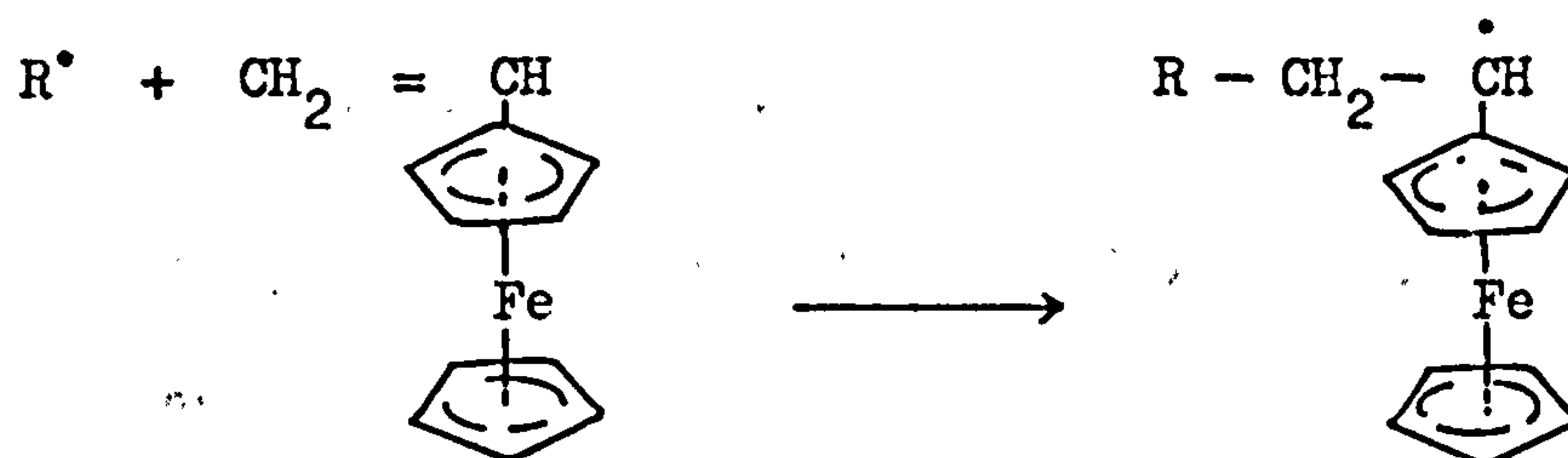
The polydispersity also tends to increase with increasing $[M]_0$. This effect is in agreement with the transfer activity of vinylferrocene. Thus, as the monomer concentration increases, transfer reactions could be more probable. This will result in a broader molecular weight distribution in the polymers prepared with a high initial monomer concentration.

The low polydispersity obtained when $[M]_0 = 5.9 \text{ mol dm}^{-3}$ and $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$ appears anomalous, since at such a high monomer concentration, transfer should occur readily. However, a value of $[M]_0 = 5.9 \text{ mol dm}^{-3}$ for vinylferrocene is equivalent to a bulk polymerization and hence the transfer activity may be altered in comparison with solution polymerization. Also in this polymerization benzene-soluble and insoluble fractions were obtained and only the soluble portion could be examined. Therefore, the low dispersity in this sample can be attributed to causes other than a lack of branching.

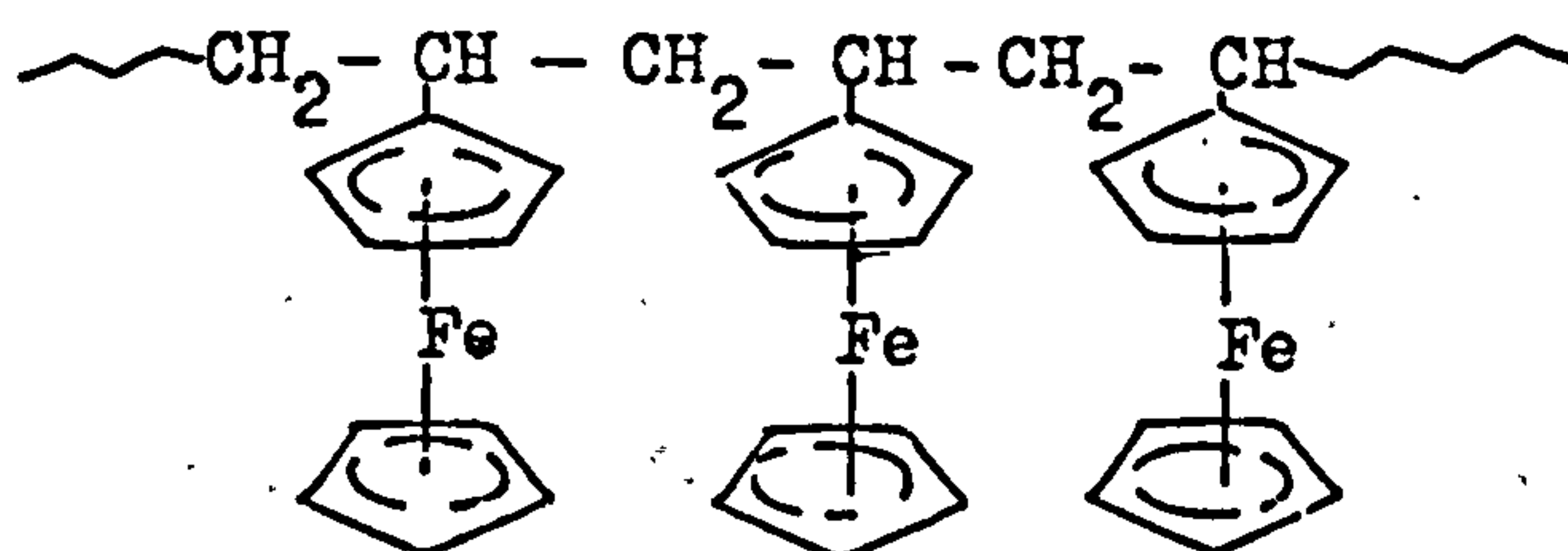
In general, the GPC results are acceptable although further work is required before the quantitative results can be regarded with confidence.

3.2.6 Structure of Polyvinylferrocene

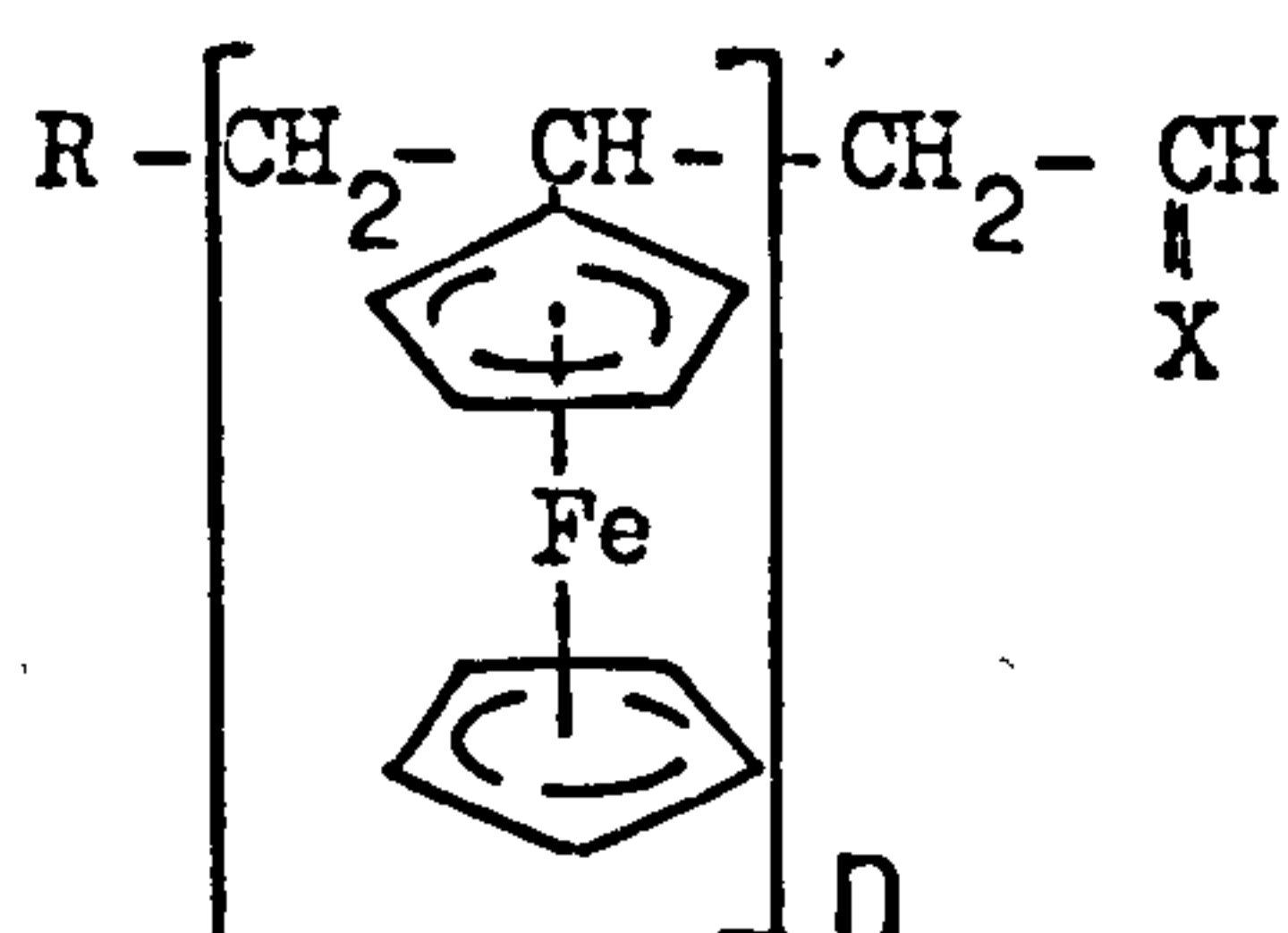
Addition of free radicals to vinylferrocene will occur to give a substituted ferrocenyl radical in the transition state.



This radical will be far more stable than one in which the unpaired electron is on the β carbon atom to the ferrocene substituent. This is expected because of the powerful electron releasing properties of ferrocene which stabilize adjacent electron deficient centres.⁸⁹ Successive addition will result in a typical vinyl polymer structure with the substituent on alternate carbon atoms i.e. the 1,3 or head-to-tail structure. Head-to-head addition is unlikely because of steric hinderance. Tail to tail addition is possible but the radical formed in the transition state will be relatively unstable.



Because of the monomolecular termination of the polymer radical, the terminal unit will differ from interchain units. Therefore, an idealized linear structure, ignoring all transfer reaction, will be

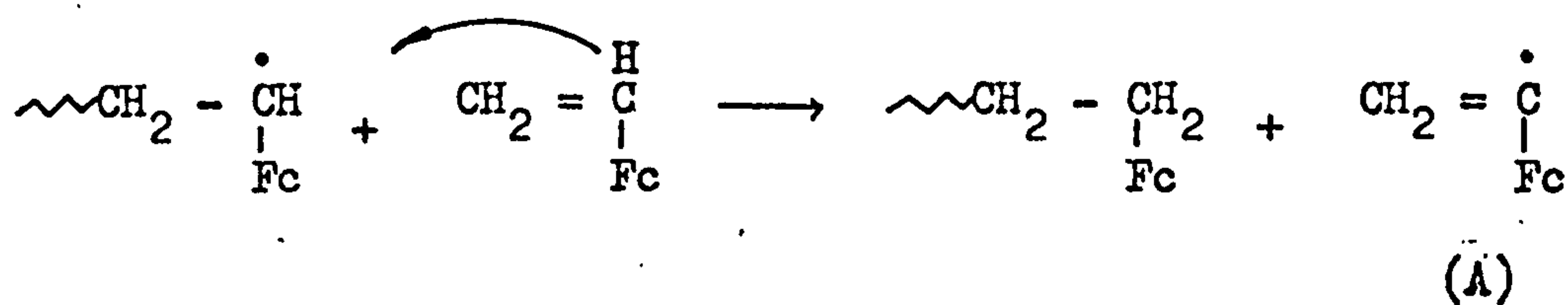


where R represents $(\text{CH}_3)_2(\text{CN})\text{C}-$ and X the Fe(III) high spin complex.

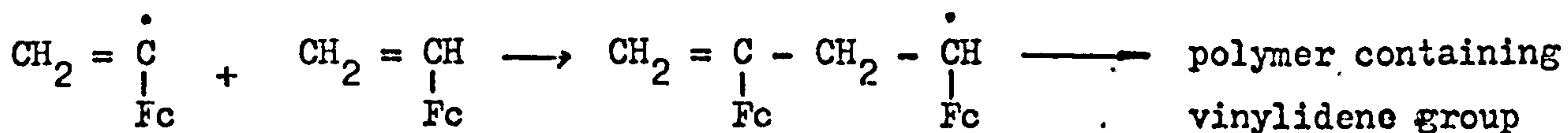
The infrared spectrum of PVF indicates the presence of unsaturation in the polymer. The absorptions at 920 cm^{-1} and 885 cm^{-1} have been ascribed to the presence of a vinylidene grouping in the polymer. Such a group is readily introduced by chain transfer reaction. Thus hydrogen abstraction from the monomer and reinitiation by the resultant radical will produce a polymer containing a $\text{CH}_2 = \text{CR}_1\text{R}_2$ grouping.

In the following scheme the ferrocenyl group ($\text{C}_{10}\text{H}_9\text{Fe}$) is represented by Fc .

(i) hydrogen abstraction from monomer:-



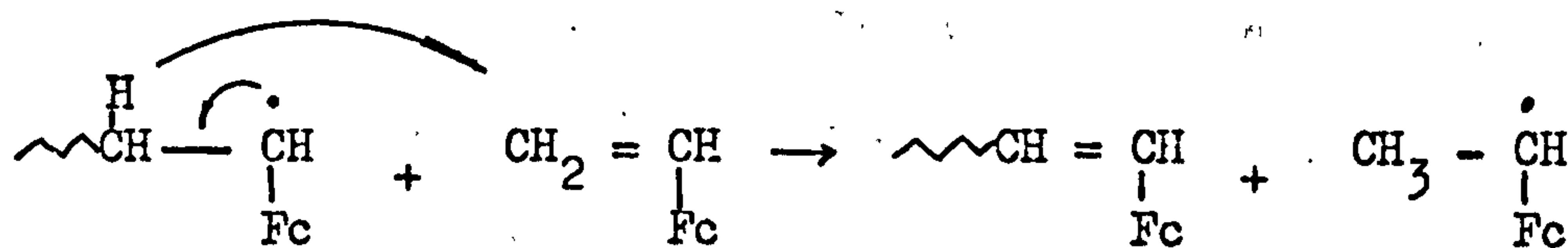
(ii) reinitiation by the α -ferrocenyl radical



The α ferrocenyl radical, species (A), will be stable because of resonance interaction with the ferrocene ring and the aliphatic double bond. Therefore hydrogen abstraction from vinylferrocene will be highly favoured. Thus, the very high transfer activity of vinylferrocene may be ascribed to the formation of this relatively stable species. However, the radical will not be so stable that it does not reinitiate further polymerization reactions.

The infrared spectrum also contains bands which may be due to a trans disubstituted ethylene group. Hydrogen abstraction is feasible from the methylene group adjacent to the chain radical centre.

Therefore, the following reaction can occur:-



The resultant polymer molecule would then contain a disubstituted ethylene group. However, abstraction of the methylene hydrogen is not as probable as abstraction from the carbon atom carrying the ferrocene substituent. The resultant radical may also reinitiate polymerization.

The presence of a vinyl group in the polymer is less likely. The introduction of this group would require a hydrogen abstraction from the ferrocene ring of the monomer followed by reinitiation. Although this reaction is possible, it is unlikely that it will compete with abstraction of the hydrogen from the α carbon atom of vinylferrocene. Also the infrared spectrum does not indicate any absorptions due to the vinyl group.

The above discussions indicate that molecules of polyvinylferrocene may contain the following structural units. These are presented in tabular form in Table 3-13.

In Table 3-13, the structural units are depicted in linear polymer molecules. This is, of course, an oversimplification, since if transfer to monomer is high, transfer to polymer will also be high and branching in the polymer structure will result.

Branching is usually disregarded in vinyl polymers isolated at low percentage conversions and of low degrees of polymerization. For example, the transfer constants to monomers and polymers are generally less than 10^{-4} . Thus, only one non-linear unit should be produced for each 10^4 monomer units polymerized, unless the conversion is taken

Table 3 - 13

Possible Structural Units in Polyvinylferrocene Prepared by Free

Radical Polymerization in Benzene at 60°C . $R = (CH_3)_2 \dot{C}(CN)$; $Fc = C_{10}H_9Fe$; $X = Fe(III)$ high spin complex.

initiating radical	termination step	structural unit
$(CH_3)_2 \dot{C}(CN)$	intraelectran*	$R - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH_2 - \begin{array}{c} CH \\ \\ X \end{array}$
"	H abstraction from monomer	$R - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH_2 - \begin{array}{c} CH_2 \\ \\ Fc \end{array}$
"	H abstraction from polymer	$R - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH = \begin{array}{c} CH \\ \\ Fc \end{array}$
$CH_2 = \begin{array}{c} \dot{C} \\ \\ Fc \end{array}$	intraelectran	$CH_2 = \begin{array}{c} C \\ \\ Fc \end{array} - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH_2 - \begin{array}{c} CH \\ \\ X \end{array}$
"	H abstraction from monomer	$CH_2 = \begin{array}{c} C \\ \\ Fc \end{array} - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH_2 - \begin{array}{c} CH \\ \\ Fc \end{array}$
"	H abstraction from polymer	$CH_2 = \begin{array}{c} C \\ \\ Fc \end{array} - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH = \begin{array}{c} CH \\ \\ Fc \end{array}$
$CH_3 - \begin{array}{c} \dot{CH} \\ \\ Fc \end{array}$	intraelectran	$CH_3 - \begin{array}{c} CH \\ \\ Fc \end{array} - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH_2 - \begin{array}{c} CH \\ \\ X \end{array}$
"	H abstraction from monomer	$CH_3 - \begin{array}{c} CH \\ \\ Fc \end{array} - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH_2 - \begin{array}{c} CH_2 \\ \\ Fc \end{array}$
"	H abstraction from polymer	$CH_3 - \begin{array}{c} CH \\ \\ Fc \end{array} - \left[\begin{array}{c} CH_2 - CH \\ \\ Fc \end{array} \right]_n - CH = \begin{array}{c} CH \\ \\ Fc \end{array}$

* intramolecular electron transfer

beyond 75 per cent.¹⁶² If the $\overline{DP}$ does not exceed ca. 10^4 , most of the polymer molecules will be linear and the structure unaffected by transfer reactions.

The main exception to this generalization is vinyl acetate. The transfer constant to monomer and polymer is high in this system. Therefore, transfer and branching occur in PVA at low percentage conversions and low degrees of polymerization.¹³³ Polyvinylferrocene appears to be similar to PVA in this respect.

Thus, GPC of polyvinylferrocene has shown the presence of branching in polymers isolated below 5 % conversion. As the concentration of polymer increases (i.e. at high conversions) the branching is even more pronounced. Therefore, transfer to polyvinylferrocene must be an important reaction. Since the transfer constant to vinylferrocene is high, a high transfer activity to polymer is expected¹³³.

Elemental analysis of the polymer also suggests that the polymer is not completely linear. Some representative iron contents are recorded in Table 3-14. At low conversions ($< 3\%$) the iron contents are in agreement with a linear polymer structure of repeat unit $(C_{12}H_{12}Fe)_n$ proposed by Arimoto and Haven.²⁵ (Calc. C = 67.96 % ; H = 5.71 % Fe = 26.33 % not corrected for the presence of end groups.)

At higher conversions, the iron contents are invariably lower. Similar results have been obtained by Pittman et al^{34,136}. They attribute the low iron content to the method of analysis.

Transfer to polymer will most probably occur by abstraction of the hydrogen atom from the carbon atom carrying the ferrocene substituent. This reaction is most probable because of the lability of this hydrogen atom plus the fact that the resultant radical will be relatively stable.

Table 3 - 14

^a
Iron Contents of PVF. Polymers prepared at 60 °C in Benzene;

$$[\text{AIBN}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$$

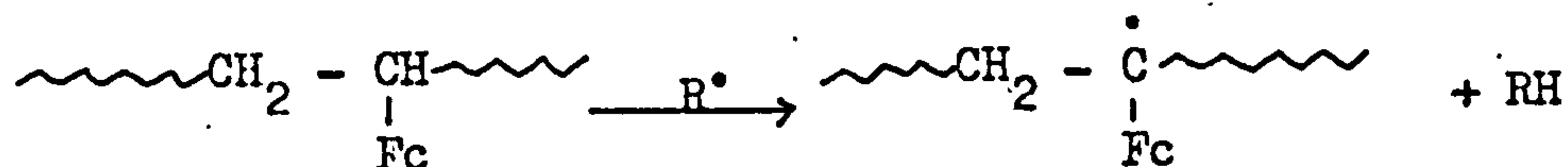
$[\text{M}]_0 \text{ mol dm}^{-3}$	conversion %	iron content %	
3.0	2.2	26.1,	26.2
4.0	1.6	26.4,	26.3
4.0	1.8	26.3,	26.3
4.0	7.0	23.6,	23.7
3.0 ^b	4.9	23.6,	23.5
2.0	10.0	23.4,	23.6
1.0	15.0	23.4,	23.1
5.9	20.0	22.4,	22.5
5.9 ^c	20.0	23.0,	22.4

a determined by polarography

b prepared at 70 °C

c benzene-insoluble fraction

Thus, the following reaction can be envisaged:



Subsequent polymerization reactions at this radical will cause branching of the polymer chain. This transfer reaction has recently been suggested by Pittman et al³⁵ to account for branching in PVF. To explain the insolubility of PVF, they also suggest that such reactions eventually produce crosslinked polymer. However, this branching process is not in itself capable of generating an infinite network structure, although a given molecule may be reactivated any number of times with subsequent branching.¹⁶²

In fact, although PVF isolated at high conversions is insoluble in benzene, it is still readily soluble in chloroform which suggests that the polymer is not crosslinked. This is to be expected, since a branched polymer should remain soluble and fusible in the absence of other processes.

The structure of polyvinylferrocene is not simple, therefore. As well as containing the possible units listed in Table 3-13, the molecules are non-linear and will be highly branched especially at high conversions.

This complex structure may well explain some of the anomalous solution properties of PVF. For example, the Mark Houwink constants in benzene³⁵ are $K = 0.64 \times 10^{-4} \text{ 100 cm}^3 \text{ g}^{-1}$ and $\alpha = 0.48$. Theoretically, however, the lowest limit of α is 0.5^{77} . Similarly,

high molecular weight polyvinylferrocene ($\bar{M}_n = 134,000$) has been found³⁵ to have very low intrinsic viscosities ($0.085 \text{ 100 cm}^3 \text{ g}^{-1}$). Also, PVF isolated at high conversions contains fractions which are insoluble in benzene, carbon disulphide DMF, THF, carbon tetrachloride, dioxan and other well known solvents. Yet these fractions are extremely soluble in chloroform.

Complex behaviour in solution has also been observed in the present study during VPO measurements and viscosity measurements. These effects will be discussed later. However, further work is required before the exact structure of PVF can be elucidated completely.

3.3 CONCLUSIONS FROM THE SPECTROSCOPIC AND PHYSICAL EXAMINATION OF POLYVINYLFERROCENE.

The results from the spectroscopic and physical examination of PVF are in excellent agreement with the results of the kinetic study of the polymerization reaction.

Thus, ESR spectroscopy has confirmed the presence of a paramagnetic species in PVF. Moreover, the concentration of this species has been found to vary with the average degree of polymerization of the polymer. Therefore, the predictions implicit in the kinetic scheme postulated for the radical polymerization of vinylferrocene (see Section 2.7.2) have been substantiated.

Mössbauer spectroscopy has confirmed the participation of an iron atom of a ferrocene nucleus in the monomolecular termination of PVF. The polymer contains iron in an Fe (III) state as well as iron, formally as Fe (II), in the ferrocene nuclei. The paramagnetic species is not a ferricenium cation but appears to be an ionic complex

of Fe (III) in a high spin configuration. The Mössbauer results also show that there is a quantitative relationship between the concentration of this species and $\overline{DP}$ in agreement with the ESR results.

A value of the magnetic moment of PVF was not obtained. However, the magnetic susceptibility measurements show that there are no oxidized impurities in the polymer. Negative results for ferric ions were also obtained from PVF in standard chemical tests. Further, the polymer does not exhibit any electrical conduction properties. These results confirm that the paramagnetism is intrinsic to the polymer molecule as required by the kinetic scheme.

In accord with the high transfer activity of vinylferrocene and PVF, infrared spectroscopy shows the presence of unsaturation in the polymer. The absorption bands at 920 cm^{-1} and 885 cm^{-1} in the IR are characteristic of the vinylidene group, $\text{CH}_2 = \text{CR}_1\text{R}_2$.

Hydrogen abstraction from the carbon atom carrying the ferrocene substituent is a favourable reaction with vinylferrocene and may account for the high transfer constant of this monomer. This reaction, followed by reinitiation by the α ferrocenyl radical, $\text{CH}_2 = \dot{\text{C}}\text{Fc}$, has been postulated to explain the presence of the vinylidene group in PVF.

The high transfer activity of vinylferrocene is further supported by ultraviolet and visible spectroscopy which indicate that the amount of unsaturation increases at high monomer concentrations.

Unfortunately, an exact interpretation of the unsaturated groups in the polymer by NMR spectroscopy was not possible due to paramagnetic broadening of the spectra.

The high transfer constant of the monomer suggests that transfer with the polymer will also occur readily. Thus, a similar hydrogen abstraction from an α carbon in the polymer chain followed by addition

at this point will produce branching in the polymer. This suggestion is supported by the GPC results which show branching of the polymer. In agreement with the expected high transfer activity of PVF, branching is evident at low conversions. At higher conversions the branching is more pronounced.

The structure of PVF is non-linear. Also, because of the structural units which can be introduced by transfer reactions and monomolecular termination, the structure is complex even at low conversions. Finally, the high T_g can be explained by the bulky nature of the ferrocene group whilst the thermal stability of the polymer is in accord with its structure.

3.3.1. Possible Mechanisms for the Termination Step in the Polymerization of Vinylferrocene.

The kinetics of the polymerization of vinylferrocene and the spectroscopic examination of the polymer have been discussed. It is now possible to postulate a mechanism for the termination reaction.

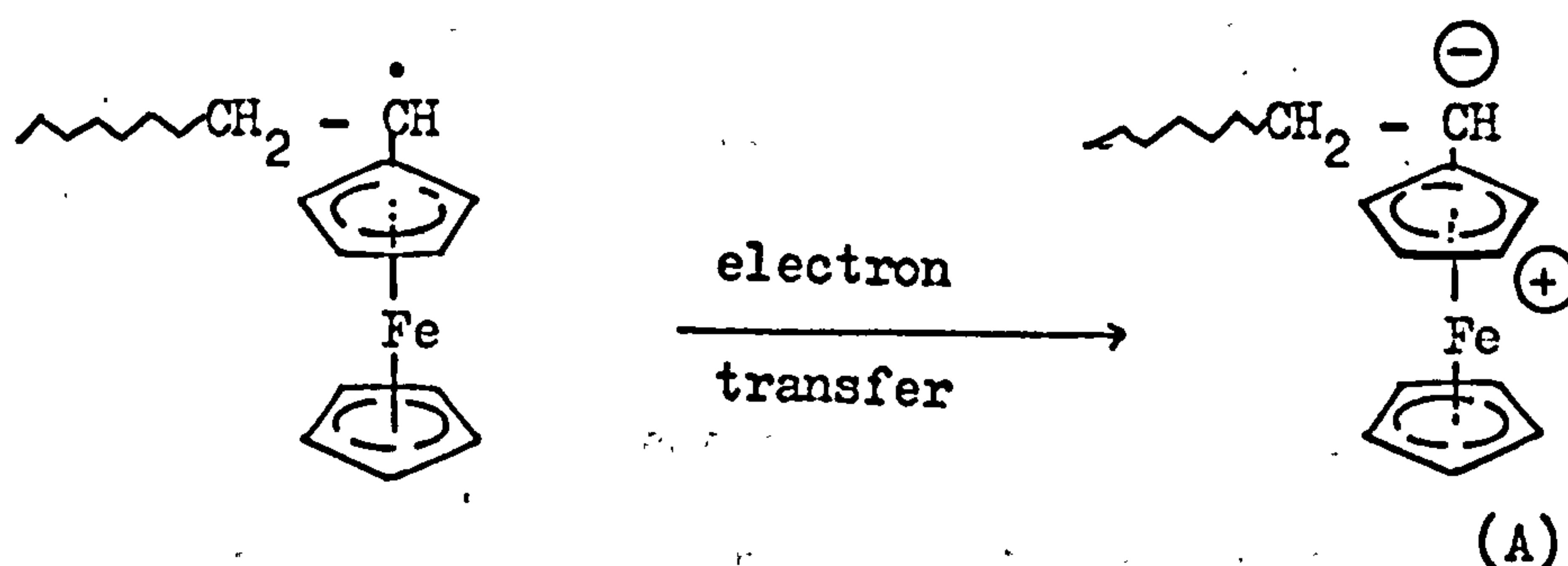
The initial rate of polymerization of vinylferrocene initiated by AIBN in benzene at 60 °C is first order in initiator concentration and monomer concentration. This rate dependence is readily explained by an intramolecular termination of the growing polymer chain radical. Such a reaction will also be monomolecular with respect to the chain radical. The resultant odd electron species which will be produced in the above reaction must be inactive in further polymerizations, as required by the first order dependence between the overall rate and the rate of initiation.¹⁶³ Thus, this termination step is different from a transfer reaction where reinitiation of the polymerization reaction takes place.

The Mössbauer results show that PVF contains an Fe (III) species. The oxidation state of the iron atom in ferrocene can be regarded formally to be Fe (II)¹⁶⁴. Therefore, an electron must have been lost from a ferrocene nucleus in the polymer chain to explain this result.

One of the most characteristic features of all metallocenes is their facile oxidation to a cationic species by loss of one or more electrons.¹⁻⁶ The ease and the extent of electron transfer between metallocenes and electron acceptors is very much dependent upon the oxidation-reduction potentials of the reactants. However, such is their reactivity that complete electron transfer occurs even with acceptor molecules of only moderate electron affinity.¹⁻⁴

Henrici - Olivé and Olivé¹⁶⁵ claim that the electron affinity of most polymer chain radicals is similar to that of compounds such as o-chloranil or tetracyanoethylene (TCNE). Moreover, ferrocene undergoes complete electron transfer with o-chloranil⁷⁴ and forms a charge transfer with TCNE⁷³.

Hence, an electron transfer from a ferrocene nucleus on the PVF chain to the chain radical will occur readily. Thus, the following reaction can be envisaged.



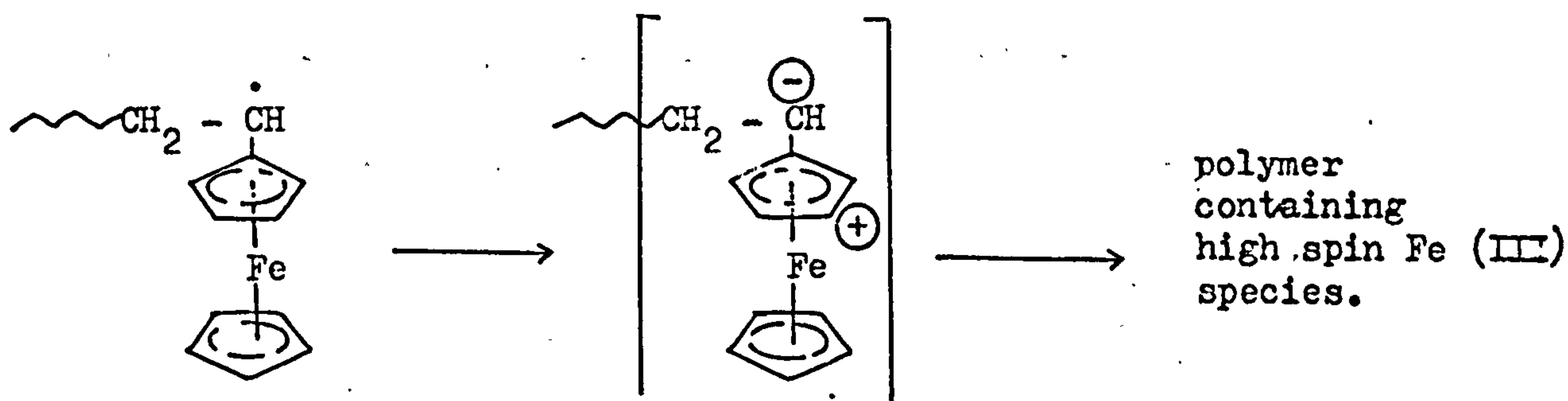
Normally, loss of an electron from ferrocene results in the formation of the ferricenium cation. The cation is characterized by

strong colours in solution¹⁶⁶ and a high reactivity towards free radicals.^{63,64} . These reactions have not been observed in the polymerization of vinylferrocene. Furthermore, ESR and Mössbauer spectroscopy show that the ferricenium cation is not present in the isolated polymer.

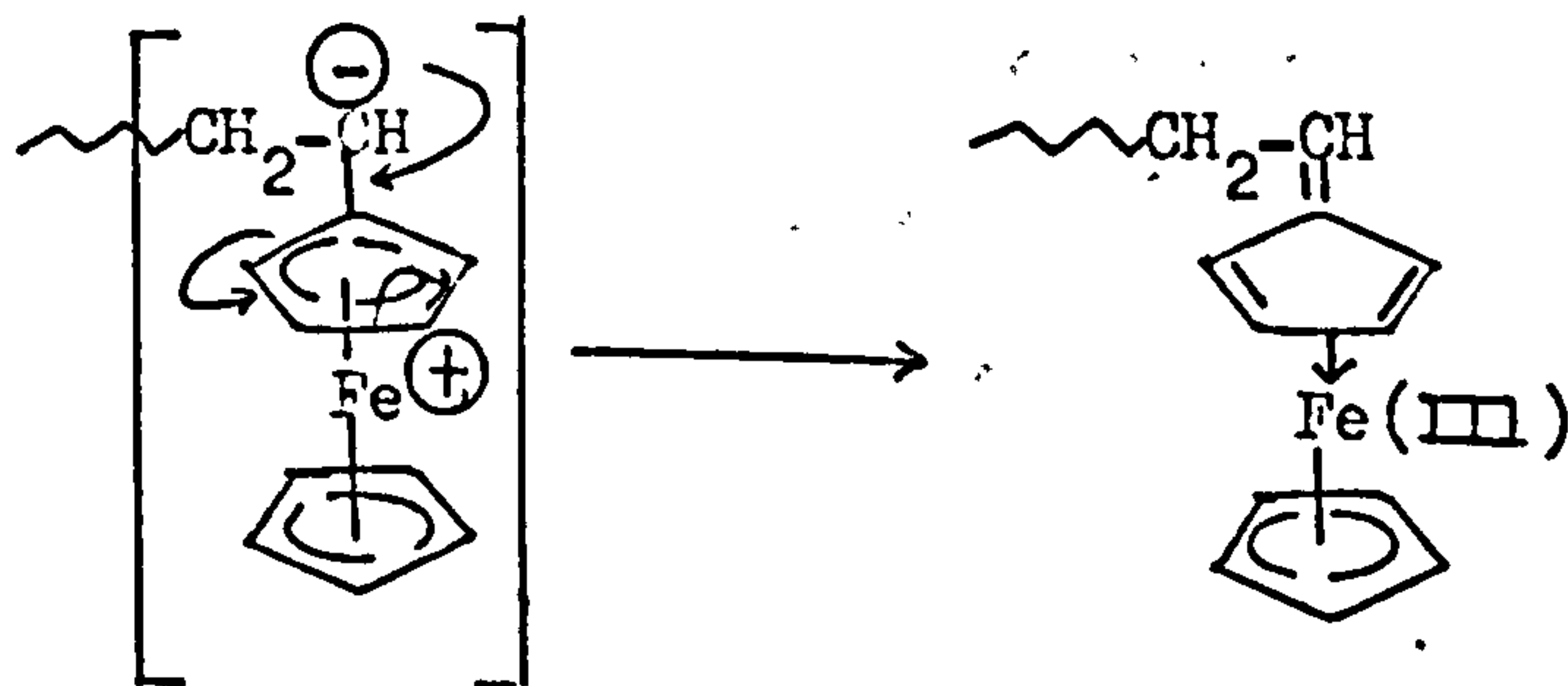
Therefore, species (A), which can be regarded as a ferricenium cation, appears to be present as a transition state only. This conclusion is in accord with the instability of the ferricenium cation in organic solutions.^{1,52}

Golding and Orgel⁵² have shown that organic solutions of ferricenium cations decompose to give iron (III) compounds. Therefore, it seems that after the initial electron transfer which terminates the polymer chain, the cation immediately undergoes further reaction to give a high spin Fe (III) species. This reaction is in accord with the results of the spectral analysis of PVF. Furthermore, the resultant odd electron species will be inactive in further polymerization reactions in accordance with the kinetic results.

The overall mechanism for the termination reaction may be depicted as follows:-



No attempt has been made to investigate the bonding between the chain carbon atom and the Fe(III) species but a redistribution of the electrons could readily form a double bond.



The first order rate constant for the initial electron transfer reaction will be high. For example, the rate constant for the mixed valence system biferrocene $\text{Fe(II) Fe(III) picrate}^{167}$ is $1.3 \times 10^{10} \text{ s}^{-1}$. It is unlikely that the termination reaction is controlled by such a high rate constant, since the rate constant for the termination reaction was estimated to be between 3.0 and 60.0 s^{-1} (see section 2.6.6.)

It is probable therefore, that the mechanism of the reaction involves a rate determining step during which the reactants are brought within an acceptable distance or take up a suitable configuration for the electron transfer reaction. Thus, k_t will be a composite constant.

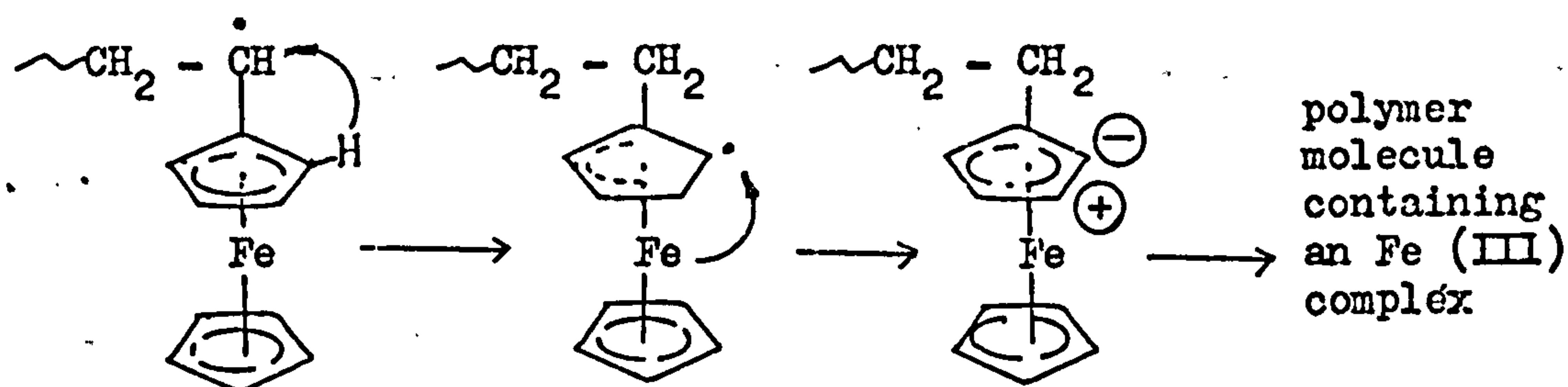
Termination by electron transfer is well known in radical polymerizations of vinyl compounds and has been demonstrated by many workers.¹⁶⁸⁻¹⁷⁰ However, in all these polymerizations, an added species, normally a metal halide, has been involved in the termination reaction. The chain radical, therefore, undergoes an intermolecular reaction.

In the vinylferrocene system the electron transfer reaction takes place between the chain and a species (in this case a ferrocene group) on the same polymer chain. Hence, the polymer chain radical is terminated by an intramolecular electron transfer reaction.

Thus, vinylferrocene is unique in comparison with other vinyl monomers. Furthermore, this study appears to be the first one which has reported intramolecular electron transfer termination of a polymer chain radical.

Direct electron transfer from the ferrocene nucleus is the most probable mechanism for the termination reaction, since electron transfer is fundamental to the chemistry of ferrocene. However, it is possible that a hydrogen abstraction reaction may precede the electron transfer.

Hydrogen abstraction from the polymer backbone can be precluded, since the resultant radical would still be active. However, hydrogen abstraction from the ferrocene ring followed by electron transfer from the iron atom would satisfy the kinetic requirements. Thus, the following reaction can be envisaged.



Hydrogen abstraction from the ferrocene ring is an important reaction in ferrocene chemistry. For example, Korshak and Nesmeyanov¹⁷¹ utilize this reaction to synthesize polyferrocenylenes. These reactions occur at elevated temperature ($> 200^{\circ}\text{C}$). However, Neuse and Rosenberg¹⁷² consider that at lower temperatures, the ferrocene ring will be as susceptible to hydrogen abstraction as benzene is. Therefore, such a reaction may occur in the polymerization of vinylferrocene at 60°C .

In conclusion, the mechanism of the termination step involves an electron transfer from the iron atom of a ferrocene nucleus. However, further work is required to ascertain whether the ferrocene nucleus involved is the terminal unit or an interchain unit, or whether a hydrogen abstraction reaction precedes the electron transfer.

4. POLYMERIZATION OF VINYLFERROCENE TO HIGH CONVERSIONS

It has been shown in the previous chapters that vinylferrocene does not polymerize to a high molecular weight linear polymer. The kinetic studies were confined to low conversions of monomer to polymer. Further studies were concerned with the polymerization of this monomer to high conversions and an examination of the properties of the resultant polymer.

4.1. EXPERIMENTAL

Vinylferrocene was polymerized in benzene at 60°C using AIBN as initiator. All materials were purified as described in Section 2.1. Reactions were carried out in sealed glass vessels after degassing the reactants by three freeze-pump-thaw cycles at 10^{-4} mm Hg. The reaction times were varied between 10 hours and 240 hours. The polymers were isolated by precipitation in methanol as before (Section 2.3.3) and the yields determined gravimetrically.

In some polymerizations, benzene-insoluble polymer was obtained. In these cases, after pouring the contents of the reaction vessels into methanol, the isolated polymer was stirred for 24 hours in benzene. The benzene-insoluble polymer was then collected on a sintered glass crucible (porosity No.4), washed repeatedly with benzene and finally dried to constant weight at 70°C, 0.1 mm Hg. The remaining benzene-soluble polymer was reprecipitated into methanol, collected, washed and dried as previously described.

The polymers were characterized by elemental analysis, infrared and ultraviolet spectroscopy, and gel permeation chromatography. (See section 2.4) . Where applicable, other techniques described in Section 2.4 were also used to examine the polymers.

4.2 RESULTS AND DISCUSSION OF POLYMERIZATION TO HIGH CONVERSIONS

4.2.1 Effect of Experimental Conditions on Conversion

The effects of varying the reaction time and initial monomer and initiator concentration on the percentage conversions of monomer to polymer are shown in Table 4-1.

In general, the yield of polymer is increased with time, as expected. Some anomalous results can be ascribed to inhibition of the polymerization reaction. Unlike dilatometry, gravimetric experiments give no indication of inhibition. Hence, gravimetry is not a generally reliable method for determining rates of polymerizations, unless inhibition reactions are unimportant. This is not the case with vinylferrocene, which is very prone to inhibition. However, the rates of polymerization in the gravimetric experiments are in reasonable agreement with those obtained by dilatometric measurements.

In Fig. 4-1 the per cent conversion is plotted against time for two sets of conditions. Fig. 4-1 shows that the percentage conversion is higher for the higher initiator concentration at any given time. Approximately the rate of polymerization is doubled by doubling the initiator concentration. This result is in accord with the dependence between the initial rate of polymerization and the initiator concentration.

The rate is linear only at low conversions and decreases with time. In these experiments there was no evidence for autoacceleration of the rate up to conversions of 55 %, even though the viscosities of the reactants became very high. For example, after 60 hours the reactants were solid at 60°C.

A well known phenomenon in vinyl polymerizations is an increase in rate as the conversion increases. This effect, often known as the

Table 4 - 1

Conversions of Polyvinylferrocene Obtained from Polymerizations With Varying Reaction Times, $[M]_0$ and $[In]_0$. All Reactions Performed at 60°C in Benzene.

$[M]_0$ mol dm ⁻³	$[In]_0 \times 10^2$ mol dm ⁻³	reaction time hours	conversion ^a %
1.0	1.0	20	8.4
"	"	23	9.9
"	"	43	16.9
"	"	45	17.3
"	"	46	18.5
"	"	62	8.9
"	"	66	23.4
2.0	"	44	10.4
3.0	"	42	7.4
"	"	90	8.8
4.0	"	26	7.2
"	1.5	44	12.5
"	"	69	16.9
"	2.0	10	20.0
"	"	24	32.3
"	"	24	33.8
"	"	48	42.7
"	"	68	54.9

^a includes benzene-insoluble material

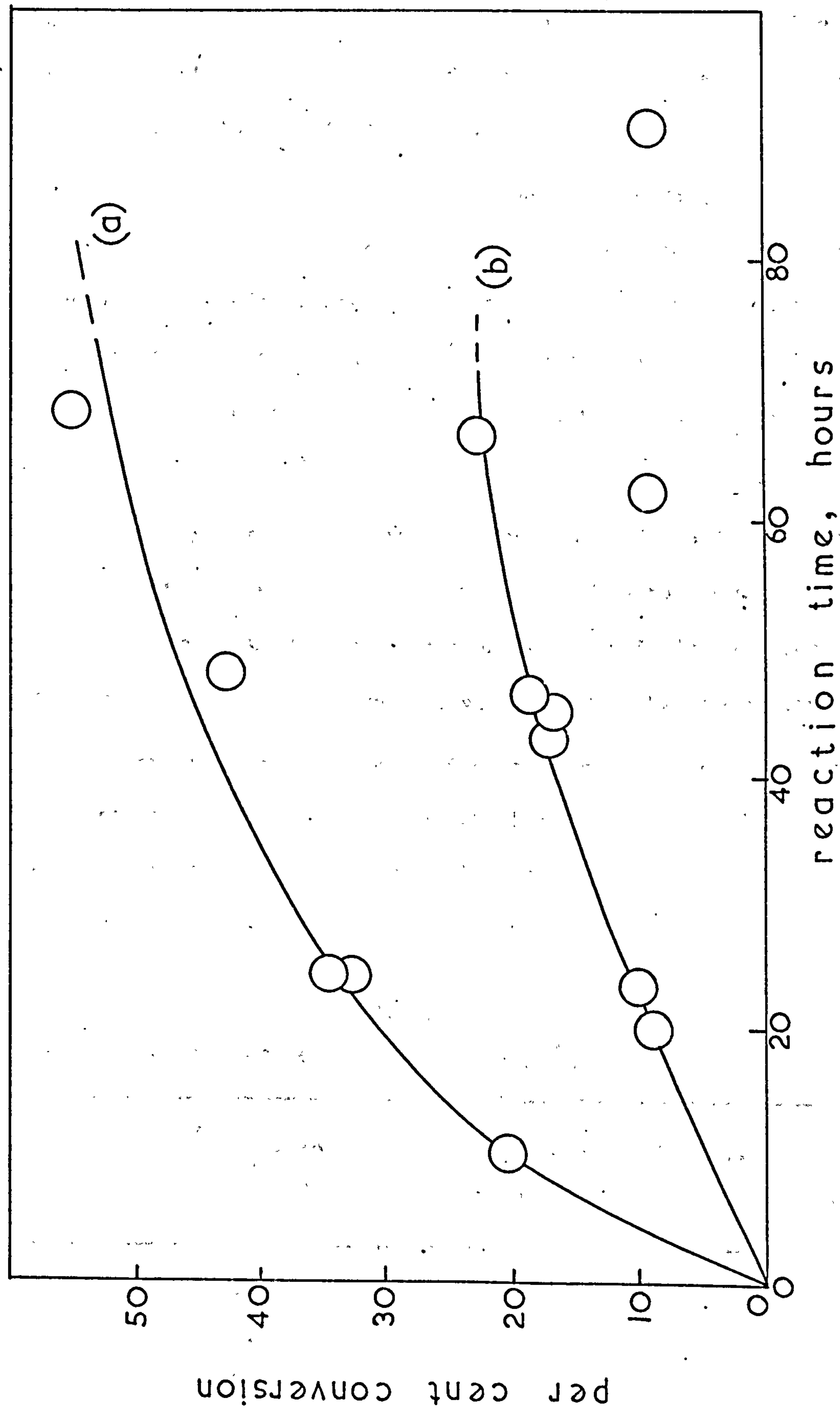


Fig 4-1. Per cent conversion as a function of time for polyvinylferrocene prepared in benzene at 60°C in the presence of AIBN. (a) $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $[In]_0 = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$; (b) $[M]_0 = 1.0 \text{ mol dm}^{-3}$, $[In]_0 = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$.

gell effect, has been ascribed to a decrease in the rate of termination which becomes diffusion controlled in the increasingly viscous medium.¹⁷³ This is possibly an oversimplification since North, Hughes and Reed¹⁷⁴ have shown that termination reactions can be diffusion controlled even before sufficient polymer has been formed in the system to increase the viscosity to a certain critical level.

The above considerations on the effects of diffusion on rates are for normal vinyl polymerizations in which the termination step is bimolecular. Therefore, the two reactants must approach each other in order to react. Since vinylferrocene undergoes a monomolecular termination, it might be expected that diffusion effects on the rate of termination will be negligible.

Thus, the absence of autoacceleration when $[M]_0 = 4.0 \text{ mol dm}^{-3}$ is in accord with the polymerization mechanisms of this monomer. The rate will also tend to decrease because of a reduction in $[M]$ and $[In]$ at high conversions as well as the effects of increased viscosity on the propagation reaction.

These conclusions are supported by bulk polymerization. Some typical results are shown in Table 4-2. Even at high initiator concentrations, and protracted reaction times, the conversions are still relatively low.

Table 4 - 2

Bulk Polymerization of Vinylferrocene at 60°C

$[M]_0$ mol dm ⁻³	$[In]_0 \times 10^2$ mol dm ⁻³	reaction time, hours	conversion %
5.9	1.0	43	23
"	4.0	240	40.8
"	8.0	40	52.3

In the reaction with $[In]_0 = 1.0 \times 10^2 \text{ mol dm}^{-3}$ the reaction mix remained fluid at 60°C . The others became solid within 40 hours. The low yield after 240 hours reaction indicates all reaction had ceased in this solid matrix. Increasing the temperature to 80°C resulted in a higher yield in similar bulk polymerization studies¹³⁶ which supports this suggestion. However, 'dead-end' polymerization may also explain the low yields obtained after long reaction times²⁰⁰.

4.2.2 Heterogeneous Polymerization at Low Monomer Concentration

In the polymerization reactions with a low monomer concentration, $[M]_0 = 1.0 \text{ mol dm}^{-3}$, the solutions became cloudy after 24 hours at 60°C . Further reaction resulted in the formation of a yellow precipitate in the bottom of the reaction vessel, the amount of which increased with time. Surprisingly, most of the polymers isolated from these reactions were soluble in benzene, although traces of insoluble material were present in some cases. Presumably, polyvinylferrocene is insoluble in certain molar ratios of benzene and vinylferrocene.

The same effect was not observed in reactions with higher monomer concentrations, although the dark colour of these reactions may have masked the formation of any precipitate.

For a typical polymerization with $[M]_0 = 1.0 \text{ mol dm}^{-3}$ and a total volume of 5.0 cm^3 , 1.0598 g of vinylferrocene is dissolved in 4.158 cm^3 of benzene and the solution is quite pale. When $[M]_0 = 4.0 \text{ mol dm}^{-3}$, 4.2394 g vinylferrocene is dissolved in 1.63 cm^3 benzene and the solution is dark brown. However, no precipitation occurred when $[M]_0 = 2.0 \text{ mol dm}^{-3}$ in which the solution is relatively clear. This suggests that the effect is quite specific to lower monomer concentrations.

The polymers obtained from reactions with low monomer concentrations have low molecular weights. The concentration of the terminal unit

produced by the electron transfer, is therefore relatively high. Since this unit is an ionically bound $\text{Fe}(\text{III})$ complex, it may impart some polar characteristics to the polymer molecule which cause precipitation in benzene.

At the higher monomer concentrations, the molecular weights of the polymers are higher and the relative polar effect of the terminal unit will be smaller. Hence, the polymers do not precipitate.

However, it is also possible that polyvinylferrocene is more soluble in its own monomer than in benzene.

The effects of precipitation on the overall rate of polymerization was not studied. However, Fig. 4-1 suggests that the presence of an extra phase has no effect on the polymerization reaction. Thus, the curve of conversion against time for $[M]_0 = 1.0 \text{ mol dm}^{-3}$ follows closely the curve in which no precipitation occurred. ($[M]_0 = 4.0 \text{ mol dm}^{-3}$)

Normally, heterogeneous polymerization produces marked increases in the rate of polymerization of vinyl monomers. This result is ascribed to the fact that many, if not all, of the polymer radicals are precipitated from the liquid phase during growth.¹²³ This 'trapping' of the radicals usually has a greater effect on termination than propagation. Thus, propagation continues whereas bimolecular termination is restricted and therefore the rate of polymerization increases.

However, in the polymerization of vinyl ferrocene the polymer is only precipitated after termination. Hence, trapping of the chain radicals does not occur. The negligible effect of the presence of solid polymer on the rate is therefore in agreement with the mechanisms of polymerizations.

4.2.3. Effect of Conversion on the Solubility of PVF

Polyvinylferrocene isolated at low conversions is completely soluble in benzene. However, benzene-insoluble polymer is formed in increasing amounts, as the percentage conversion of monomer to polymer increases. Some typical results are given in Table 4-3, which shows that at conversions above 40 % an appreciable amount of benzene-insoluble polymer was isolated from the polymerization reaction.

Table 4 - 3

Amount of Benzene-Insoluble PVF Obtained from Polymerizations to High Conversions. All Reactions at 60°C.

$[M]_0$ mol dm ⁻³	$[In]_0 \times 10^2$ mol dm ⁻³	conversion per cent	benzene-insoluble fraction %
1.0	1.0	17.4	trace
4.0	2.0	32.3	0
"	"	33.8	0
"	"	42.7	17.5
"	"	54.9	37.3
5.9	1.0	23	10
"	4.0	40.8	20.2
"	8.0	52.3	30.0

The small amounts of benzene-insoluble polymer obtained below 20 % conversion in reactions with low monomer concentrations, might be due to some polar effects in these polymers. At higher monomer and initiator concentrations, some other effects seem to be causing the

formation of benzene-insoluble polymers. The per cent of benzene-insoluble polymer is plotted against per cent conversion in Fig.4-2. This plot suggests that there is a linear relationship between the amount of benzene insoluble material and the per cent conversion.

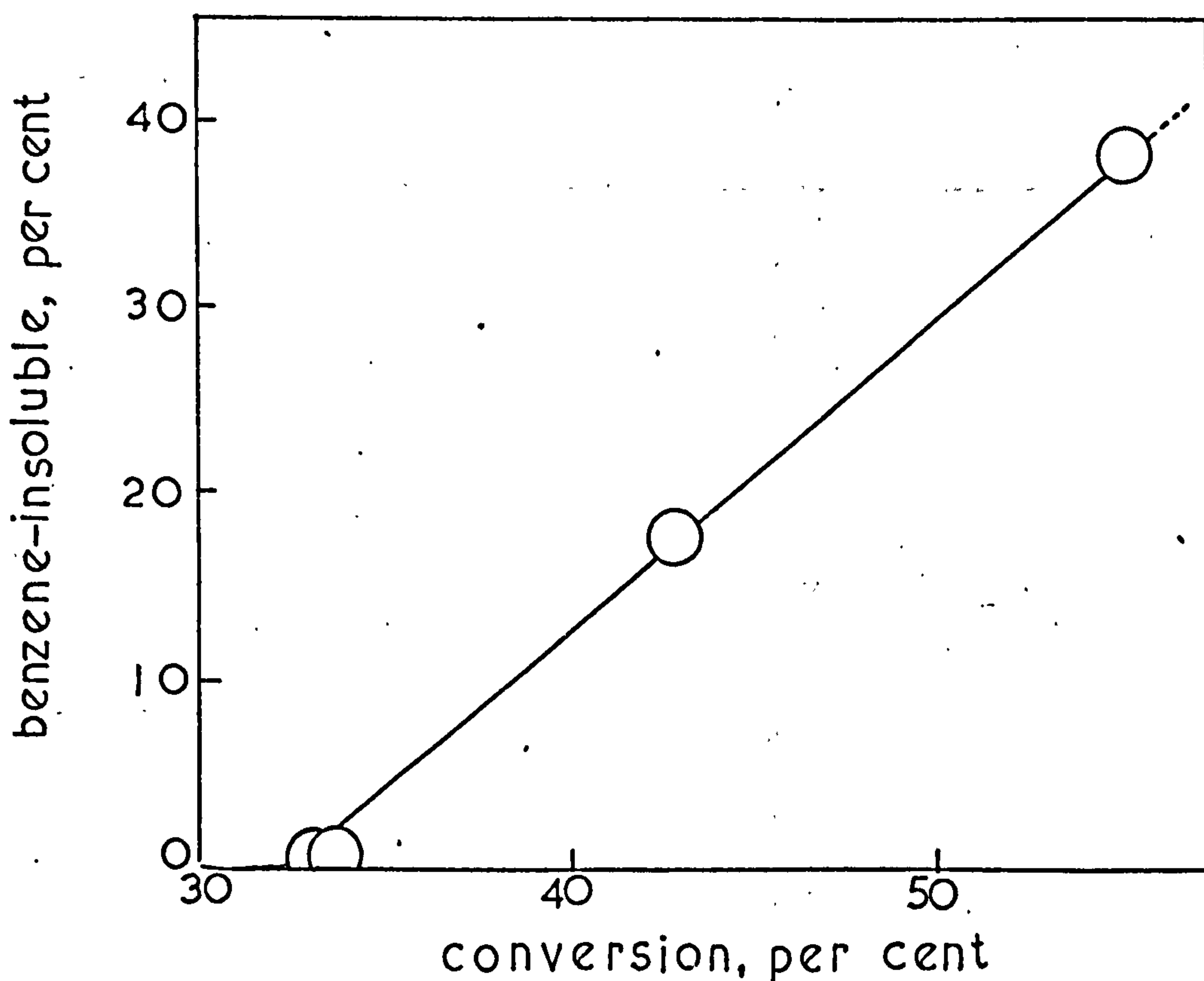


Fig.4-2 Per cent of benzene-insoluble polyvinylferrocene as a function of conversion from polymerizations of vinylferrocene in benzene at 60°C in the presence of AIBN. $[M]_0 = 4.0 \text{ mol dm}^{-3}$
 $[In]_0 = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$

It also appears that all the polymer will be insoluble in benzene at conversions above 90 %. Further work is required to confirm these suggestions.

The solubility of polyvinylferrocene obtained at high conversions was tested in a number of solvents. Pittman et al ³⁶ have reported that benzene-insoluble PVF is insoluble in all organic solvents. However, this conclusion is not supported by the results of the present study. The solubility of the benzene-insoluble fractions of PVF, obtained at high conversions, are recorded below.

Solubility of Benzene-Insoluble PVF Isolated from Polymerizations to High Conversions. Samples Shaken with Various Solvents for Twentyfour Hours at Room Temperature.

Solvent	Solubility
Benzene	insoluble
toluene	"
dioxan	"
DMSO	"
carbon disulphide	partly soluble
DMF	insoluble
carbon tetrachloride	"
THF	"
chloroform	readily soluble

It can be seen that the material is insoluble in the majority of solvents. With CS_2 a slight amount dissolved after shaking for 24 hours. However, with chloroform, the polymer dissolves immediately to give low viscosity, crystal clear solutions. The effect of chloroform is quite marked. For example, the polymer is insoluble in CCl_4 and methylene dichloride. The above results suggest that some specific type of complex formation is occurring between PVF and chloroform.

4.2.4 Structure of Benzene-Insoluble Polyvinylferrocene

The structure of the benzene-insoluble PVF was examined by elemental analysis, infrared spectroscopy and ultraviolet and visible spectroscopy.

Some typical results for the iron contents of the benzene-insoluble and benzene-soluble polymers isolated at high conversions are recorded in Table 4 - 4. In general, the iron contents of both fractions lay between 22 % and 24 %. These results suggest that both fractions have similar structures. The iron contents are lower than calculated for a linear $(-\text{CH}_2-\text{CHFc})_n$ repeat unit in accordance with the transfer activity of vinylferrocene.

Table 4 - 4

Iron Contents of Benzene-Soluble and Benzene-Insoluble Polyvinylferrocene Isolated at High Conversions ($> 20\%$)

$[M]_0$ mol dm ⁻³	$[In]_0 \times 10^2$ mol dm ⁻³	iron content %	
		benzene-soluble	benzene-insoluble
4.0	2.0	24.1, 23.2	23.1, 22.2
4.0	2.0	22.9, 23.0	22.0, 24.0
5.9	1.0	22.4, 22.5	23.0, 22.4
5.9	4.0	23.6, 23.1	24.2, 23.7

The infrared spectra of benzene-soluble and-insoluble samples are shown in Fig. 4-3. The spectra were examined as KBr discs and show that the two samples are identical. Similar spectra were obtained from all the samples.

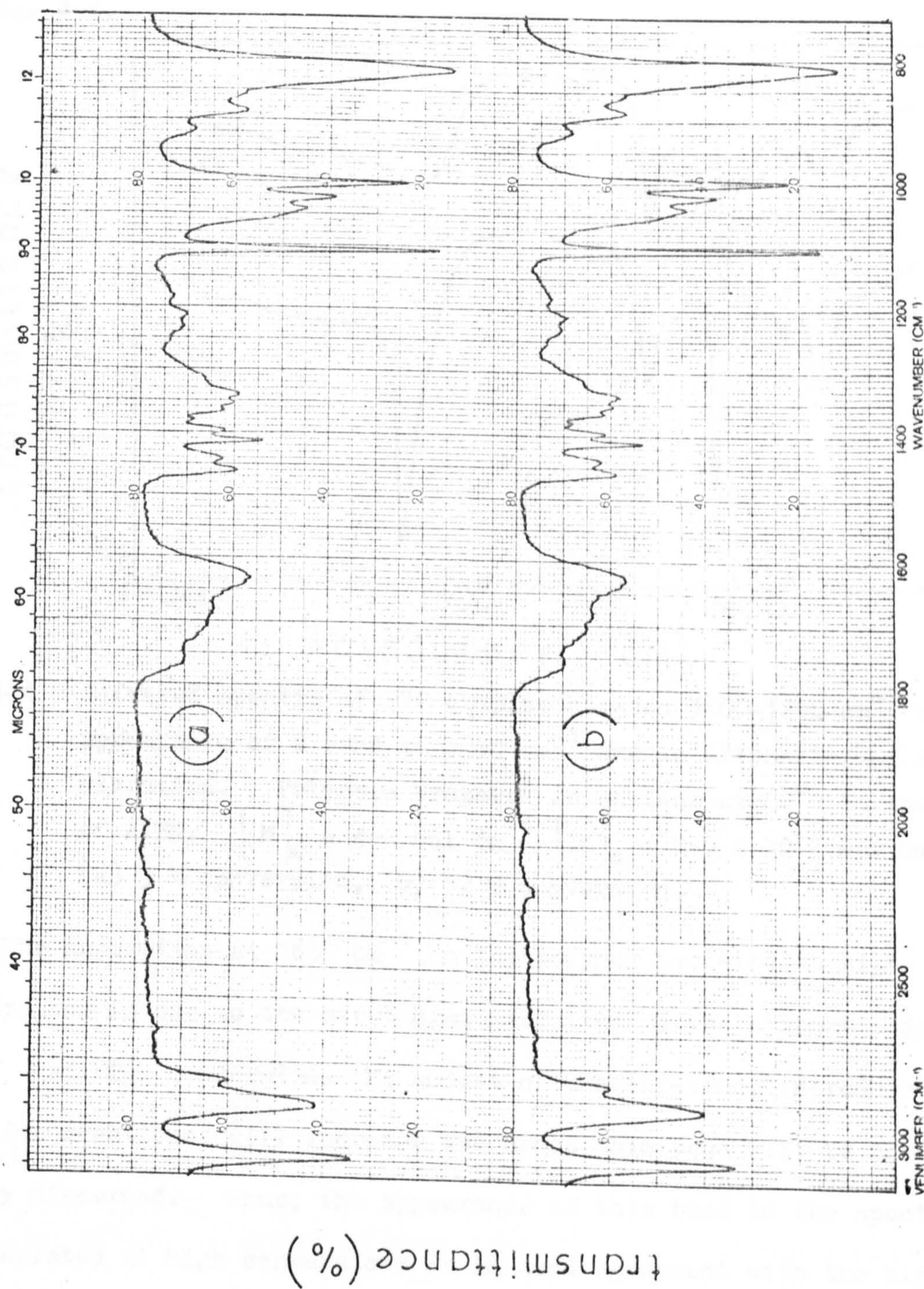


Fig 4-3. Infrared spectra of polyvinylferrocene samples examined as KBr discs. Polymer prepared by radical initiation in benzene at 60°C. $[M]_0 = 4.0 \text{ mol dm}^{-3}$, $[In]_0 = 2.0 \times 10^{-2} \text{ mol dm}^{-3}$ and isolated at 43% conversion. (a) benzene-soluble fraction, (b) benzene-insoluble fraction.

A comparison of Fig. 3-1 and Fig. 4-3 also shows that the spectrum of PVF isolated at low conversions is essentially the same as those obtained from PVF isolated at high conversions. The main difference is the appearance of a band near 1630 cm^{-1} in the spectra of the latter samples. This band is sharper in films cast from benzene as can be seen in Fig. 4-4.

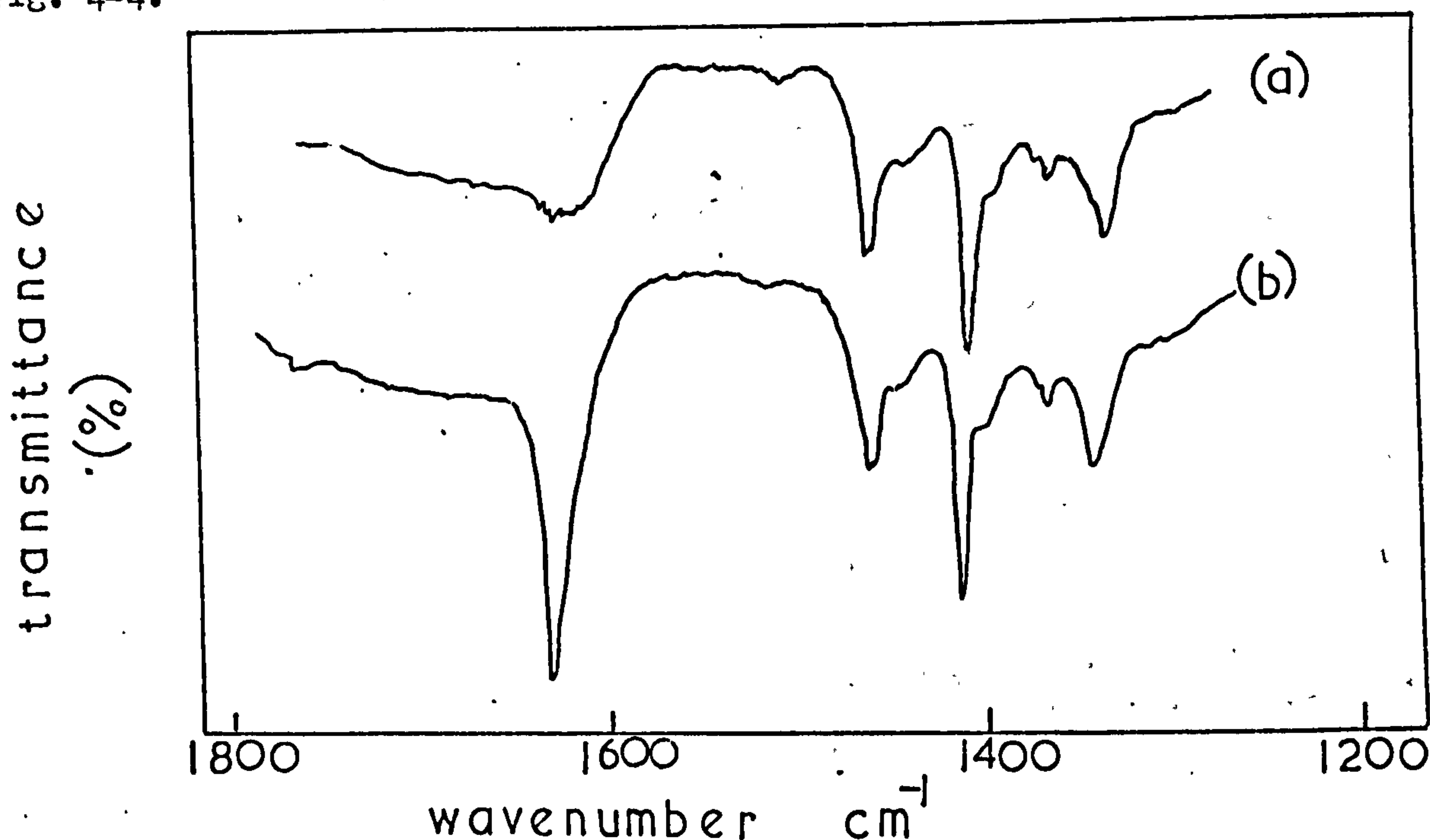


Fig. 4-4 Infrared spectra of PVF samples between $1800\text{--}1200\text{ cm}^{-1}$ showing the appearance of a band at 1630 cm^{-1} due to aliphatic $\text{C}=\text{C}$ stretching vibration. Polymers prepared in benzene at 60°C in the presence of AIBN. $[M]_0 = 4.0\text{ mol dm}^{-3}$ $[In]_0 = 2.0 \times 10^{-2}\text{ mol dm}^{-3}$
(a) 3 % conversion, (b) 32 % conversion.

The absorption at 1630 cm^{-1} in the polymer isolated at high conversions is due to the stretching vibration of the aliphatic double bond. At high conversions the amount of unsaturation, introduced by transfer reactions, will increase and hence this band will be more easily discerned. Thus, the appearance of this band in the spectra of PVF isolated at high conversions is in good agreement with the high transfer activity of the system.

The structure of the polymers prepared to high conversions appears to be very similar to that of polymers isolated at low conversions apart

from the increase in the absorptions near 1630 cm^{-1} . This conclusion is applicable to the benzene-soluble and-insoluble fractions. Therefore, in agreement with the iron contents, the IR results indicate that both fractions have the same type of structure.

The UV/visible spectra of the polymers were examined in chloroform since both fractions are completely soluble in this solvent. Typical spectra are shown in Fig. 4-5.

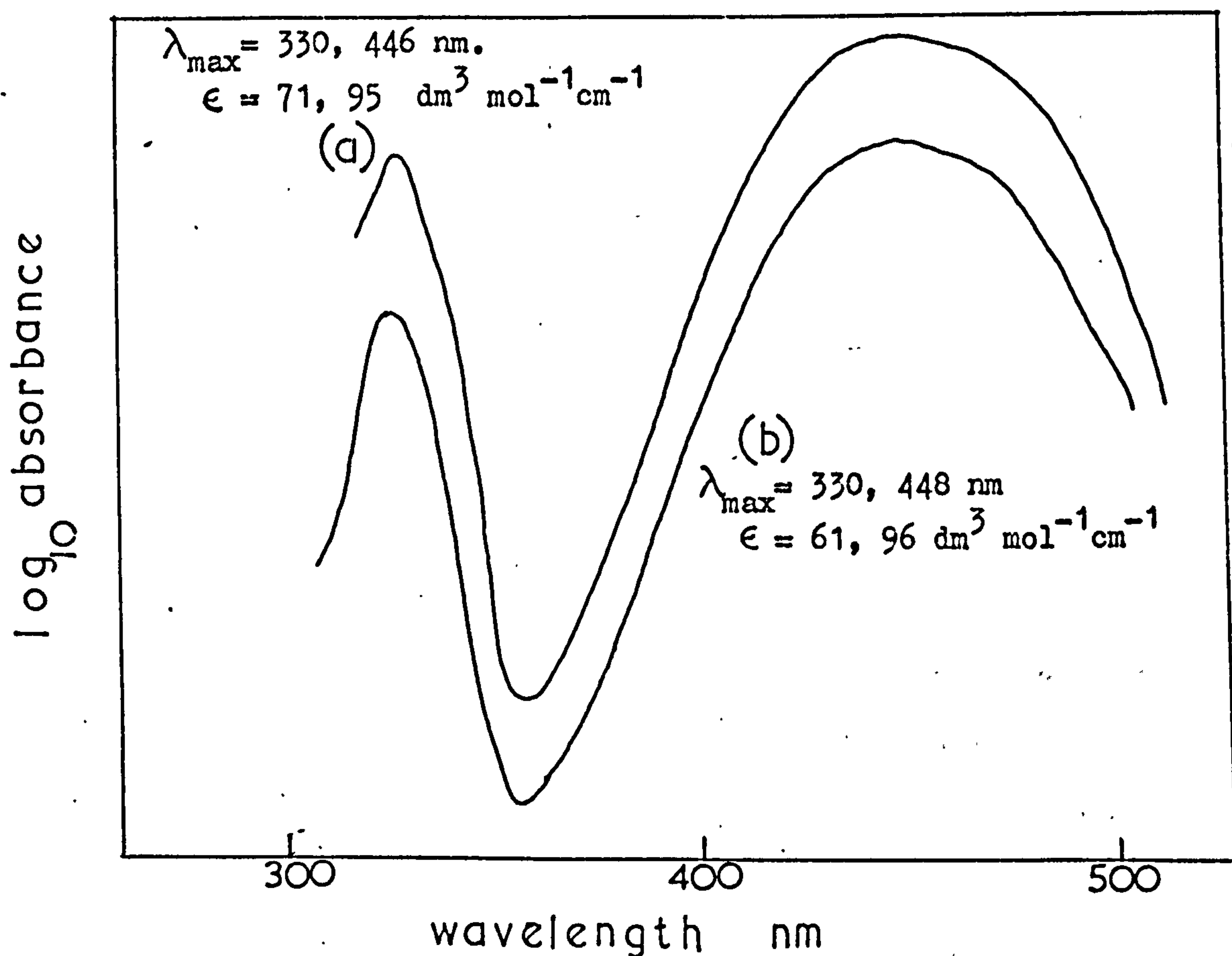


Fig.4-5. Electronic spectra of polyvinylferrocene in chloroform. $[M]_0 = 4.0\text{ mol dm}^{-3}$; $[In]_0 = 2.0 \times 10^{-2}\text{ mol dm}^{-3}$. Polymers isolated above 30 % conversion. (a) benzene-soluble polymer (b) benzene-insoluble polymer.

It can be seen that the spectra of the two fractions are identical.

The values for the molar absorptivities are in general agreement. The discrepancy in the values may be due to the use of a repeat unit based on $(\text{CH}_2\text{-CHFc})_n$ to calculate ϵ , since this unit will not be the only one present at high conversions.

However, the spectra are typical of those found for polyvinylferrocene by other workers.^{32,34}

The above results suggest that the benzene-insoluble PVF has the same structure as the benzene-soluble polymer. The insolubility of the polymer in benzene is not caused therefore, by cross-linking as proposed by Pittman et al³⁶. The ease with which the benzene-insoluble polymers dissolve in chloroform also suggests that cross-linking is not present.

It appears that the polymers become insoluble in benzene and other solvents at high conversions because of some type of polymer-polymer interaction, such as aggregation. The interaction must be quite specific since chloroform is the only solvent which destroys the interactions and solubilizes the polymer molecule.

4.2.5 Intrinsic Viscosities of Polyvinylferrocene

If association is present in the polymers obtained at high conversions, it might be expected that some effects on intrinsic viscosities may be apparent. Accordingly, the intrinsic viscosities of PVF were determined in benzene and chloroform and mixtures of the two at 25°C using a suspended-level viscometer.¹⁰⁹ A polymer sample isolated at 32.3 % conversion and completely soluble in benzene was used for all the determinations. The number average molecular weight of this sample was $\bar{M}_n = 28,000 \pm 10\%$ (determined by VPO in benzene at 37 °C).

The relationship between dilute solution viscosity and polymer concentration, c , has been described by various functions all of which

have been used to obtain the intrinsic viscosity $[\eta]$ by extrapolation to zero concentration.¹⁷⁵ The commonest relationship called the Huggins equation is

$$\eta_{sp}/c = [\eta] + k^1 [\eta]^2 c \quad (4.2.1)$$

where η_{sp} is the specific viscosity and k^1 is the Huggins or slope constant. Thus a plot of η_{sp}/c against c will give $[\eta]$ as the intercept on the ordinate axis.

Alternately, the following equation can be used where η_r is the reduced viscosity or viscosity number

$$(\ln \eta_r)/c = [\eta] + k^1 [\eta]^2 c \quad (4.2.2)$$

since the plot of $(\ln \eta_r)/c$ against c is often less steep.

The plots of equations (4.1) and (4.2) have the same ordinate intercept and therefore, it is convenient to plot them on the same graph to facilitate extrapolation to zero concentration. If the lines do not meet at this point, it is usual to take the mid-point of the intersections of each with the ordinate as the intrinsic viscosity.

Table 4-5 records values of the reduced viscosity of PVF in benzene and chloroform at 25°C.

Typical plots of η_{sp}/c against c are shown in Fig. 4-6.

The best straight lines for these plots were obtained by the method of least squares.

The values of $[\eta]$ obtained from these plots are recorded in Table 4-6 and are in agreement with the results of other studies.³⁶

The efflux times of the solvent and solution were measured to a tenth of a second consistently and the average of three readings used to obtain η_{sp} .

Table 4 - 5

Reduced Viscosity of PVF in Benzene and Chloroform at 25°C.

solvent	concentration g/100 cm ³	η_{sp}/c 100 cm ³ /g
chloroform	0.0450	0.0856
"	0.0813	0.0918
"	0.1346	0.1008
"	0.2020	0.1142
benzene	0.0568	0.0888
"	0.1024	0.0845
"	0.1706	0.0929
"	0.2560	0.0901

Since the viscosities were low, the efflux time of pure solvent and solution did not differ by more than four seconds. At low concentrations, the relative difference was less, and hence the errors in these points may be high..

However, the intrinsic viscosities obtained were in good agreement with those reported by Pittman et al³⁶.

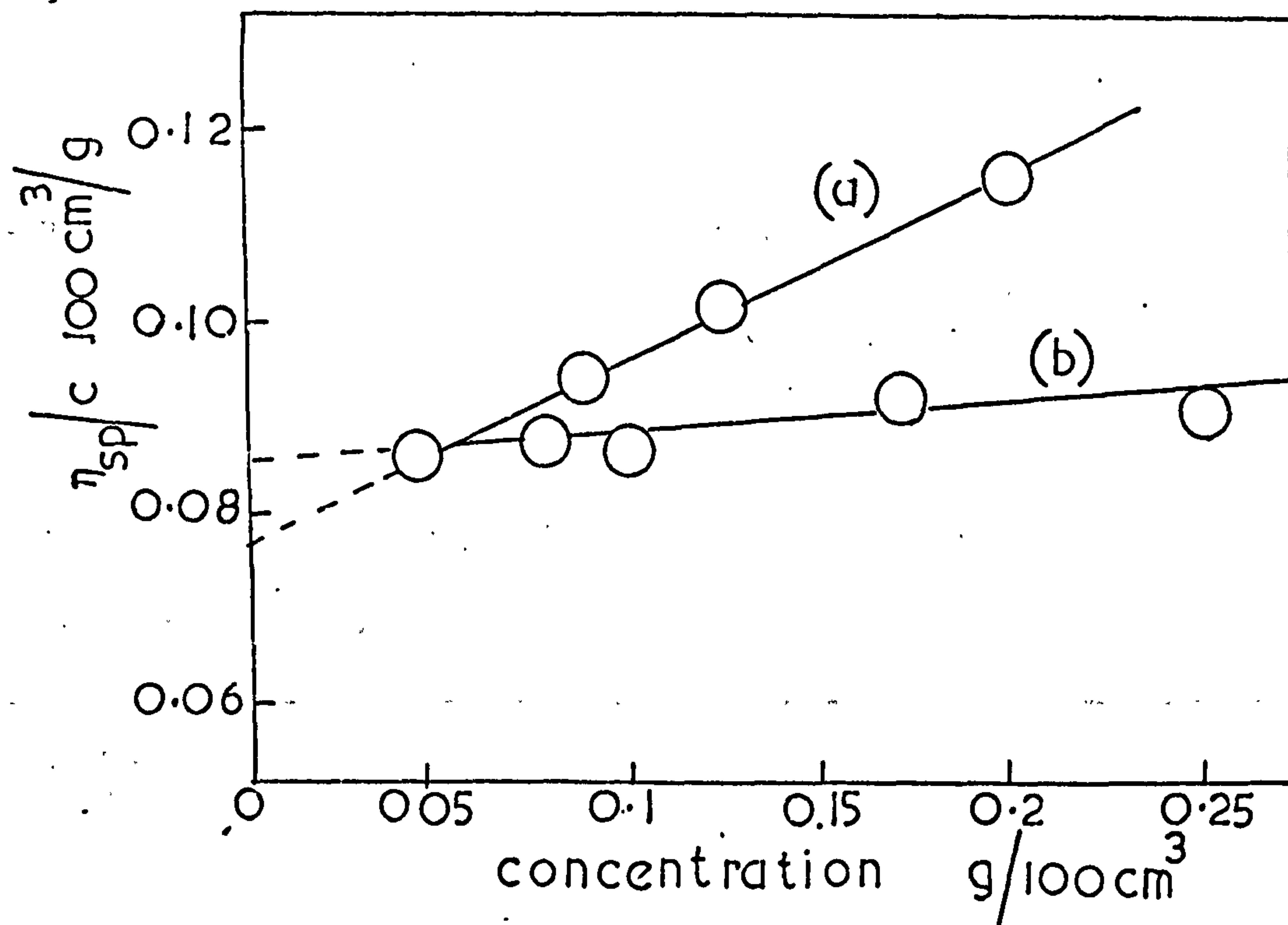


Fig. 4-6 Reduced viscosities of polyvinylferrocene solutions as a function of concentration at 25°C (a) in chloroform (b) in benzene.

Table 4 - 6

Intrinsic Viscosities of Polyvinylferrocene at 25°C

solvent	$[\eta] 100 \text{ cm}^3/\text{g}$	$\bar{M}_n$ (VFO)
benzene	0.071	28,000
chloroform	0.063	"
benzene ^a	0.073	23,000
THF ^a	0.096	"

a at 30°C see ref. 36.

The reduced viscosity of the PVF sample was also determined in mixtures of benzene and chloroform. Typical results are given in Table 4-7. At a 50 : 50 mole ratio the usual plots of η_{sp}/c and $(\ln \eta_r)/c$ against c were obtained. However, at intermediate ratios

the plot of η_{sp}/c against c produced negative slopes, whereas the plot of $(\ln \eta_r)/c$ against c showed distinct curvature.

Table 4 - 7

Reduced Viscosities of PVF in Different Mole per cent of Benzene and Chloroform at 25°C.

benzene/chloroform mole %	concentration g/100 cm ³	η_{sp}/c 100 cm ³ /g
75 : 25	0.0455	0.1345
	0.0820	0.1119
	0.1366	0.1088
	0.2050	0.0981
65 : 35	0.0576	0.1136
	0.1036	0.1083
	0.1727	0.1001
	0.2590	0.0974
50 : 50	0.0569	0.0754
	0.1138	0.0889
	0.1517	0.0943
	0.2276	0.1077
25 : 75	0.0644	0.1297
	0.1160	0.1260
	0.1933	0.1235
	0.2900	0.1193

Some typical plots are shown in Fig. 4-7. These plots show that the viscosity of the polymer solution is increasing with dilution, which must mean that the effective size of the polymer molecules is larger at low concentrations.

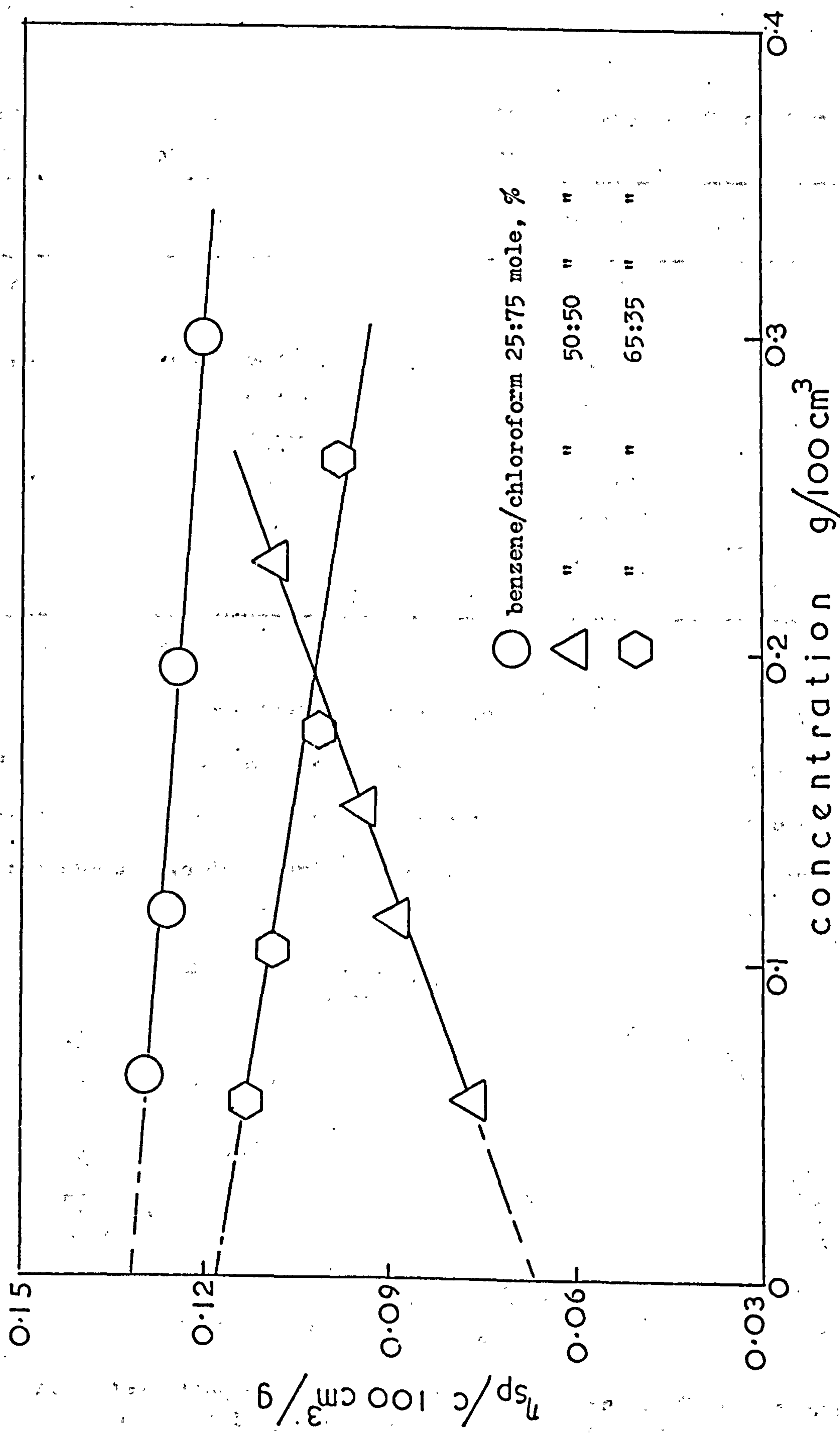


Fig 4-7. Reduced viscosities of solutions of polyvinylferrocene ($\bar{M}_n = 28,000$) in mixtures of benzene and chloroform as a function of concentration at 25°C.

The intrinsic viscosities were determined from the plots of η_{sp}/c against c since these slopes were linear. The intrinsic viscosities of PVF in different mole % of benzene to chloroform are given in Table 4-8.

Table 4-8

Intrinsic Viscosities of PVF ($\bar{M}_n = 28,000$) in Benzene, Chloroform and Mixtures of Benzene and Chloroform at 25°C.

solvent			$[\eta] \text{ } 100 \text{ cm}^3/\text{g}$
benzene			0.071
chloroform			0.063
benzene/chloroform 90/10 ^a			0.078
"	"	75/25	0.137
"	"	65/35	0.132
"	"	50/50	0.066
"	"	40/60	0.092
"	"	25/75	0.132

a mole %

The table shows that the intrinsic viscosities of the solutions vary with the mole % of the benzene/chloroform mixture. These results are plotted in Fig. 4-8. The curve shows that the intrinsic viscosity reaches a maximum at two different mole ratios of benzene to chloroform.

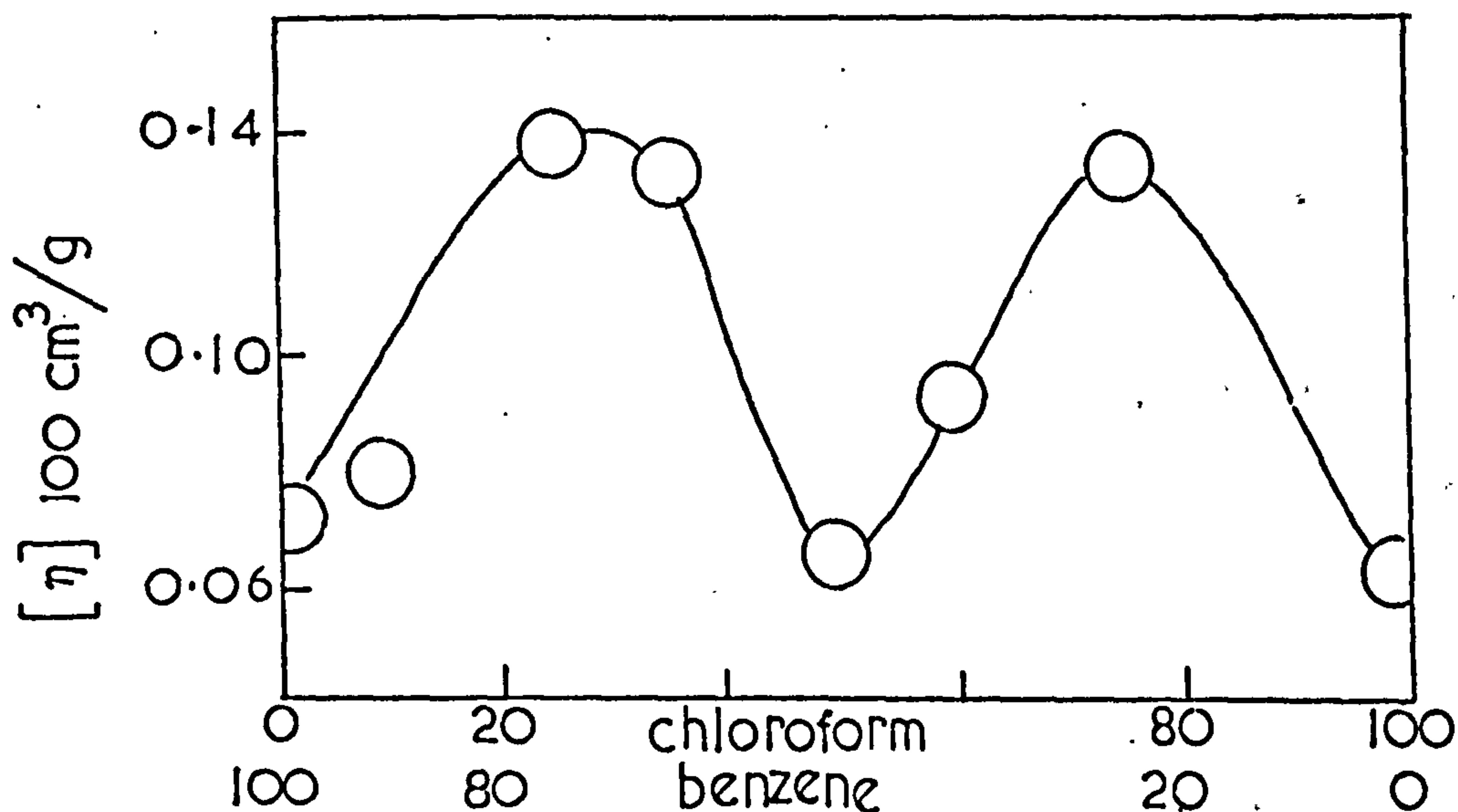


Fig.4-8 Variation in the intrinsic viscosities of PVF solutions as a function of the mole per cent of benzene and chloroform in the solvent mixture.

This result is unusual for a homopolymer. When $[\eta]$ is examined in a mixture of two solvents, the presence of interaction is indicated

by a displacement of the curve from linearity. If no interactions are present, a linear relationship between $[\eta]$ and mole fraction of the cosolvent is often found. The double hump in the curve in Fig. 4-8, however, suggests that specific interactions are only occurring at certain mole fractions. Benoit¹⁸¹ points out that similar behaviour is observed with block copolymers, but is never observed with homopolymers. A change in conformation is involved but the mechanism is not clear. The dielectric characteristics of the solvent mix may also be exerting an influence.

4.2.6. Aggregation of Polyvinylferrocene in Solution.

The results obtained from the intrinsic viscosity measurements indicate that association is occurring. Association effects were observed in vapour pressure osmometry of PVF, whilst the low value of $\alpha = 0.48$ in the Mark Houwink equation, can also be explained by aggregation phenomena.

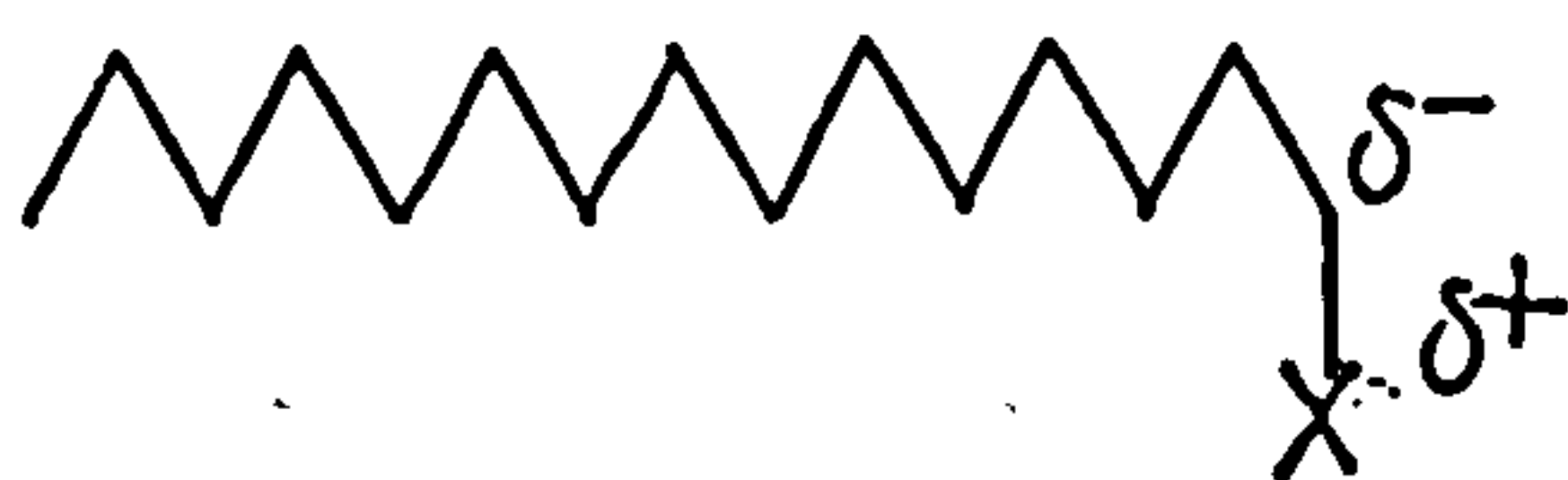
The measurements of the reduced viscosity of PVF shows that the viscosity is increasing with dilution in some solvent mixtures. This result means that the effective size of the polymer molecules must be increasing with dilution.

A similar dependence between viscosity and concentration is shown only by polyelectrolytes. Thus, these latter polymers are unique in that the reduced viscosity η_{sp}/c undergoes a marked increase with dilution.¹⁷⁶ In contrast, η_{sp}/c of nonionic polymers increases only gradually with increasing concentration.

With uncharged chain molecules, effects of particle interaction are eliminated by an extrapolation of η_{sp}/c to zero concentration. This extrapolation is possible only because the shape of the individual polymer coil depends only slightly on solution concentration.

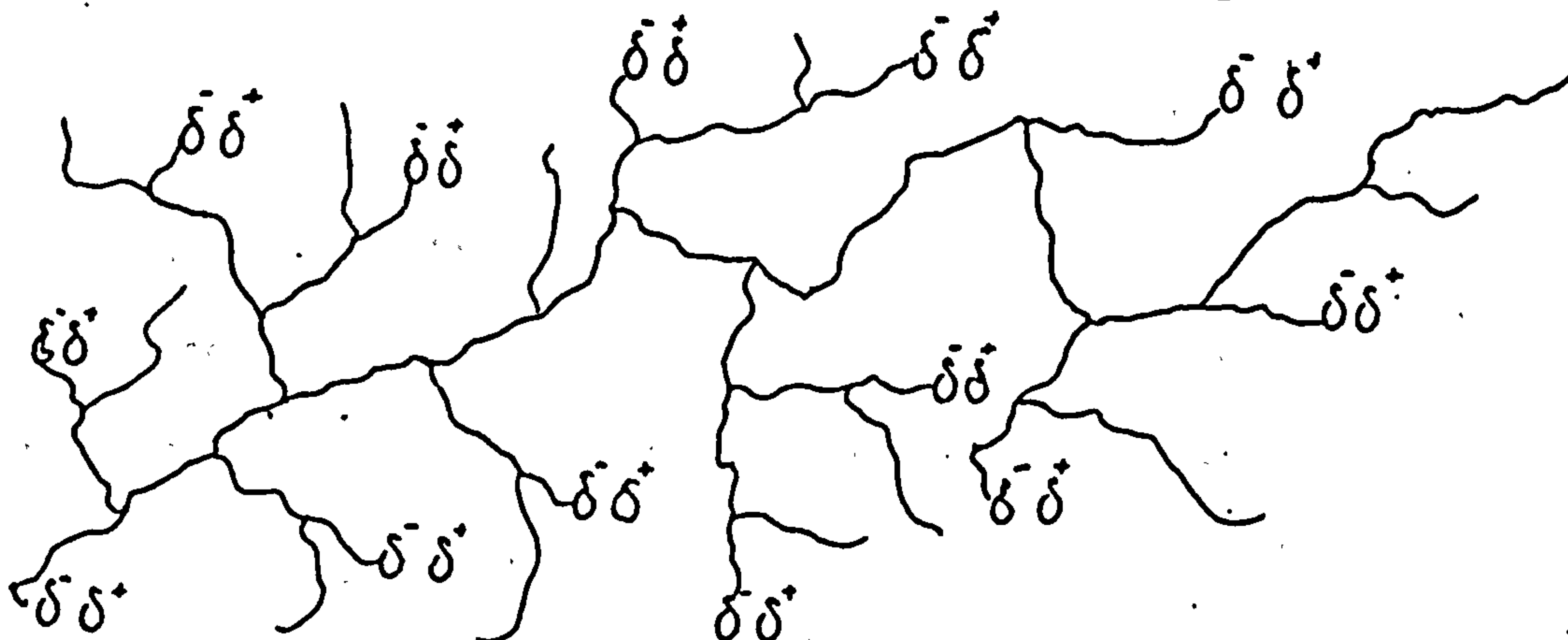
The situation is very different in polyelectrolyte solutions. In this case, increasing dilution provides increasing volume for the counterions, which will then tend to distribute themselves at larger distances from the polyion. As a consequence, the shielding of the fixed charges will be reduced, their mutual repulsion will increase, and the polyion will tend to expand. Hence it is not surprising to find that reduced viscosities of polyelectrolytes will typically increase on dilution.

From the above considerations, it appears the PVF molecule is behaving like a polyelectrolyte in benzene/chloroform solutions. This behaviour is, in fact, in accord with other results of the present study. For example, Mössbauer spectroscopy has shown that PVF contains an ionic-type complex of Fe(III). Thus, it can be expected that some charge distribution will occur between this unit and the polymer chain. The polymer molecule can be depicted, therefore, as follows :-



where X represents the Fe(III) high spin complex.

It has also been shown that PVF is highly branched at high conversions. For the sample under consideration, the conversion was 32.3 % and hence the following structure can be envisaged:



Even allowing for termination by transfer reactions, monomolecular termination of the chain radical by electron transfer will result in

the polymer molecule containing an unspecified number of ionic charges. Thus, this situation is very similar to that existing with a poly-electrolyte.

At high concentrations, when polymer-polymer interactions are present, mutual repulsion will tend to cause the polymer molecules to contract. However, at high dilutions in the absence of intermolecular effects, mutual repulsion of neighbouring charged sites in the molecule will cause it to expand and separate the charges to a maximum distance. These influences are depicted schematically below in Fig. 4-9.

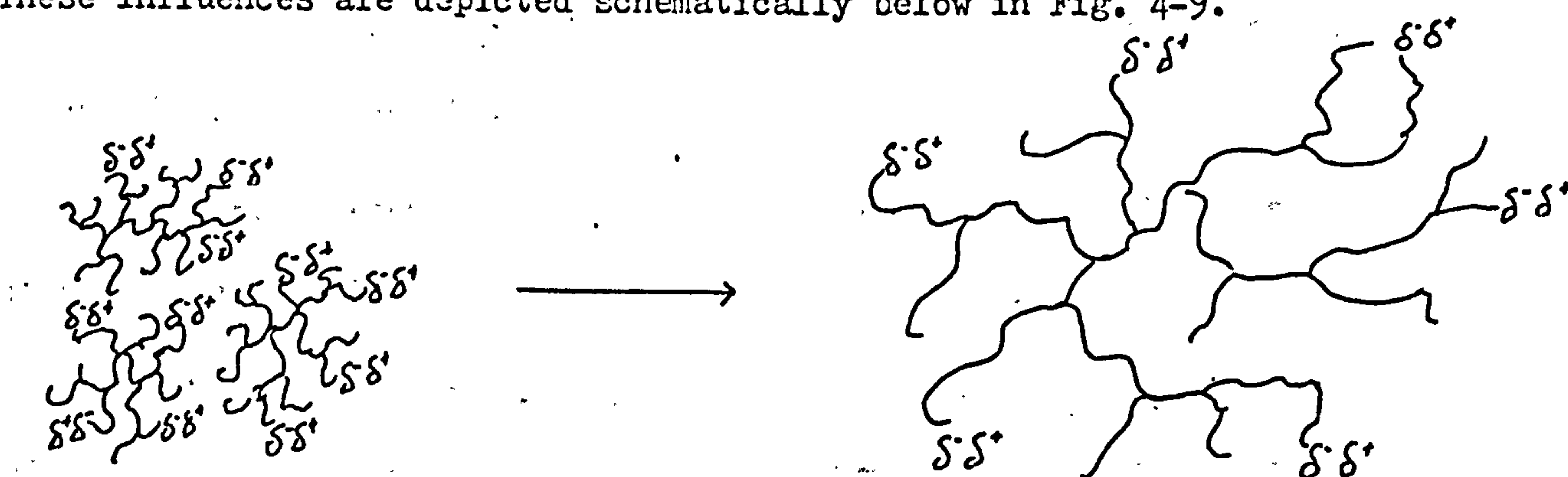


Fig.4-9 Scheme to explain the increase in the reduced viscosity observed on dilution of polyvinylferrocene solutions. In concentrated solution, intermolecular repulsion between neighbouring polymer molecules tends to keep the molecules relatively coiled. On dilution the polymer molecules tend to expand in order to separate adjacent charges on the same molecule.

Thus, the interactions discussed above, can account for the increase in η_{sp}/c of FVF solutions in benzene/chloroform mixtures. The observed association phenomena is also in accord with the physical and chemical properties of the polyvinylferrocene molecule.

Why two maxima should occur in the plot of $[\eta]$ against mole % of cosolvent is not so clear. Kruyt¹⁷⁷ points out that association in

macromolecules is a complex subject and some of the phenomena are not completely understood. The extent to which $[\eta]$ will depend on aggregation, is discussed at length in his compilation. In association colloids Booi¹⁷⁸ shows that the shape of the aggregate will effect $[\eta]$ either increasing it, decreasing it, or leaving it unchanged. The shape of the PVF molecule alters as the mole per cent of cosolvent alters, as indicated by the changes in $[\eta]$. It is possible that similar shapes occur at benzene/chloroform mole % of 75/25 and 25/75 due to different mechanisms. Alternately, the changes in $[\eta]$ may be caused by solvation or electroviscous effects.¹⁷⁹ Further work is required to clarify these results.

However, it seems that the PVF solutions fall into the class of macromolecular sols which have electrolytic nature.

If the analogy with a polyelectrolyte is correct, then the relationship between reduced viscosity and concentration, according to Fuoss¹⁸⁰ is best expressed by the following empirical equation.

$$\eta_r = A/(1 + Bc^{0.5}) \quad (4.2.3)$$

where A and B are constants.

Thus a plot of η_r^{-1} against $c^{0.5}$ should give a straight line and the intrinsic viscosity will be given by A assuming that there are no deviations at lower concentrations than those at which the measurements were made.

Typical values of these parameters were calculated from Table 4-7 for solutions which showed increasing viscosities with dilution. The plots are shown in Fig. 4-10.

The plots show that the relationships are linear, which supports the concept of the polyelectrolytic behaviour of PVF. The intrinsic

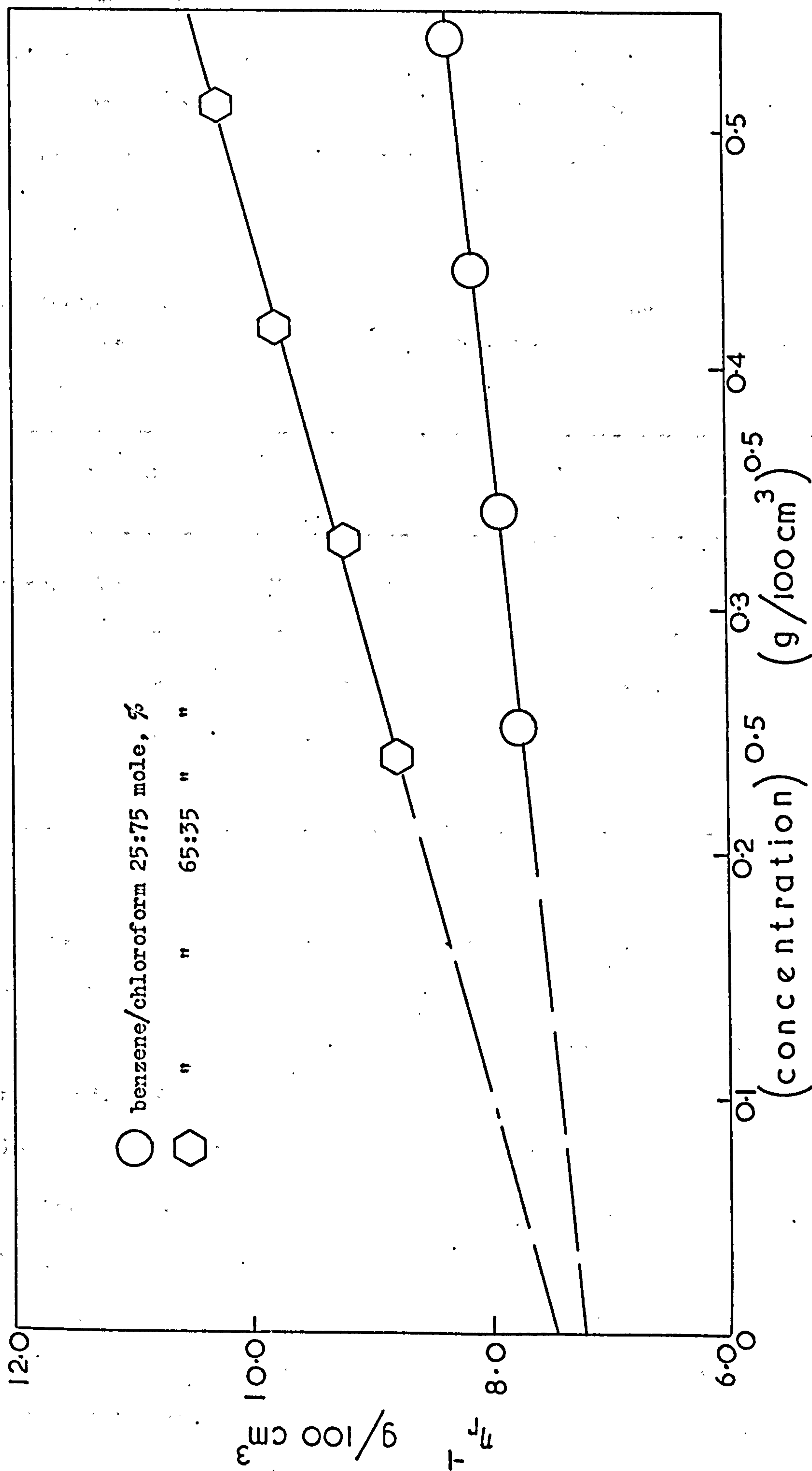


Fig 4-10. Reciprocal of the reduced viscosity of polyvinylferrocene ($\bar{M}_n = 28,000$) in mixtures of benzene and chloroform as a function of $C^{0.5}$ at 25°C.

viscosities obtained from these plots are given in Table 4-9. The values are slightly higher than those recorded in Table 4-8. but are in reasonable agreement. They can only be regarded as approximate, since no account has been taken of shear and polyelectrolyte solutions often exhibit dependence between shear and viscosity.¹⁷⁷

Table 4-9

Intrinsic Viscosities of PVF for Solutions which show Increasing Reduced Viscosities with Dilution. $[\eta]$ Obtained by the method of Fucss.¹⁸⁰

Solvent Mix		$[\eta]$ 100 cm ³ /g
benzene/chloroform	75 : 25	0.222
"	" 65 : 35	0.133
"	" 40 : 60	0.09
"	" 25 : 75	0.138

The association phenomena cannot be caused by degradation of the polymers in chloroform. All the measurements were carried out within 6 hours. Efflux times were checked after 24 hours and found to be unchanged. Furthermore, the degradation of PVF in chloroform is a slow process and only occurs after more than 4 days in dilute solutions.

The presence of the ionically bound Fe(III) complex in PVF has been shown to explain the association behaviour of the polymer. This ionic character can also explain the insolubility of the polymer in benzene at high conversions. At high conversions, the polymer molecule will be highly branched and therefore, each molecule will contain more than

one Fe (III) species. Interactions of these ionic sites may occur and form clusters which are impenetrable by non-polar solvents.

Solubility of polymers can be highly specific^{176,177} and presumably chloroform has the correct balance of polarization and solvation properties to dissolve the molecule. The insolubility of polyvinylferrocene in benzene cannot be explained by cohesive energy density considerations, since the Hildebrand solubility parameter for both solvents is the same ($\delta = 9.2$)¹⁷⁷

Similar solution properties to those of PVF have recently been discussed by Benoit¹⁸¹. Thus, block copolymers of monomer A and B show a dependence between $[\eta]$ and mole fraction of cosolvent. Also, a good solvent for A but not for B can dissolve the polymer. Benoit uses the analogy of a soap micelle to explain this effect i.e. part A solubilizes B and keeps the copolymer in solution. The same analogy may also apply to PVF.

4.3. CONCLUSIONS FROM THE POLYMERIZATION OF VINYLFERROCENE TO HIGH CONVERSIONS.

The results of the polymerization of vinylferrocene to high conversions, are in good agreement with the earlier results of the present study.

Thus, no autoacceleration was observed in the rates of polymerization at high conversions or in the presence of precipitated polymer. Autoacceleration is caused by a decrease in the rates of bimolecular radical termination reactions. Since PVF undergoes a monomolecular termination reaction, the absence of autoacceleration is to be expected.

In agreement with the high transfer activity of vinylferrocene, the amount of branched material in the polymer increases with conversion. This is shown by the presence of absorptions at 1630 cm^{-1} in the

IR spectra of polymer samples isolated at high conversions.

As the conversion of monomer to polymer increases, benzene-insoluble polymer is formed in increasing amounts. This fraction is not crosslinked, as suggested by Pittman et al,³⁶ since it is readily soluble in chloroform. Furthermore, the structure of the benzene-insoluble polymer is identical to the benzene-soluble fractions.

The intrinsic viscosities of a benzene-soluble fraction ($M_n = 28,000$) were determined in benzene and chloroform and found to be similar to previous results.³⁶ The values are not much higher than predicted for spherical particles¹⁷⁷ indicating that the polymer chains are tightly coiled in these solvents.

In mixed benzene/chloroform solvent, the viscosity was found to increase with dilutions which suggests association phenomena occur in these systems. Similar effects were also observed with osmometry. These results have been explained by proposing that PVF is behaving like a polyelectrolyte. This suggestion has been supported by the linear plots of η_r^{-1} against $c^{0.5}$. Such plots are typical for polyelectrolytes.¹⁸⁰

The presence of ionic charges in the polymer is in accord with the polymerization mechanisms of this monomer. Thus, the electron transfer termination has been shown to produce an ionically-bound Fe(III) complex. This species must contribute polar character to the polymer molecule.

The insolubility of PVF in the majority of solvents has been ascribed to cluster formation due to mutual interaction of these ionic sites. These effects must be highly specific since chloroform is the only solvent which breaks down the interactions and dissolves the polymer.

The solution properties of PVF have only been examined relatively briefly. It has been conclusively shown that these properties are unusual. Thus, PVF shows many solution properties characteristic of block copolymers.¹⁸¹ It has also been shown that the observed effects can be explained by the results of the kinetic studies of the polymerization reaction.

However, further work is required before all the interesting facets of this system can be fully explained.

5 POLYMERIZATION OF VINYLFERROCENE IN CHLOROFORM WITHOUT ANY ADDED
FREE RADICAL INITIATOR.

Simonescu et al³⁵ and Rausch and Siegal³⁸ have reported that vinylferrocene decomposes in chloroform. Pittman et al³⁶ have also found that the polymer decomposes in halogenated solvents. In the present study, the monomer and polymer have been observed to change colour on standing in chloroform. This is illustrated in Fig.5-1 which shows the change which occurs with time, in the UV/visible spectrum of PVF in chloroform.

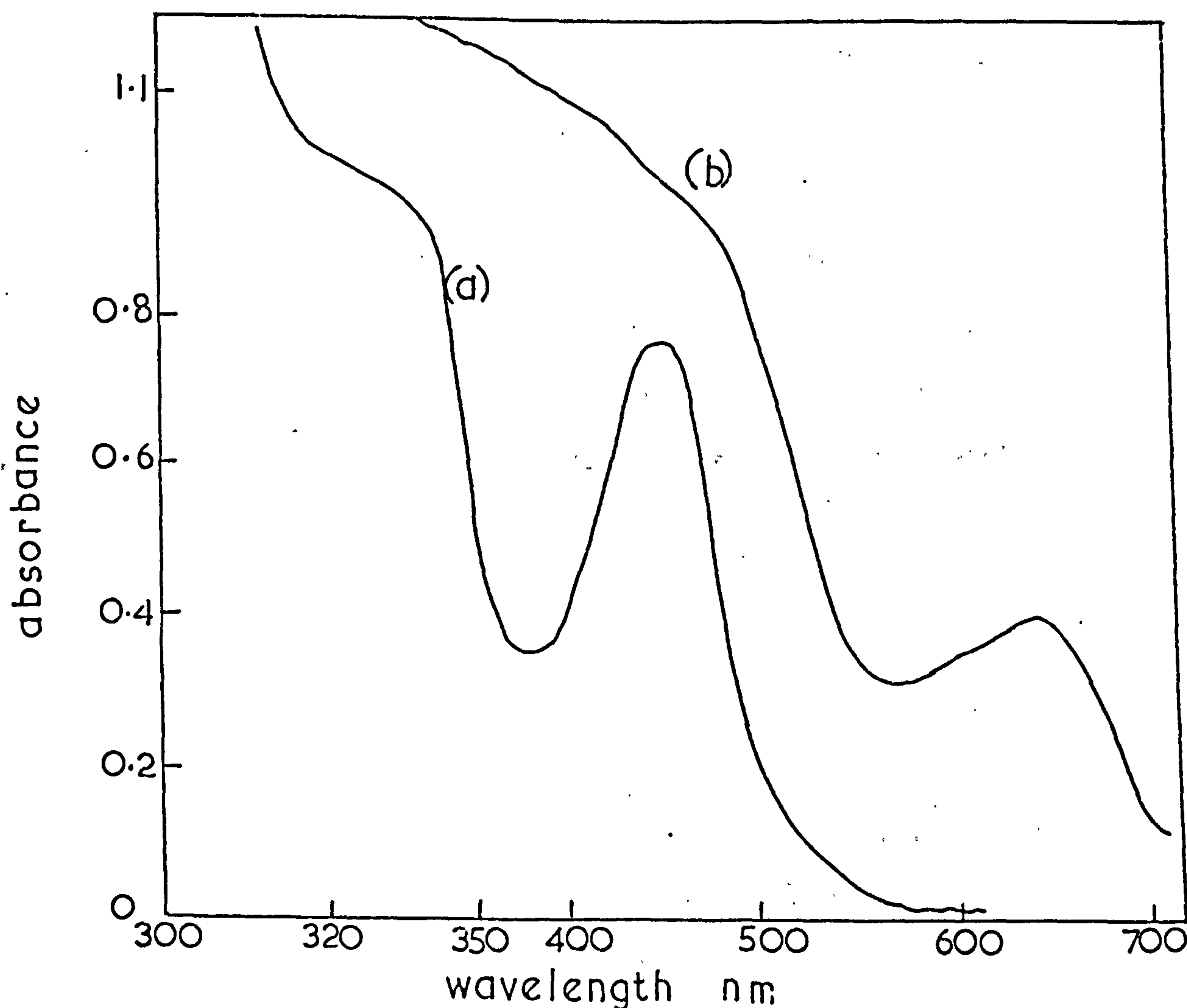
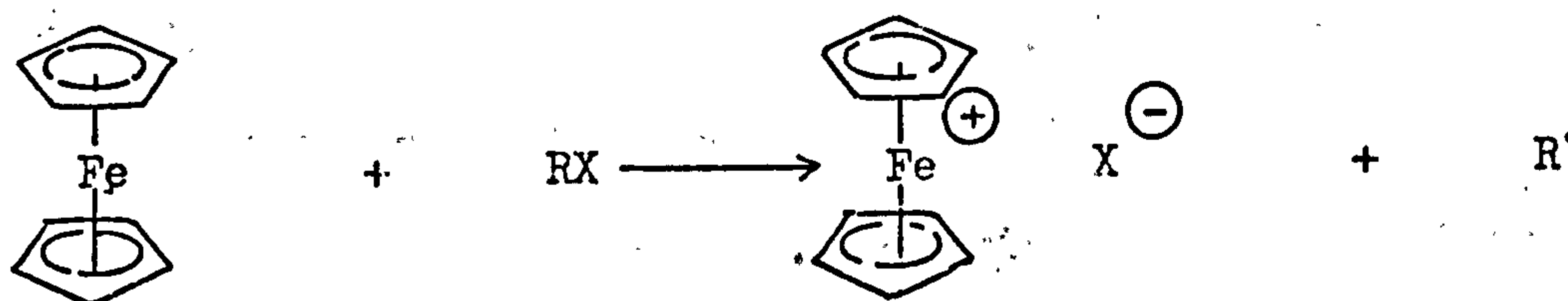


Fig.5-1 Changes in the electronic spectrum of polyvinylferrocene in chloroform as a function of time. Polymer prepared by free radical initiation in benzene at 60°C and then dissolved in chloroform (40 mg/10 cm³) (a) as prepared. (b) after standing for 24 hours in the presence of light.

The appearance of an absorption band at 635 nm is ascribed to oxidation of the ferrocene nucleus to the ferricenium cation.^{1,14} Thus, the following reaction of ferrocene and its derivatives is generally accepted to occur in halogenated solvents.^{1,14,35,36}



The ferricenium ion formed is unstable in organic solvents in the presence of air, and decomposes to ferric ion species, probably complex oxides.⁵² However, in common with many redox reactions, free radicals are also produced. Therefore, decomposition of a suitable ferrocene derivative, such as vinylferrocene, in solvents which promote this electron transfer reaction, may also result in polymerization of the ferrocene compound. To examine this possibility the polymerization of vinylferrocene in chloroform at 60°C was studied.

5.1 EXPERIMENTAL AND CHARACTERIZATION.

Vinylferrocene was purified as described in section 2.1. AnalaR chloroform was dried over Linde molecular sieves (3A) and distilled under reduced pressure just prior to use, only the middle fraction being collected and used. Reactions were carried out in sealed glass vessels after degassing the reactants by three successive freeze-pump-thaw cycles at 10^{-4} mm Hg. Other reactions, in which oxygen-free

nitrogen was passed over the frozen reactants before sealing, were also examined. Since oxygen cannot be totally eliminated by this method, these systems contained traces of oxygen.

After sealing the vessels, they were warmed to room temperature, shaken to ensure all the monomer had dissolved and placed in a water bath at $60^{\circ}\text{C} \pm 0.01^{\circ}\text{C}$ for 7 days.

After freezing and cracking the vessels open, the contents were poured into Analar methanol. The precipitates were collected, redissolved in chloroform where possible, reprecipitated into methanol and collected on a sintered glass crucible (porosity 3). They were washed repeatedly with methanol and finally dried to constant weight at 30°C , 0.1 mm Hg.

The filtrate remaining after isolation of the precipitates was evaporated to dryness and examined for the presence of unreacted monomer.

The precipitates were characterized by elemental analysis, infrared and ultraviolet spectroscopy. Number average molecular weights were determined by vapour pressure osmometry and molecular weight distribution was examined by gel permeation chromatography. The precipitates were also examined by NMR, ESR and Activation Analysis.

5.2 RESULTS AND DISCUSSION.

5.2.1 Products Isolated from Reactions of Vinylferrocene in Chloroform.

The results of the reactions in chloroform at 60°C are given in Table 5-1. For comparison, some results from attempted polymerizations in benzene at 60°C in the absence of AIBN are also shown. Heating the monomer at 60°C in chloroform produced a marked colour change. In the case of reactions conducted in vacuo, the colour of the reactants

changed from dark red to green. In the presence of oxygen, the reaction mix became muddy brown and precipitated a brown solid. Heating vinylferrocene in benzene without AIBN did not produce any observable effect.

Table 5 - 1

Effect of Heating Vinylferrocene in Chloroform and Benzene in the Absence of Any Added Free Radical Initiator. All Reactions Carried Out at 60°C for 7 days.

$[M]_0$ mol dm ⁻³	solvent	product	yield %	iron content %
1.0	CHCl ₃	greenish powder	30	23.1, 23.4
1.0	"	" "	32	23.9, 23.6
4.0	"	yellow "	77	24.0, 24.1
4.0	"	" "	76	24.6, 24.9
4.0 ^a	"	brown "	3	56.0, -
4.0 ^a	"	" "	2	- , -
3.0	"	yellow "	41	23.7, 23.8
3.0	benzene	unreacted monomer	>96	26.4, 26.3
4.0 ^a	"	" "	>96	26.5, 26.3

a reacted in the presence of oxygen.

The reactions in chloroform in the absence of air, produced good yields of a solid yellow powder. At low monomer concentrations the powder had a definite greenish cast. The iron contents of these powders are similar to those obtained for PVF prepared by free radical initiation in benzene (see Table 4-4).

In the presence of oxygen, a low yield of a brown ionic solid was obtained together with a gummy residue. Only a small amount of

unreacted vinylferrocene was recovered from these reactions. Heating vinylferrocene in benzene without AIBN produced no polymer. This was expected since vinylferrocene does not react with benzene. The absence of any polymerization also suggests that thermal polymerization of vinylferrocene does not occur readily at 60°C.

5.2.2. Infrared and UV/visible spectra of Products Obtained from Reactions in Chloroform.

Iron analysis of the powders obtained from heating vinylferrocene in chloroform in the absence of air suggests that polymerization has occurred. This suggestion was confirmed by spectroscopic examination of the powders.

Thus, the yellow powders were readily soluble in benzene and the IR spectra of the cast films were identical to PVF prepared by free radical initiation in benzene. Typical spectra are shown in Fig.5-2.

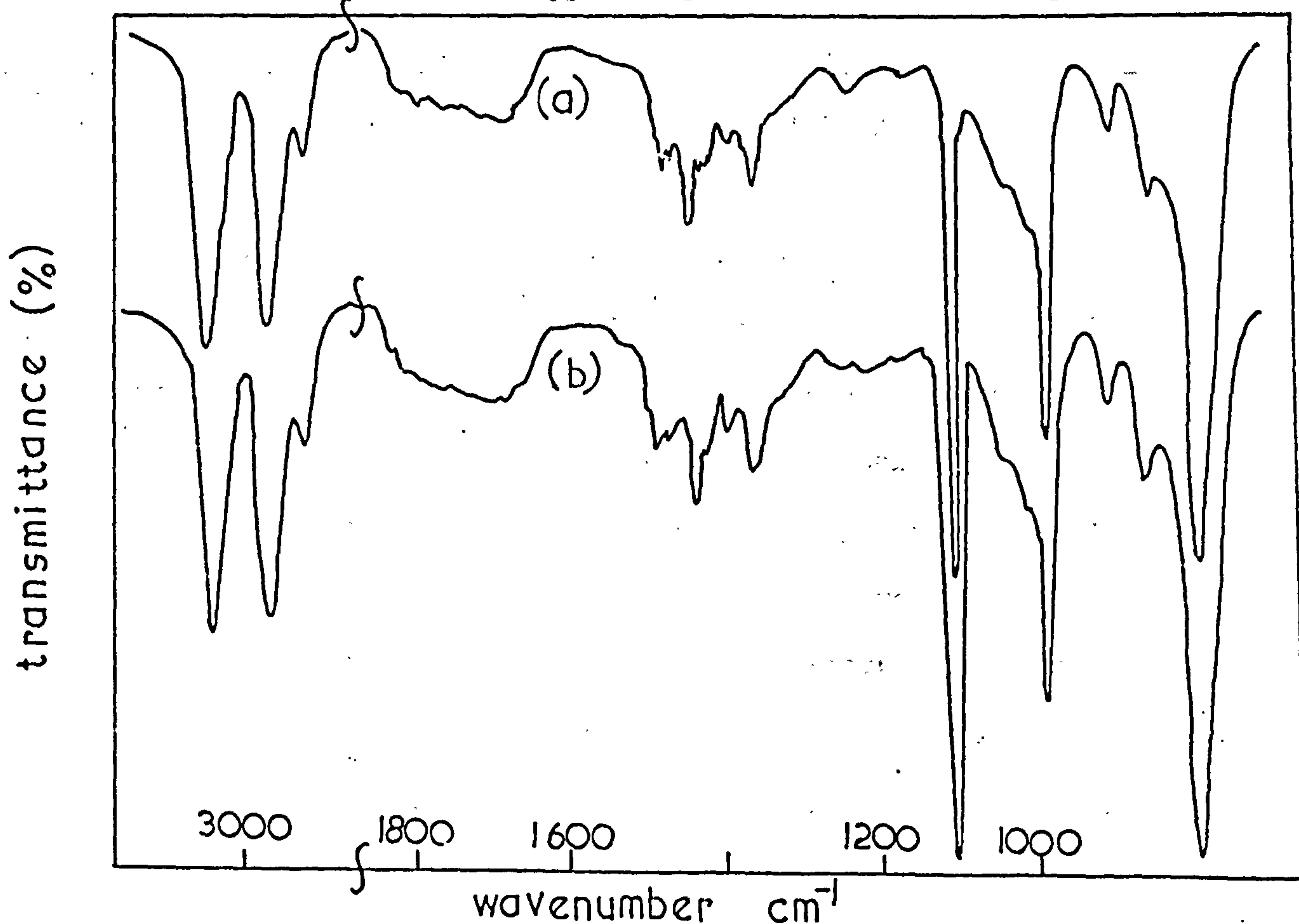


Fig. 5-2 Infrared spectra of polyvinylferrocene examined as films cast from benzene (a) prepared in CHCl₃ without any added initiator (b) prepared in benzene with AIBN.

Likewise, the UV/visible spectra of the yellow powders are identical to authentic polyvinylferrocene. Typical results are given in Table 5-2. The greenish powder also produced a similar spectrum after being purified.

Table 5 - 2

Ultraviolet and Visible Spectra of Polymers Obtained from Reacting Vinylferrocene in Chloroform at 60°C. No added initiator.

$[M]_0$ mol dm ⁻³	λ_{max}	ϵ dm ³ mol ⁻¹ cm ⁻¹	solvent
1.0	330 450	54, 81	CHCl ₃
3.0	330 448	65, 81	"
4.0	330 450	55, 71	"
1.0 ^a	330 446	88, 99	"
2.0 ^a	330 446	86, 96	"
4.0 ^a	330 442	53, 91	benzene

a. PVF obtained by AIBN initiation in benzene at 60°C.

The brown powder obtained from heating vinylferrocene in chloroform in the presence of air was insoluble in benzene and chloroform. Its IR spectrum showed none of the absorptions which characterize the ferrocene ring. The product was similar to that obtained in the present study from attempted polymerizations of vinylferrocene in benzene using benzoyl peroxide as initiator. In the latter reaction, the benzoyloxy radicals are presumed to oxidize and decompose the ferrocene ring rather than initiate polymerization of the vinyl group.^{34,37}

A similar reaction appears to have occurred with vinylferrocene in chloroform in the presence of air. Thus, the ferrocene ring was

oxidized as judged by the change in colour. Decomposition of the oxidized species must then occur immediately. The gummy residue also obtained from these reactions indicates, however, that some low molecular weight products have been formed.

The above results show that vinylferrocene does, in fact, undergo polymerization when heated in chloroform in the absence of any added polymerization initiator. However, polymerization only occurs in oxygen-free conditions. In the presence of oxygen, the monomer is decomposed to a brown ionic solid, probably iron oxides.

5.2.3. Molecular Weights of Polyvinylferrocene Prepared in Chloroform

The number average molecular weights of the polymers prepared in chloroform are recorded in Table 5-3. Good correlation between the VPO and GPC results were obtained with these polymers.

Table 5 - 3

Number Average Molecular Weights of PVF prepared in Chloroform at 60°C without Any Added Initiator.

$[M]_0$ mol dm ⁻³	$\bar{M}_n$ (VPO) ^a	$\bar{M}_n$ (GPC) ^b	$\bar{M}_w/\bar{M}_n$
1.0	1,140	1,060	1.42
1.0	1,100		
3.0	1,000		
4.0	1,200	1,280	1.84
4.0	1,250		

a in benzene at 37°C

b in THF at ambient temperature.

The molecular weights in general, are lower than those of PVF prepared by free radical initiation in benzene, although similar values have been obtained by other workers.^{32,34} The consistency in the values suggests that the molecular weight of PVF prepared in chloroform may be controlled by transfer reactions.

The molecular weight distributions are similar to those of PVF prepared by AIBN in benzene. Typical curves of $dw/d(\log M)$ against $\log M$ are shown in Fig. 5-3.

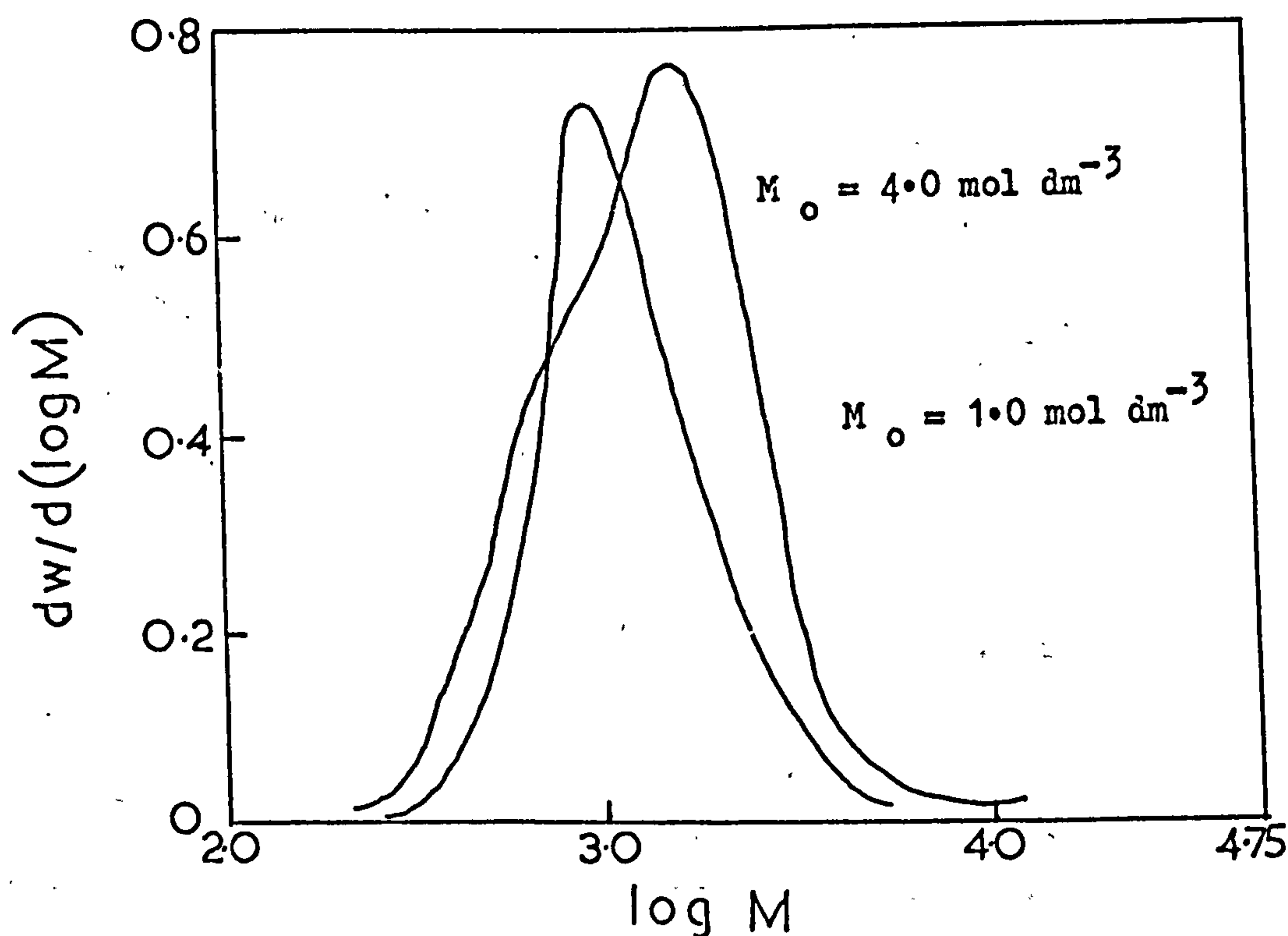


Fig. 5-3. Plot of weight fraction per log molecular weight increment as a function of log molecular weight for polyvinylferrocene prepared in chloroform at 60°C without any added initiator.

A broader distribution was obtained for the reactions with the higher initial monomer concentration. This result is in accord with high transfer activity of vinylferrocene. Thus, when $[M]_0 = 4.0 \text{ mol dm}^{-3}$ transfer with monomer should be higher than when $[M]_0 = 1.0 \text{ mol dm}^{-3}$.

5.2.4 Electron Spin Resonance of PVF Prepared in Chloroform.

The polymers prepared in chloroform without any added initiator produced a similar ESR signal to PVF prepared in benzene using AIBN initiation. Typical ESR spectra are shown in Fig.5-4.

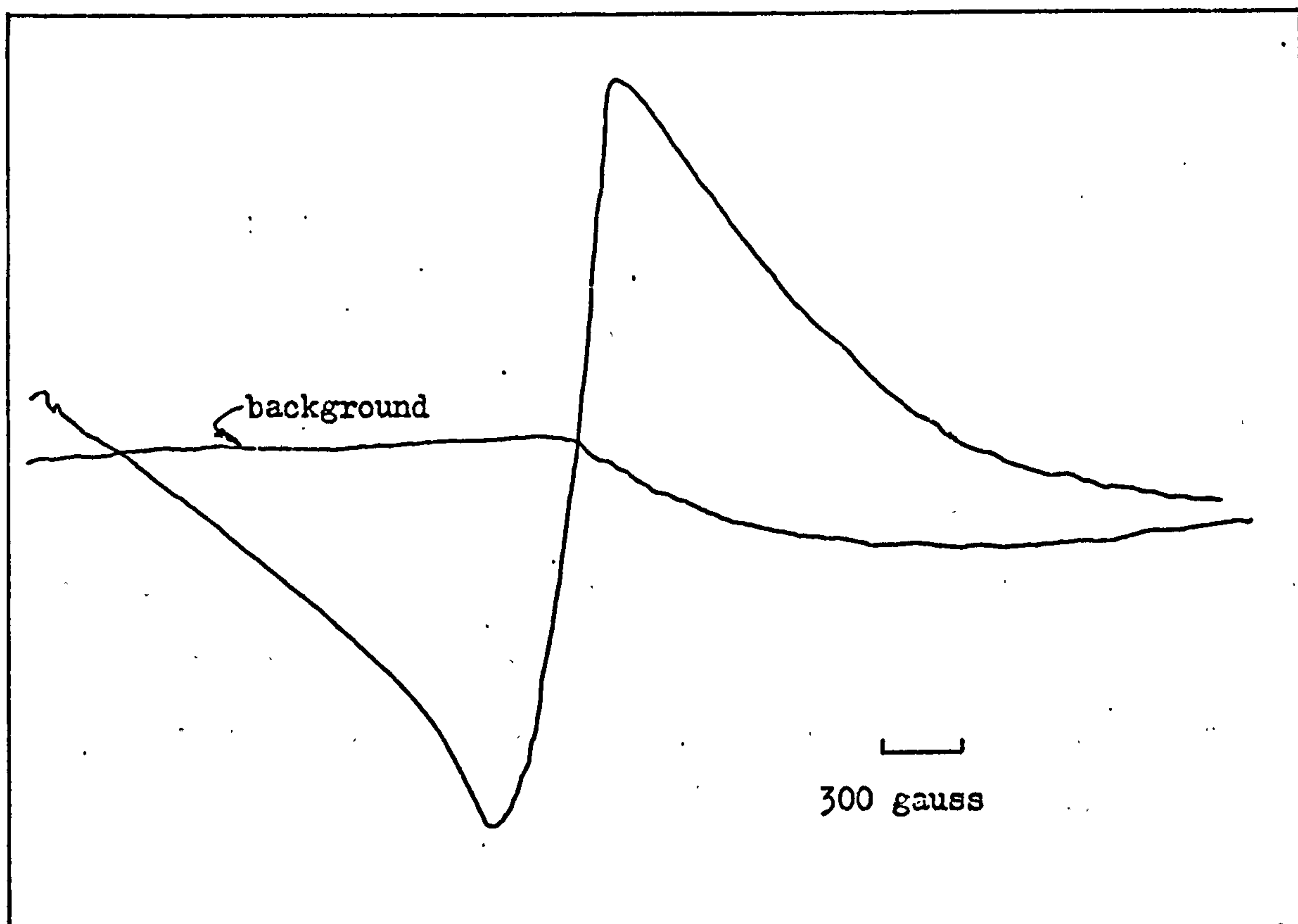


Fig. 5-4 Electron spin resonance signal from polyvinylferrocene prepared in chloroform at 60°C without any added free radical initiator. $[M]_0 = 4.0 \text{ mol dm}^{-3}$. Modulation 1000 Hz; Gain 400 powdered sample examined at room temperature.

The linewidth was ~ 600 gauss and the 'g' value for the centre of the peak was 2.06. Thus, PVF prepared in chloroform contains the same high spin Fe(III) species previously observed in the ESR spectra of PVF prepared in benzene with AIBN. These results suggest that a similar polymerization mechanism may be operative in both cases.

The ESR signal was much stronger from polymers prepared with $[M]_0 = 1.0 \text{ mol dm}^{-3}$. This result may indicate that electron transfer termination occurs more readily at lower monomer concentrations.

At higher monomer concentrations, termination by transfer reactions may be more favourable.

5.2.5. Activation Analysis of PVF Prepared in Chloroform.

The polymerization of vinylferrocene occurs in chloroform in the absence of any added initiator. This results suggests that chloroform is involved in the polymerization reaction. Therefore, the polymer may contain chlorine. For example, initiation by a chlorine-containing species will result in chlorine in the polymer.

Alternately, because of the high transfer activity of vinylferrocene, chlorine may be introduced by transfer reactions with chloroform.

To investigate these possibilities and confirm the presence of chlorine in the polymers, they were examined by activation analysis.¹⁸² Quantitative determination of chlorine, using standard chemical techniques, is difficult in the presence of iron and hence neutron activation analysis is the preferred method.

Activation analysis is based on the principle that when a material is irradiated by nuclear particles, some of the atoms present in the material will interact with the bombarding particles and will be converted into different isotopes of the same element or isotopes of different elements depending on the nature of the bombarding particles. Separation and measurement of each different induced radioactivity then gives the identity and quantity of the parent isotope present in the sample. A convenient method for distinguishing the induced radioactivities for certain elements is by measurement of their γ - activities.

Neutron capture reactions produce activated nuclides which decay by prompt emission of γ - rays. The ^{38}Cl nuclide has a half-life

of 37 minutes and therefore its γ -ray spectrum can be readily obtained. Since the nuclear characteristics of chlorine and its activation products are well known, this technique is very suitable for its detection.

Polymer and monomer samples were irradiated in the pneumatic tube facility of the HERALD reactor (Atomic Weapons Research Establishment, Aldermaston) at a thermal neutron flux of $4 \times 10^{12} \text{ N cm}^{-2} \text{ s}^{-1}$. Irradiation times were 1 and 5 minutes and the 37.5 minute ^{38}Cl activity was measured with a multichannel γ -scintillation spectrometer using a Ge (Li) detector. A typical γ -spectrum of PVF prepared in chloroform is shown in Fig.5-5 and representative quantitative results for the chlorine contents of polyvinylferrocene and vinylferrocene are given in Table 5-4.

This table shows that small amounts of chlorine are also present in the monomer and in PVF prepared by AIBN initiation in benzene. However, these quantities are due to trace impurities. The amounts in the polymers prepared in chloroform are too high to be ascribed to impurities.

Table 5 - 4

Chlorine Content of Vinylferrocene and PVF Prepared in Chloroform Without any Added Initiator. Determined by Activation Analysis.

$[M]_0 \text{ mol dm}^{-3}$	chlorine % $\pm$ 5 %
1.0	0.84
1.0	0.80
4.0	0.54
4.0 ^a	0.01
vinylferrocene	0.01

a prepared in benzene using AIBN initiation.

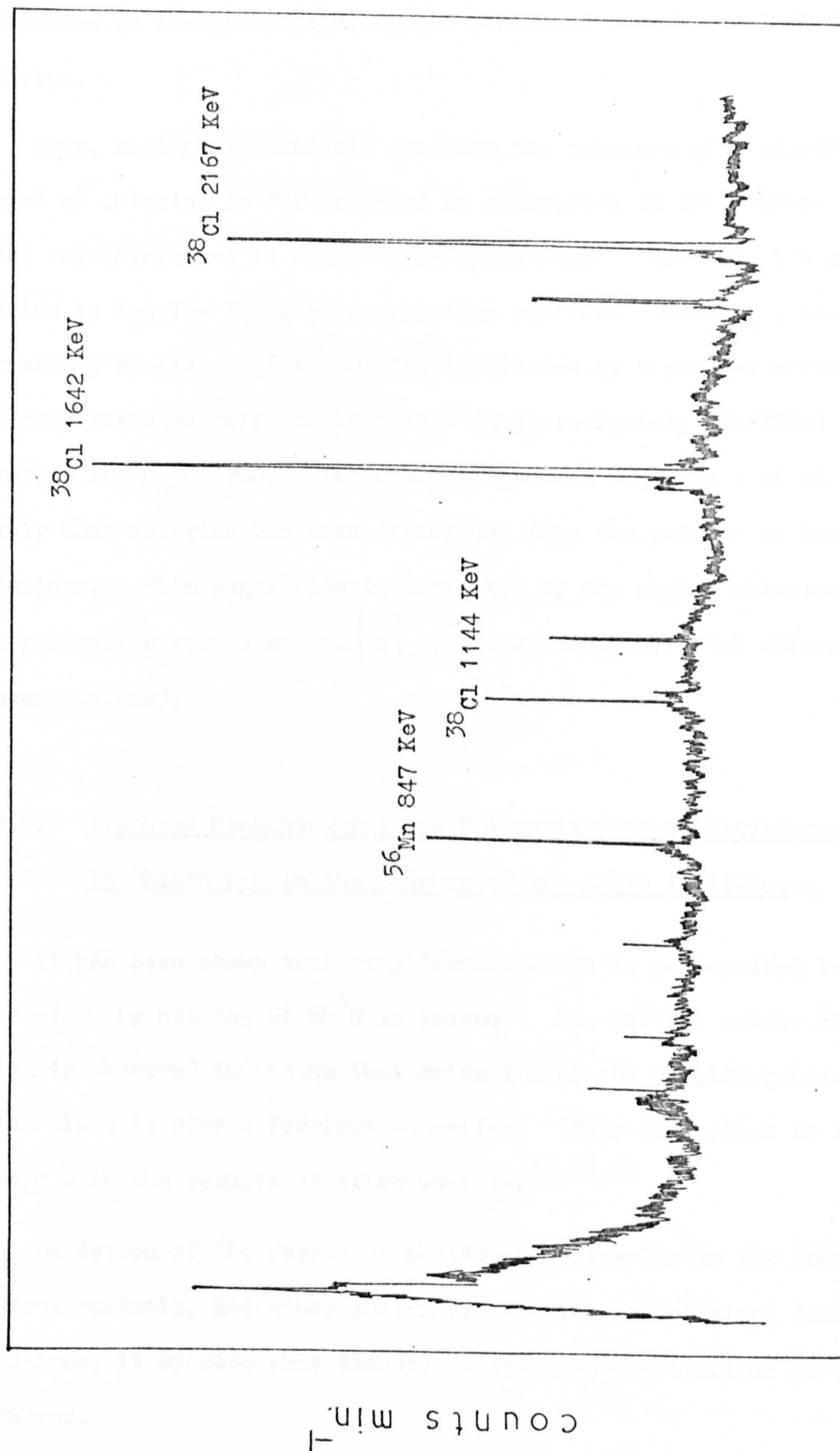


Fig 5-5. γ -spectrum of polyvinylferrocene showing peaks due to ^{38}Cl . Polymer prepared in chloroform without any added initiator. $[\text{M}]_0 = 4.0 \text{ mol dm}^{-3}$. Counted for 5 minutes after a 5 minute irradiation in a neutron flux $\sim 4 \times 10^{12} \text{ N cm}^{-2} \text{ s}^{-1}$.

The brown ionic solids obtained by heating vinylferrocene in chloroform in the presence of oxygen contained 0.08 % and 0.11 % chlorine.

Thus, activation analysis confirms the presence of a significant amount of chlorine in PVF prepared in chloroform in the absence of added initiators and in oxygen-free conditions. However, the concentration is too low for a polymerization reaction involving a chlorine-containing species. For example, initiation by a species containing one chlorine atom only should result in approximately $(35/1200) \times 100 = 3\%$ chlorine for $\bar{M}_n = 1200$. The chlorine content suggests that it is more likely that chlorine has been introduced into the polymer by transfer reactions. This suggestion is supported by the higher chlorine content for polymers prepared at low $[M]_0$ (and consequently high chloroform concentrations).

5.2.6. Proposed Mechanism for the Polymerization of Vinylferrocene in Chloroform in the Absence of Any Added Initiator.

It has been shown that vinylferrocene can be polymerized in chloroform by heating at 60°C in vacuum. The initial colour change which is observed indicates that oxidation of the vinylferrocene has taken place to give a ferricenium cation. This suggestion is in accord with the results of other workers.^{35,36,38}

Oxidation of the ferrocene nucleus also results in the production of free radicals, and since polyvinylferrocene was obtained from these reactions, it appears that radical addition to the olefinic group has occurred.

A radical polymerization mechanism is supported by the effects of oxygen on the reaction. Heating vinylferrocene in the presence of

oxygen did not produce any polyvinylferrocene. The colour change in these systems showed that ferricenium cations were formed and hence radicals must also have been present. Suppression of radical addition to the double bond is in accord with the effects of oxygen on radical polymerizations mechanisms.¹²¹⁻¹²⁵ Thus, the radical addition reaction was inhibited, and decomposition of the ferricenium cation occurred.

Further evidence in support of a free radical mechanism for the polymers prepared in chloroform is given by their IR and UV/visible spectra. These spectra were identical to those of PVF prepared by AIBN initiation in benzene.

Finally, the ESR spectra of the polymers prepared in chloroform is indicative that a radical mechanism has occurred in these reactions. The ESR signal has been shown to be due to the presence of a high spin Fe(III) complex in polyvinylferrocene prepared by free radical initiation in benzene. This complex is formed as a result of the electron transfer termination reaction from the ferrocene nucleus to the growing polymer chain radical.

The presence of an identical paramagnetic species in PVF prepared in chloroform suggests that a similar termination reaction also occurs in these polymerization and consequently, that a free radical mechanism is operative.

A radical mechanism for the polymerization of vinylferrocene in chloroform is in agreement with the observations from other studies. For example, Bamford et al¹⁸³ have shown that the polymerization of vinylmonomers by metal carbonyls in carbon tetrachloride occurs by a radical mechanism. Similarly, the polymerization of butadiene and isoprene by metal acetylacetonates has been shown to proceed by a radical mechanism.¹⁸⁴ More recently, Kaeriyama¹⁸⁵ has initiated polymerization of methyl methacrylate by using ferrocene in oxygenated solvents and has proposed a radical

polymerization mechanism to explain his results.

In all these reactions, the radicals which initiate polymerization are generated as a result of an electron transfer reaction between the metal nucleus and the solvent. The general reaction can be depicted as follows

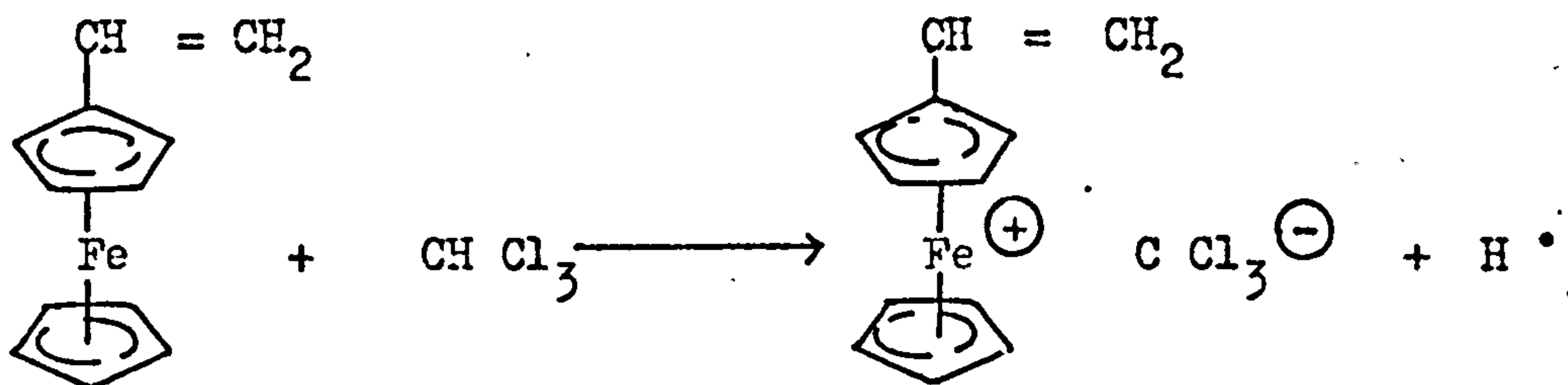


where M represents the metal and RX the solvent.

Since vinylferrocene undergoes a similar electron transfer reaction with chloroform, a radical polymerization reaction of this monomer in chloroform is not unexpected.

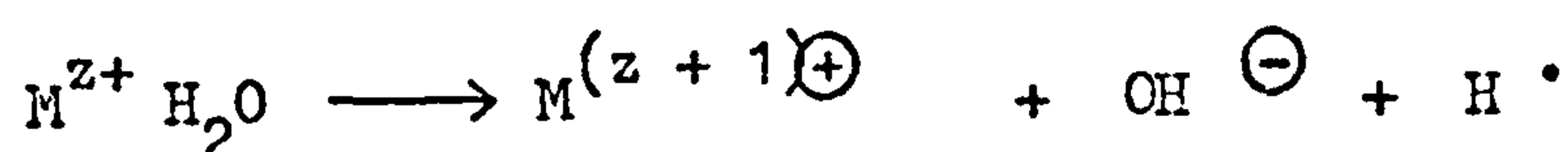
The radical species which initiates the polymerization reaction is produced as a result of the oxidation of vinylferrocene to the ferricenium species. If the structure of this species were known then the resultant radical could also be identified.

Chloroform is known to form a relatively stable $CCl_3^{\ominus}$ anion. For example, this anion is involved in the facile proton exchange of chloroform and also in its hydrolysis.¹⁸⁶ Since the ferrocene nucleus also readily forms a cationic species, the following electron transfer reaction between vinylferrocene and chloroform is postulated:-



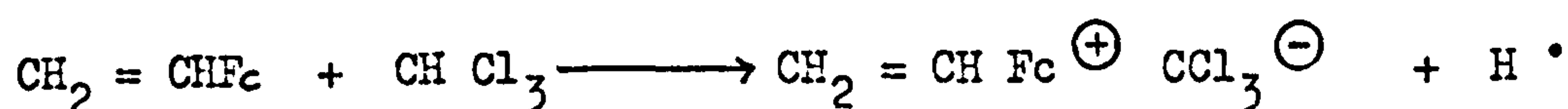
The above reaction is very similar to photochemical electron

transfers of the general form



Dainton and James¹⁸⁷ have shown that the hydrogen atoms liberated in these reactions will initiate radical polymerizations.

Therefore, the following reaction scheme is proposed to account for the polymerization of vinylferrocene in chloroform



Since hydrogen atoms are extremely reactive, they will be easily poisoned which explains why polymerization does not occur when traces of oxygen are present.

The proposed scheme for the polymerization reaction is supported by the chlorine contents of the polymers. The percentage by weight of chlorine found in the polymers was below 1 %. This suggests that the initiating species does not contain chlorine. For example, consider initiation by $Cl \cdot$ and assume a bimolecular termination reaction. If all transfer reactions are ignored, then each polymer molecule will contain two chlorine atoms, which for a polymer of $\bar{M}_n \sim 1200$ will be $(2 \times 35.5/1200) \times 100$ or approximately 6 % by weight chlorine.

Even allowing for monomolecular termination and transfer reactions, there should still be, on average, one chlorine atom per molecule which will give ~ 3 % by weight of chlorine in the polymers.

Chlorine contents this high were not found experimentally. The only other possible product from chloroform which does not contain

chlorine is the hydrogen atom. Thus, the low chlorine contents suggest intuitively, that initiation by hydrogen radicals has occurred.

The presence of chlorine in the polymers can be ascribed to transfer reactions. The low molecular weights of the polymers indicate that transfer reactions are important which is in accord with the high transfer activity of vinylferrocene.

The transfer activity of chloroform is also relatively high. For example, although it is 180 times less reactive than carbon tetrachloride with styrene at 60°C, it is 4 times more reactive than toluene.¹⁸⁸ Thus, it is sufficiently reactive to undergo some transfer reactions which will introduce chlorine into the polymer. The higher chlorine content in polymers prepared at higher mole fractions of solvent supports this conclusion.

Because of the unusual nature of the vinylferrocene/chloroform system, it is possible that a more obscure mechanism, such as charge transfer initiation, may be responsible for the polymerization reaction. However, the proposed radical mechanism is more likely.

The green ferricenium species formed in the initial electron transfer reaction contains a vinyl group. It is possible, therefore, that this species may undergo radical polymerization. Thus, a green polymer was obtained from reactions when $[M]_0 = 1.0 \text{ mol dm}^{-3}$. However, it is more probable that the colour in these systems is due to oxidation of the polyvinylferrocene formed initially. This is supported by the fact that yellow solutions of PVF in carbon tetrachloride turn green on standing.³⁶ Similar results have been observed in chloroform in the present study.

Free radicals readily undergo ring substitution reactions with the ferricenium species⁶¹⁻⁶⁴. Thus, this species will act as a radical

scavenger. It is probable that radical addition to the olefinic double bond is preferred because of the lower activation energy for this reaction compared with ring substitution. However, ring substitution reactions cannot be precluded. Further work is required to clarify these points.

5.3. CONCLUSIONS FROM THE POLYMERIZATION OF VINYLFERROCENE IN CHLOROFORM.

It has been shown that the oxidation reaction of vinylferrocene in chloroform can be used to initiate polymerization of this monomer under suitable conditions.

Thus, this polymerization is novel since the monomer initiates its own polymerization. Furthermore, the reaction is quite general and should be applicable to any unsaturated metallocene derivative in solvents which promote electron transfer from the metal nucleus.

Polyvinylferrocene prepared in chloroform without any added free radical initiator has been shown to be similar to the polymer prepared by AIBN initiation in benzene. Both have identical IR and UV/visible spectra, and contain the same paramagnetic species.

A radical mechanism has been postulated to describe the polymerization reaction. This scheme proposes that, as a result of the initial electron transfer from the ferrocene nucleus to form the ferricenium species, hydrogen atoms are released from the chloroform. These radicals then add to the double bond to initiate the polymerization reaction. Experimental evidence has been presented in support of this scheme.

PVF prepared in chloroform without any added initiator has a low molecular weight and contains $\sim 1.0\%$ chlorine. These results have been explained by the high transfer activity of the system.

6. COPOLYMERIZATION OF BUTADIENE AND VINYLFERROCENE .

In the previous chapters, the characteristics of the homopolymerization of vinylferrocene have been examined. This chapter is concerned with the synthesis and examination of some potentially useful materials.

6.1 MATERIALS

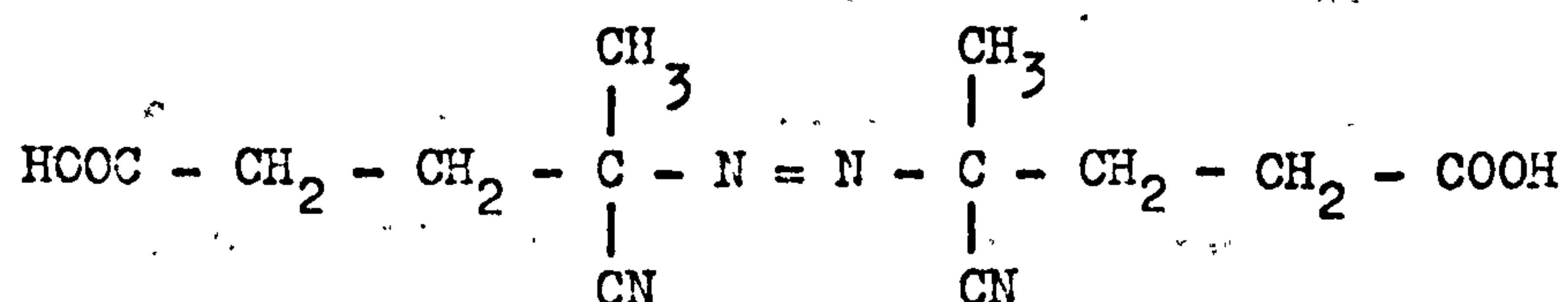
6.1.1. Monomers

Vinylferrocene was purified as described in Section 2.1.1

Research grade butadiene (99.9 % pure) was obtained from Cambrian Chemicals Ltd., Croydon. It was passed over potassium hydroxide and calcium hydride before use.

6.1.2. Initiator

The initiator used in the copolymerization study was 4,4' azobis-(4 - cyanovaleric acid) ACVA



It was obtained from the Aldrich Chemical Co., Inc., Milwaukee, and used as received.

6.1.3 Solvents

The most suitable solvents for the initiator were dimethylformamide (DMF) and 1,4 dioxan. However, attempted polymerizations in DMF resulted in precipitation of the copolymer during the reaction. Hence, 1,4 dioxan (AnalaR) was used in all the copolymerizations. It was purified by refluxing for 4 hours at atmospheric pressure in the presence of sodium metal. It was then distilled from fresh sodium metal under reduced pressure and the middle fraction collected. This was stored over molecular

sieves (No.3A) and used within 24 hours.

6.2. EXPERIMENTAL

The initiator, solvent and vinylferrocene were added to the reaction vessels using the procedure described in Section 2.3.1. The reaction vessels were made of heavy wall tubing of 18 mm internal diameter and $\sim 50 \text{ cm}^3$ capacity. They were attached to the manifold of a high vacuum line via a 319 socket and the contents degassed at 10^{-4} mm Hg by three successive freeze-pump-thaw cycles.

Butadiene was condensed into a second vessel and degassed in a similar manner. The butadiene was then transferred to a calibrated vessel and its volume measured at 80°C . This temperature was obtained, using a saturated solution of solid carbon dioxide in methanol. The variation in the density of liquid butadiene with temperature from the data of Blont and Mark,¹⁸⁹ is given in Table 6-1. A plot of these results is shown in Fig. 6-1. The density at the temperatures of the freezing mixtures was obtained by extrapolation. The volumes of butadiene and vinylferrocene were found to be additive in solution at the reaction temperature. The total volumes were in good agreement with those predicted from the densities of the two monomers and the solvent.

The volumes of butadiene at -80°C required to give predetermined molar concentrations at $+60^\circ\text{C}$ were transferred from the calibrated vessels to the reaction vessels. These vessels were then separated from the manifold by sealing at constrictions in the necks of the tubes. The vessels were sheathed in glass cloth and placed in a water bath at $60^\circ\text{C} \pm 0.01$ for 48 hours.

Table 6 - 1

Densities of Liquid Butadiene at Different Temperatures¹⁸⁹

temperature °C	density g cm ⁻³
-20	0.6687
-15	0.6631
-10	0.6574
- 5	0.6516
0	0.6457
10	0.6337
20	0.6212
30	0.6085
40	0.5947
50	0.5822
60	0.5684

6.2.1. Isolation and Characterization of Copolymers.

The vessels were removed from the bath, frozen in liquid nitrogen and cracked open. Excess butadiene was allowed to evaporate off and the contents precipitated into AnalaR methanol containing a trace of N-phenyl-1-naphthylamine (BDH Chemicals Ltd.)

Dependent upon the amount of vinylferrocene in the copolymers, they varied between soft gums and tough elastomers. In all cases, they proved to be unsuitable for filtration. Therefore, unreacted vinylferrocene was removed by repeated washing with methanol followed by decanting of the supernatant liquid. The copolymers were then

dissolved in benzene, reprecipitated into methanol and the washing process repeated. Final purification was achieved by soxhlet extraction with methanol.

The copolymers were characterized by the techniques described in Section 2.4.

6.3. RESULTS AND DISCUSSION OF COPOLYMERIZATION OF BUTADIENE AND VINYLFERROCENE.

6.3.1. Monomer Feed Compositions.

The ratio of butadiene to vinylferrocene in the initial monomer feed was varied between 90:10 to 30:70 mole per cent. A typical reaction mix is given in Table 6-2. In most cases, the total monomer concentration was 0.2 moles in 10 cm³ dioxan. This was reduced by half at high mole fractions of vinylferrocene to avoid undue waste of this expensive monomer. 0.4 mole % initiator was used in all the reactions.

Table 6 - 2

Typical Reaction Mix for Copolymerization of Butadiene and Vinylferrocene at 60 °C

reactant	molecular weight	weight g	volume cm ³	moles	molar monomer feed
butadiene	54.09	8.654	11.7 ^a	0.16	80
vinyl-ferrocene	211.97	8.478	6.74 ^b	0.04	20
ACVA	280.0	0.224	-	0.0008	0.4
1,4 dioxan		-	10		

a at -80 °C

b at +60 °C

6.3.2. Composition of Butadiene/Vinylferrocene Copolymers.

The composition of the copolymers of butadiene and vinylferrocene was readily determined from the iron contents of the polymers. Thus, the iron content accurately fixes the amount of vinylferrocene present and hence the mole fraction of butadiene. Typical results, in Table 6-3 show that relatively high amounts of vinylferrocene can be incorporated into the copolymers.

Table 6 - 3

Composition of Copolymers of Butadiene and Vinylferrocene.

vinylferrocene in monomer feed. mole %	iron content per cent	vinylferrocene in copolymer mole %	butadiene in copolymer mole %
10	3.2, 3.6	3.3	96.7
15	3.5, 3.5	3.8	96.2
20	5.5, 5.3	6.2	93.8
20	5.6, 5.3	6.2	93.8
23	4.3, 4.6	4.9	95.1
30	7.1, 6.9	8.4	91.6
40	11.8, 11.9	18.1	81.9
50	13.0, 12.8	20.3	79.7
60	15.2, 15.5	26.3	76.7
70	17.8, 18.1	35.3	64.7

The copolymer composition curve is shown in Fig. 6-2.

The shape of the curve shows that vinylferrocene is not incorporated into the copolymer as readily as butadiene. Thus, even at 70 mole % vinylferrocene in the monomer feed, the copolymer only contains 35 mole % vinylferrocene. This result indicates that vinylferrocene is less

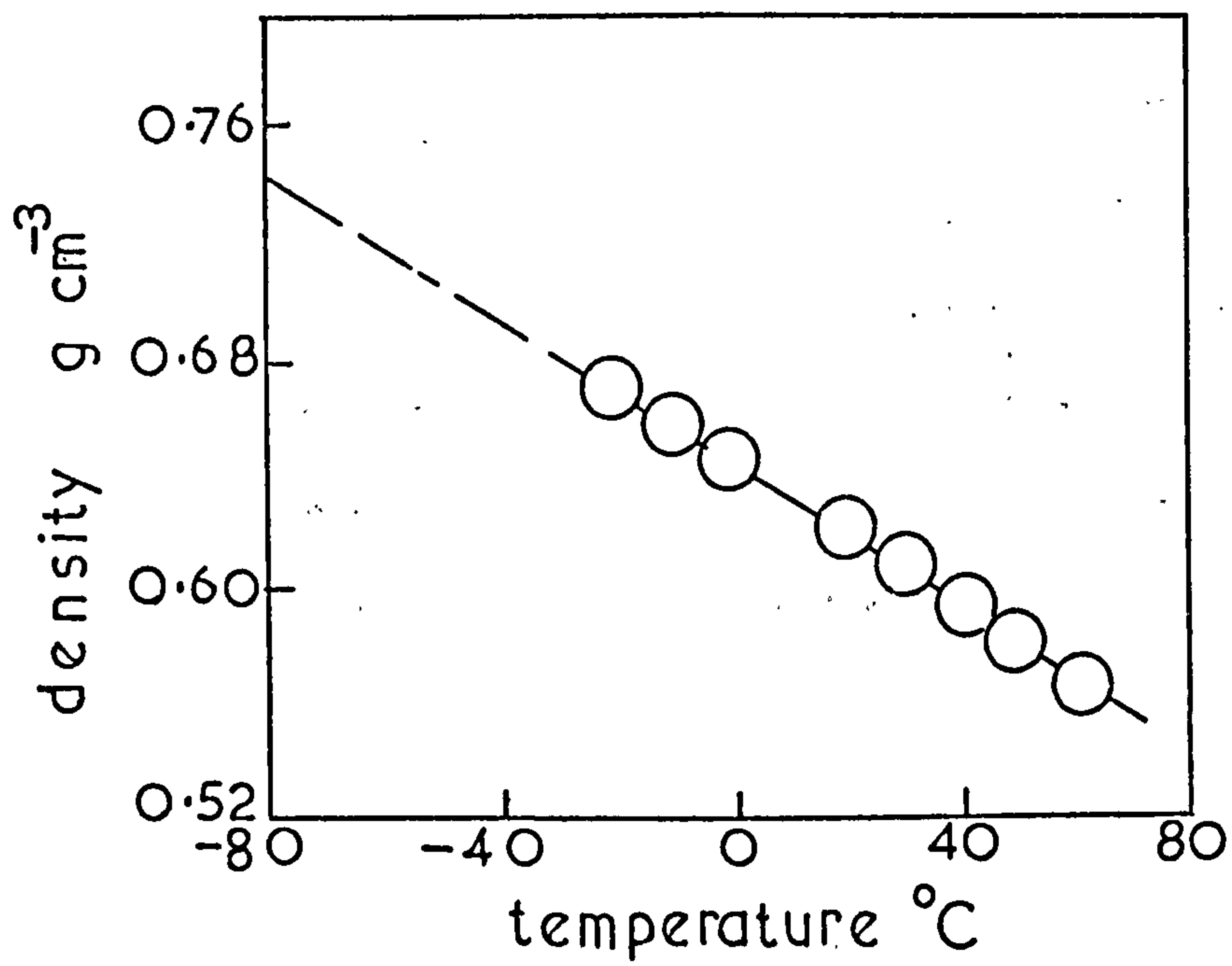


Fig.6-1 Density of liquid butadiene as a function of temperature from the data of Blont and Mark.¹⁸⁹

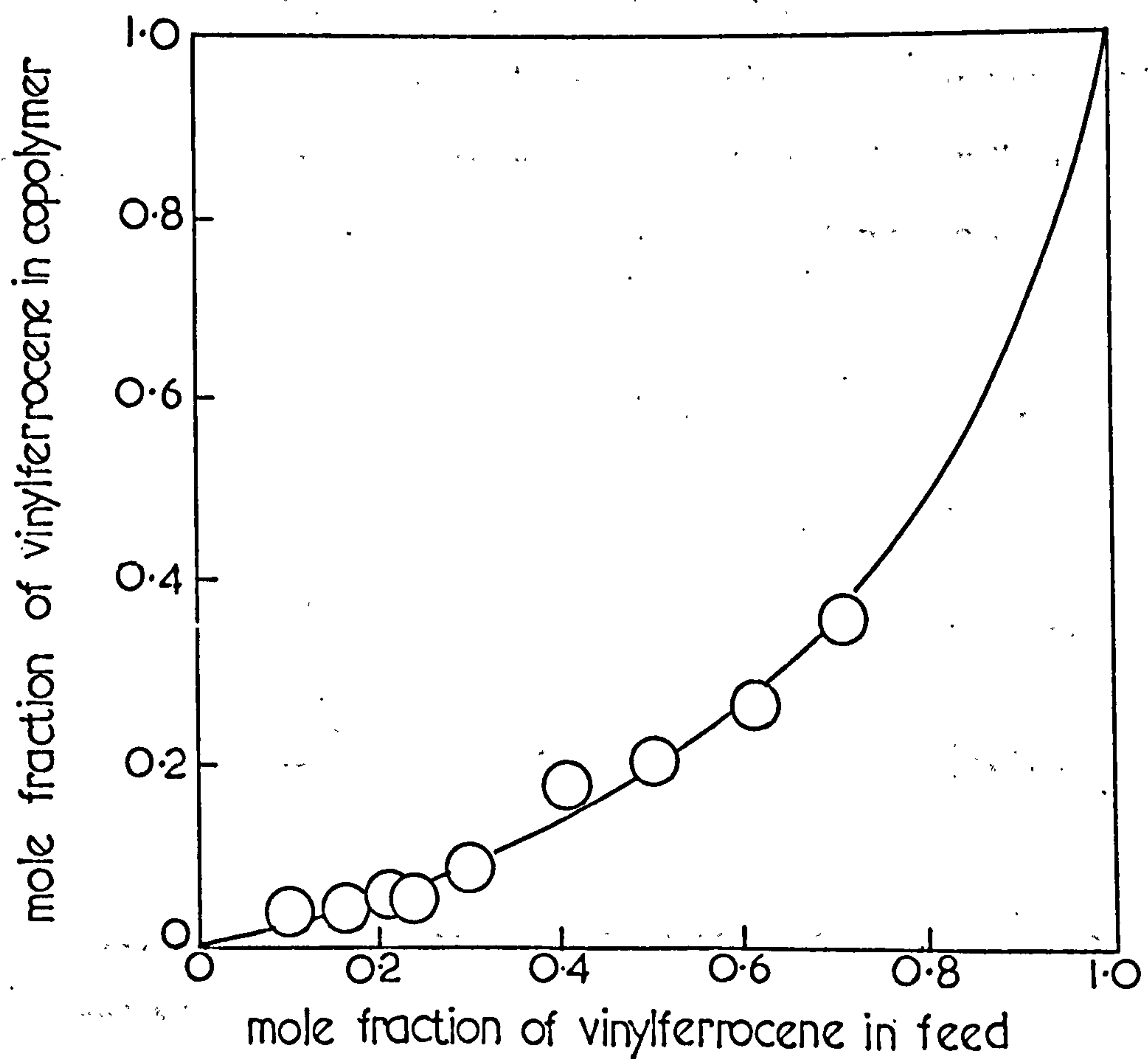


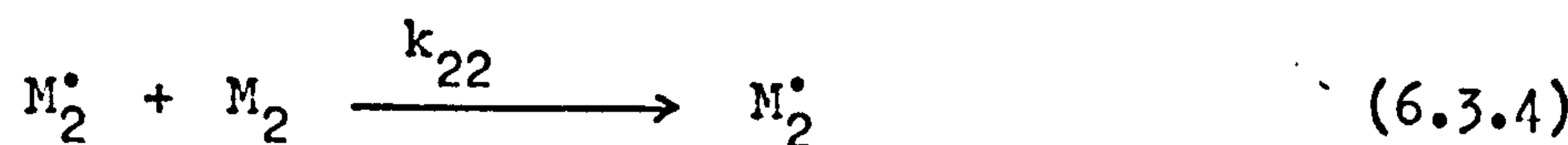
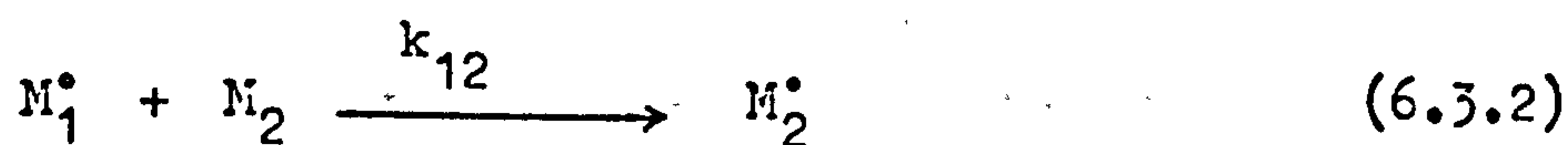
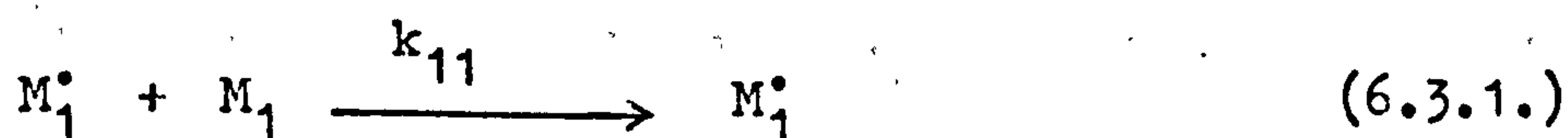
Fig.6-2 Composition curve for copolymers of butadiene and vinylferrocene prepared in 1,4 dioxan at 60°C in the presence of ACVA.

reactive than butadiene towards both its own radical and the butadiene radical.

However, it is obvious that vinylferrocene will copolymerize with butadiene using free radical initiation. This result is at variance with those of Pittman⁸² who found that vinylferrocene and butadiene did not copolymerize using radical initiators.

6.3.3. Reactivity Ratios of Butadiene and Vinylferrocene

The theoretical aspects of radical copolymerizations have been well established^{117,123,124,190} Essentially, in a polymerizing system containing two monomers M_1 and M_2 there will be two types of radical present, $M_1^\bullet$ and $M_2^\bullet$. It has been shown that the reactivity of the growing polymer chain is dependent only on the reactivity of the terminal unit and not on the length or composition of the chain as a whole, providing that the chains are long. Therefore, the growing polymer chain ending in a terminal unit $M_1^\bullet$ can react with either monomer M_1 or monomer M_2 and similarly $M_2^\bullet$ can react with monomer M_1 or M_2 . Thus, the copolymer is formed as a result of four competing propagation reactions



where k_{11}, k_{12}, k_{21} , and k_{22} are the rate constants for the respective reactions and $M_1^\bullet$ and $M_2^\bullet$ represent polymer chains ending in monomer units M_1 and M_2 .

Radicals of type $M_1^\bullet$ are formed by primary initiation and by inter-conversion in the reaction depicted in equation (6.3.3). They are destroyed by termination reactions (transfer reactions are not considered in this present treatment) and also in reaction (6.3.2)

In the steady state, the rate of initiation is practically equal to the rate of termination and for long chains the occurrence of initiation and termination reactions is rare compared with propagation reactions. Hence, in a steady state condition, the main pathway by which radicals $M_1^\bullet$ and $M_2^\bullet$ are formed and destroyed is by interconversion of one to the other.

Therefore, the following equation is applicable in the steady state

$$k_{21} [M_2^\bullet] [M_1] = k_{12} [M_1^\bullet] [M_2] \quad (6.3.5)$$

A similar expression can be obtained for radicals of type $M_2^\bullet$ using the steady state assumption.

The rate of disappearance of Monomer M_1 is given by:-

$$-d[M_1]/dt = k_{11} [M_1^\bullet] [M_1] + k_{21} [M_2^\bullet] [M_1] \quad (6.3.6)$$

Similarly, the rate of disappearance of M_2 is given by:-

$$-d[M_2]/dt = k_{12} [M_1^\bullet] [M_2] + k_{22} [M_2^\bullet] [M_2] \quad (6.3.7)$$

Eliminating radical concentrations by using equation (6.3.5) and dividing equation (6.3.6) by (6.3.7) gives the classical

copolymer composition equation:-

$$\frac{d[M_1]}{d[M_2]} = \left\{ \frac{[M_1]}{[M_2]} \right\} \left\{ \frac{k_{11}/k_{12}[M_1] + [M_2]}{k_{22}/k_{21}[M_2] + [M_1]} \right\} \quad (6.3.8)$$

This equation is usually written as

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]}{[M_2]} \left\{ \frac{r_1[M_1] + [M_2]}{r_2[M_2] + [M_1]} \right\} \quad (6.3.9)$$

where r_1 and r_2 are defined as the monomer reactivity ratios.

The reactivity ratio r_1 represents the ratio of the rate constants for the reaction of a radical of type $M_1^\bullet$ with monomer M_1 and M_2 . The monomer reactivity ratio r_2 similarly expresses the relative reactivity of an $M_2^\bullet$ radical toward an M_2 monomer compared with an M_1 monomer.

Equation 6.3.9 relates the instantaneous composition of the copolymer with the instantaneous monomer composition. Various methods are available for determining reactivity ratios from this equation. Possibly, the most accurate methods are based on integrated forms of equation (6.3.9) using computerized procedures.¹⁹¹ However, in order to use the integrated form of the copolymer equation, it is necessary to determine the conversion of monomers to copolymer exactly.¹⁹² This is best achieved gravimetrically which requires that the copolymers can be precipitated and recovered quantitatively.

Unfortunately, the gummy nature of the copolymers of butadiene and vinylferrocene precluded accurate quantitative determination of conversions by gravimetric techniques even at low temperatures.

Since the use of the integrated form of the differential copolymer equation was not justified, a linearized form was used to determine the monomer reactivity ratios.

In equation (6.3.9) the ratio of the rates of addition of the two monomer is also the ratio of the molar concentrations of the two monomers in the resulting copolymer. Therefore, for low conversions equation (3.6.9) can be written as

$$\frac{m_1}{m_2} = \frac{[M_1]_0}{[M_2]_0} \left\{ \frac{r_1[M_1]_0 + [M_2]_0}{r_2[M_2]_0 + [M_1]_0} \right\} \quad (6.3.10)$$

where m_1/m_2 denotes the molar concentrations of the two monomers in the resulting copolymer. Equation (3.6.10) is strictly only valid for the initial copolymer formed at monomer concentrations $[M_1]_0$ and $[M_2]_0$. However, it allows a linearized form of the differential equation to be used to obtain values of r_1 and r_2 . According to the method of Fineman and Ross,¹⁹³ if $f = m_1/m_2$ and $F = [M_1]/[M_2]$ then equation (3.6.10) can be written as

$$f = F \left\{ \frac{r_1 F + 1}{r_2 + F} \right\} \quad (6.3.11)$$

$$\text{or} \quad F/f (f - 1) = r_1 (F^2/f) - r_2 \quad (6.3.12)$$

Thus, a plot of $F/f (f - 1)$ against F^2/f is a straight line whose slope = r_1 and whose intercept is minus r_2 . Equation (6.3.11) can also be rearranged to give the intercept as r_1 and the slope as minus r_2 .

Values of the mole fractions of butadiene and vinylferrocene in the monomer feeds and resulting copolymers are recorded in Table 6-4 for a series of copolymerizations.

Table 6 - 4

Mole Fractions of Butadiene and Vinylferrocene in Monomer Feeds and Resulting Copolymers M_1 = butadiene, M_2 = vinylferrocene

mole fraction in monomer feed		mole fraction in copolymer	
M_1	M_2	m_1	m_2
0.90	0.10	0.9642	0.0358
0.85	0.15	0.9624	0.0376
0.80	0.20	0.9383	0.0617
0.77	0.23	0.9507	0.0493
0.70	0.30	0.9155	0.0845
0.60	0.40	0.8188	0.1812
0.50	0.50	0.7973	0.2027
0.40	0.60	0.7374	0.2626
0.30	0.70	0.6471	0.3529

The Fineman - Ross parameters $f = m_1/m_2$ and $F = M_1/M_2$ are recorded in Table 6-5 and a plot of $F/f (f - 1)$ against F^2/f is shown in Fig. 6-3. The slope and intercept of the straight line was obtained from a least squares fit of the data. The reactivity ratios thus obtained were :-

$$r_1 = \text{butadiene} = 3.5 \pm 0.2$$

$$r_2 = \text{vinylferrocene} = 0.3 \pm 0.05$$

Table 6 - 5

Fineman-Ross Parameters for Copolymers of Butadiene and Vinylferrocene

mole fraction of butadiene in monomer feed, m	f	F	F/f (f - 1)	F ² /f
0.90	26.9330	9.0	9.0013	3.0075
0.85	25.5957	5.6666	5.4455	1.2545
0.80	15.2075	4.0	3.7366	1.0521
0.80	15.2075	4.0	3.7366	1.0521
0.77	19.2840	3.3290	3.1558	0.5747
0.70	10.8343	2.3333	2.1183	0.5025
0.60	4.5188	1.5	1.1682	0.4979
0.50	3.9334	1.0	0.7457	0.2542
0.40	2.8081	0.6666	0.4294	0.1583
0.30	1.8337	0.4284	0.1948	0.1002

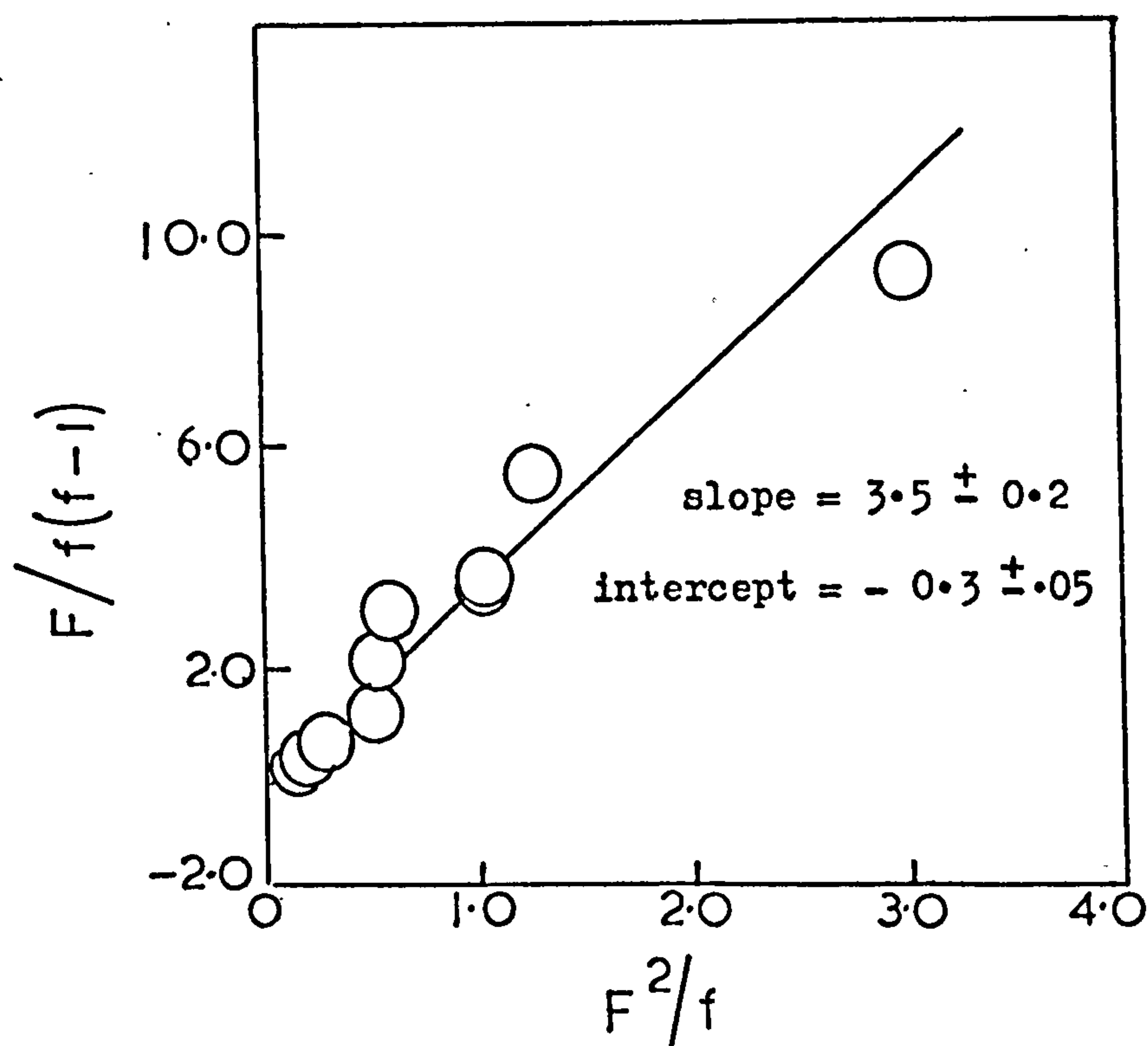


Fig.6-3 Fineman-Ross plot of copolymer composition equation for butadiene and vinylferrocene copolymers prepared at 60°C in 1,4 dioxan in the presence of ACVA.

Before discussing the experimental significance of the reactivity ratios it is worthwhile considering their quantitative accuracy. Tidwell and Mortimer¹⁹⁴ have recently examined the mathematical errors involved in determining reactivity ratios, whilst Alfrey, Bohrer and Mark¹⁹⁵ and others^{117,123,190} have pointed out the uncertainty of many experimental determinations.

One major difficulty concerns the significance of the analytical data obtained with copolymers, since the elemental analysis of pure polymers tends to be difficult. A particular example is the nitrogen content of polyacrylonitrile, which is consistently found to be lower than expected.

Hence, accurate analysis of the copolymer compositions is essential in order to obtain exact reactivity ratios.

Analysis of the copolymers presented no difficulty in the present study since the estimation of iron by polarography can be achieved with a precision of $\pm 0.1\%$. Therefore, the composition of the copolymers can be regarded with confidence as the probable analytical errors are quite small.

Some mathematical errors were unavoidably introduced by using the linearized form of the copolymer equation to obtain the reactivity ratios,¹⁹⁴ since the use of the more mathematically correct integrated form of the equation was not justified in the present study. To be meaningful, this method relies on accurate determinations of the percentage conversions. Such accuracy was not possible because of the gummy nature of the copolymers which made quantitative isolation unreliable.

In order to obtain sufficient copolymer for examination, the copolymerizations were taken to approximately 10 % conversion. Hence, the linearized form of the copolymer equation is not strictly correct,

since it only applies to low conversions. However, after correction for the average monomer feed from 0 % to 10 % conversion, the values of r_1 and r_2 obtained from equation (6.3.10) are within the experimental errors associated with handling gaseous monomers.

Probably the most important feature of the reactivity ratios is that their product $r_1 r_2$, is approximately equal to 1.0 within experimental error.

Thus the ratio of the rate constants for the reaction of the butadiene radical with butadiene and vinylferrocene is equal to the corresponding ratio for the reaction of the vinylferrocene radical to the respective monomers.

$$k_{11}/k_{12} = k_{22}/k_{21}$$

Therefore, the probability of a butadiene unit following a vinylferrocene unit is the same as a butadiene unit following a butadiene unit. Hence, there will be a random arrangement of units along the polymer chain with no tendency for alternation.

Since $r_1 r_2$ equals unity, equation (6.3.9) can be simplified to give

$$\frac{d [M_1]}{d [M_2]} = r_1 [M_1] / [M_2] \quad (6.3.13)$$

When $r_1 r_2 \approx 1.0$ the system is termed an ideal copolymerization.^{190,195} In this respect vinylferrocene is similar to styrene which also behaves ideally in copolymerization with butadiene.¹⁹⁶

The reactivity of butadiene, $r_1 = 3.5$ is much higher than that of vinylferrocene, $r_2 = 0.3$. Hence, the initial copolymer will consist almost entirely of polybutadiene. At high conversions, when the more reactive monomer is exhausted, the copolymer will be essentially pure

polyvinylferrocene.

6.3.4 Q and e Values for Vinylferrocene

The Q - e scheme is an attempt to combine the recognized effects of resonance stabilization and polarity on the relative reactivities of various monomers with various radicals.^{190,195} Thus, Q gives a measure of the monomer reactivity whilst e describes its polar properties. The method is essentially empirical although there is some semi-quantitative basis.

However, for the present purposes the actual values are not as important as their relative magnitude and sign, particularly the e values since Aso et al⁸¹ found e for vinylferrocene = - 1.3 whilst Pittman et al³⁴ report e = + 0.47 and + 0.73 .

The two reactivity ratios, r_1 and r_2 in a binary copolymerization can be written as^{190,195}

$$r_1 = (k_{11}/k_{12}) = (Q_1/Q_2) \exp \left\{ - e_1 (e_1 - e_2) \right\} \quad (6.3.14)$$

$$r_2 = (k_{22}/k_{21}) = (Q_2/Q_1) \exp \left\{ - e_2 (e_2 - e_1) \right\} \quad (6.3.15)$$

$$\text{from which } r_1 r_2 = \exp \left\{ - (e_1 - e_2)^2 \right\}$$

$$\text{or } \ln r_1 r_2 = -(e_1 - e_2)^2$$

Thus, knowing the values of r_1, r_2 and also e , for butadiene e ₂ for vinylferrocene can be obtained.

The exact values of e for butadiene do not always agree and hence an exact value for vinylferrocene is not possible. However, e

for butadiene is definitely negative and the averaged value from Young¹⁹⁷ can be used $\underline{e} = -1.05$.

Since the product of the reactivity ratios for butadiene and vinylferrocene is essentially equal to unity, then $\underline{e}_1$ must equal $\underline{e}_2$ and $\underline{e}$ for vinylferrocene must also be negative.

Thus, the results from this study support the results of Aso et al.⁸¹ and contradict those of Pittman et al.³⁴ A large negative value for vinylferrocene is in fact expected because of the exceptional electron releasing capacity of the ferrocene nucleus.

As butadiene and vinylferrocene have the same $\underline{e}$ value, then from equations (6.3.14) and (6.3.15)

$$r_1 = 1/r_2 = Q_1/Q_2$$

Using Young's value for butadiene, $Q_1 = 2.39$ gives Q_2 for vinylferrocene equal to 0.86. This value is in agreement with the value reported by Aso et al.⁸¹ ($Q = 0.47$)

6.3.5 Spectroscopic Examination of Butadiene/Vinylferrocene Copolymers

Infrared spectra of the copolymers were examined as films cast from benzene. The spectra over the whole range of compositions were very similar and characteristic. A typical spectrum is shown in Fig.6-4. The spectrum shows, almost unmodified, all the absorption bands of both polybutadiene and polyvinylferrocene.

Thus, the bands associated with the ferrocene ring appear at 1411 cm^{-1} , 1108 cm^{-1} , 1002 cm^{-1} and 813 cm^{-1} . The aliphatic stretch from the butadiene is present at 1630 cm^{-1} . The bands which characterize the modes of addition of this monomer are present at 968 cm^{-1} (trans-1:4) 911 cm^{-1} (vinyl- 1:2) and 720 cm^{-1} (cis- 1:4). There is

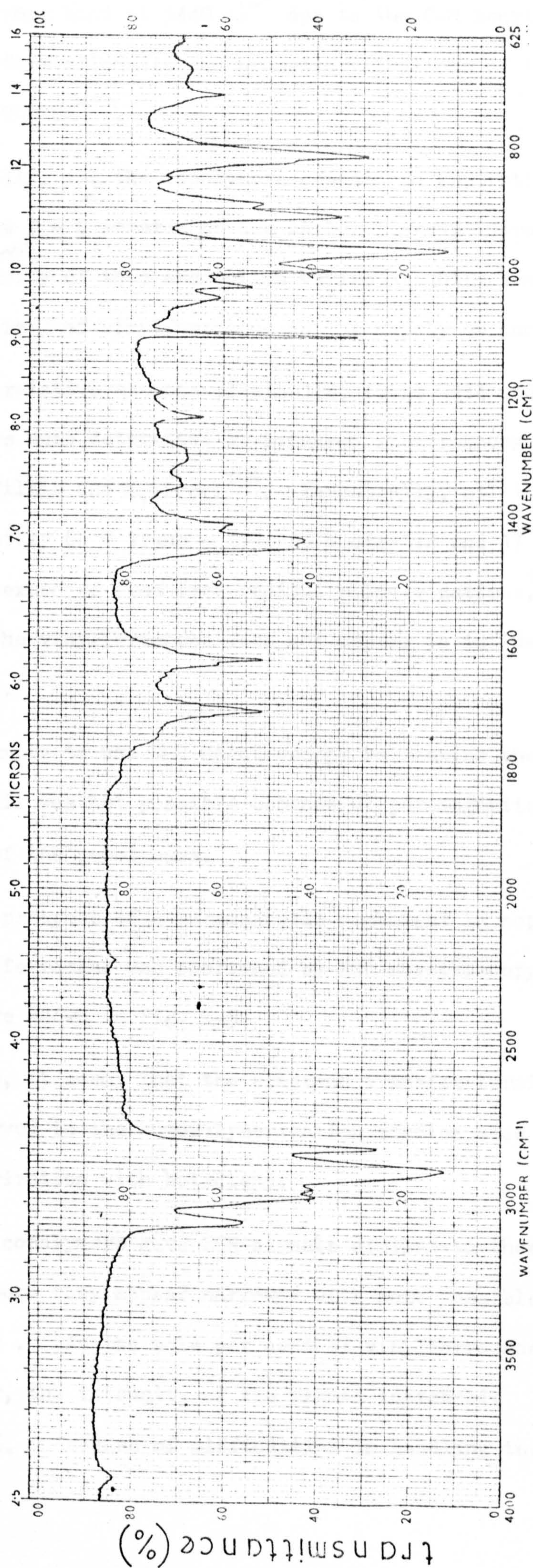


Fig 6-4. Infrared spectrum of a copolymer of butadiene and vinylferrocene containing 8.4 mole % vinylferrocene. Spectrum obtained from a film cast from benzene. Copolymer prepared by radical initiation at 60°C in 1,4 dioxan.

also a strong band at 1440 cm^{-1} due to the C-H bending vibrations. Various other aliphatic and aromatic vibrations of the CH_2 group appear around $2,800\text{ cm}^{-1}$.

Finally, all the copolymers contain an absorption at 1710 cm^{-1} due to the C = O stretch of the carboxyl group introduced by the initiator. The intensity of this absorption varies slightly tending to become weaker as the mole % of vinylferrocene in the copolymer increases.

The relative amounts of cis-1:4, trans -1:4 and vinyl units in the copolymers were determined by infrared spectroscopy using the method of Haslam, Willis and Squirrel¹⁹⁸. Essentially, all the copolymers contained approximately 64 % trans - 1:4, 19 % cis-1:4 and 17 % 1:2 vinyl. Thus, as expected from free radical polymerizations,¹⁹⁹ the presence of iron in the vinylferrocene does not appear to influence the polymer micro structure.

Attempts to use NMR spectroscopy to examine the microstructure in more detail was not possible because of paramagnetic broadening in the spectra of the copolymers.

The presence of a paramagnetic component in copolymers of butadiene and vinylferrocene was confirmed by ESR spectroscopy. Some typical traces are shown in Fig. 6-5

Thus, it seems that the electron transfer termination step which was observed in the homopolymerization studies also occurs in the copolymerization with butadiene.

The copolymers gave ESR signals similar to those obtained from PVF although they appear narrower with some possible evidence of fine structure. As the mole per cent of vinylferrocene increased in the copolymer, the intensity of the signal increased. This is shown in Table 6-6. Because of difficulties in handling the viscous copolymers

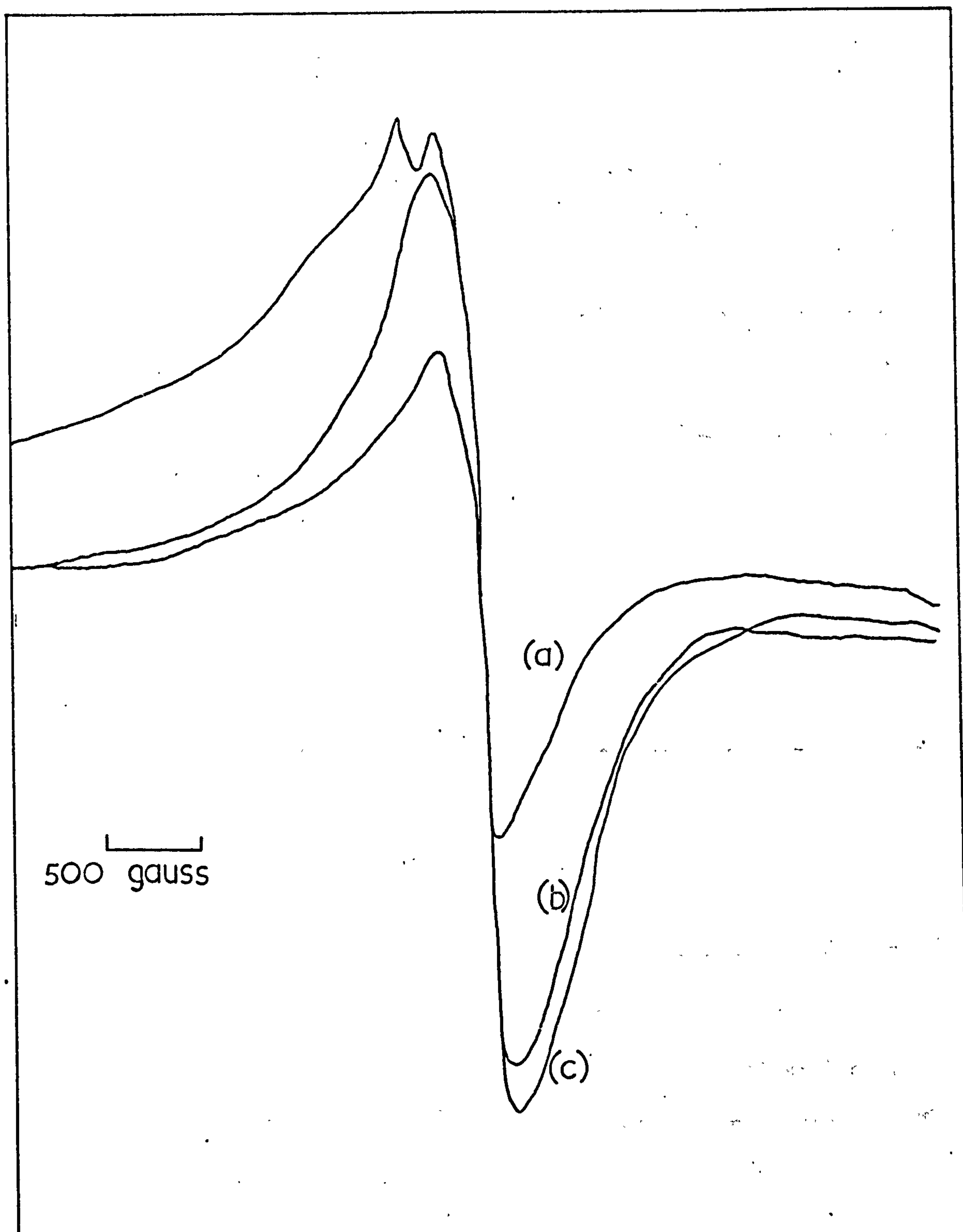


Fig.6-5 Electron spin resonance signals from copolymers of butadiene and vinylferrocene. Spectra obtained from solid samples at room temperature. Field modulation 1000 Hz. Gain 100.

- (a) 20 mole % vinylferrocene; (b) 26 mole % vinylferrocene
(c) 35 mole % vinylferrocene.

in the ESR sample tubes, the absolute intensities were not determined.

Table 6-6

Relative Intensities of ESR Signals from Butadiene/Vinylferrocene Copolymers.

Sample	mole % vinylferrocene in copolymer	Relative Intensity of ESR Signal
1	4.9	30
2	6.2 ^a	110
3	18.1	40
4	26.3	60
5	35.3	200

a repeat of sample 1 taken to high conversion

The trend to increased paramagnetism with increasing vinylferrocene content is reasonable. As more vinylferrocene is incorporated into the growing polymer chain, there is more possibility of intramolecular electron transfer termination occurring. Hence the concentration of the Fe (III) high spin species must increase.

6.3.6 Number Average Molecular Weights and Molecular Weight Distribution

The molecular weights of the copolymers were all below 10,000. Representative results are given in Table 6-7. The highest value was obtained from the copolymer with the lowest vinylferrocene content.

Table 6 - 7

Number Average Molecular Weights of Copolymers of Butadiene and Vinylferrocene. Determined by VPO in benzene at 37°C.

Mole % vinylferrocene in copolymer	$\bar{M}_n$
3.3	8,700
3.8	6,600
6.2	5,300
8.4	5,700
20.3	8,300
35.3	6,400

The copolymers all gave a single broad GPC curve. Thus, the samples were true copolymers and not mixtures of homopolymers. Some curves had a shoulder on the higher molecular weight side which indicates branching in the copolymers. Branching in these copolymers could be high because of the transfer activity of vinylferrocene and the possibility of 1,2 addition with butadiene.

6.3.7 Glass Transition Temperatures.

For a random copolymer the T_g should be determined by a simple relationship between the T_g of the pure homopolymers and the mole fraction of each in the copolymer

$$T_g \text{ (copolymer AB)} = \frac{T_g \text{ A} \times \text{mole fraction A} + T_g \text{ B} \times \text{mole fraction B}}{\text{total number of moles}}$$

Since the reactivity ratios show that butadiene and vinylferrocene form a random copolymer, the T_g of the copolymer should be related linearly to those of polybutadiene and polyvinylferrocene.

The copolymer T_g values obtained experimentally and those calculated from the above expression are given in Table 6 - 8. The T_g for polybutadiene was taken as 193 K whilst that for PVF was 497 K.

Table 6 - 8

Glass Transition Temperatures of Copolymers of Butadiene and Vinylferrocene.

Mole fraction of vinylferrocene	T_g K (experimental value ^a)	T_g K, (calculated value for a random copolymer)
0.033	199	204
0.038	206	205
0.049	212	208
0.062	210	212
0.084	226	219
0.181	248	249
0.203	259	254
0.263	266	272
0.353	291	300

a determined by DSC in sealed pans.

The results are plotted in Fig. 6-6 and show that the experimental points are in good agreement with the theoretical curve generated for a random copolymer.

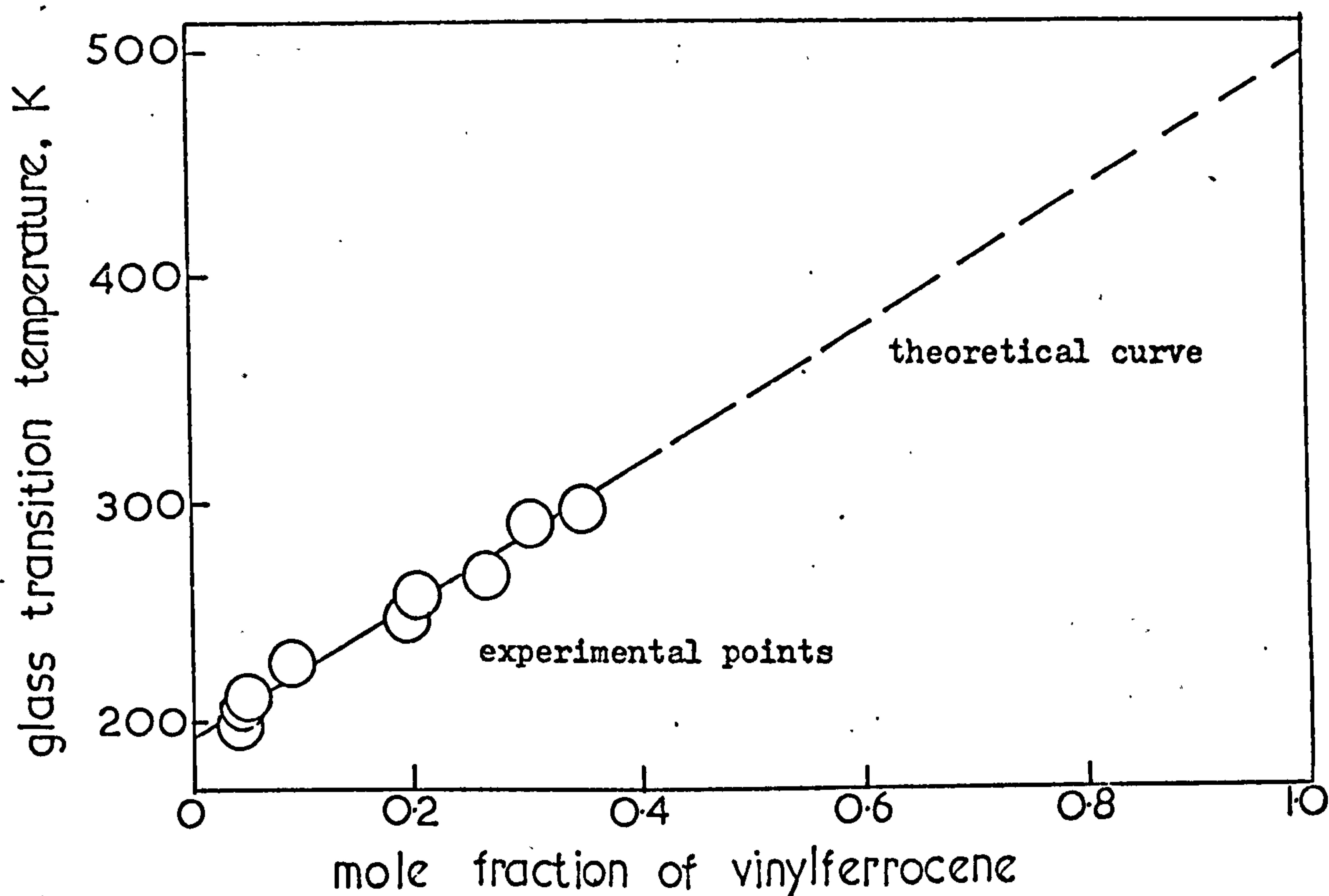


Fig. 6-6. Glass transition temperatures of copolymers of butadiene and vinylferrocene as a function of mole fraction of vinylferrocene in the copolymer.

6.4. CONCLUSIONS FROM THE COPOLYMERIZATION STUDIES OF BUTADIENE AND VINYLFERROCENE.

It has been shown that butadiene and vinylferrocene readily copolymerize using free radical initiation. Pittman's suggestion,⁸² therefore, that butadiene and vinylferrocene do not copolymerize using free radical initiation, is not supported by the experimental results of the present study.

The reactivity ratios for butadiene (r_1) and vinylferrocene (r_2) were found to be $r_1 = 3.5 \pm 0.2$ and $r_2 = 0.3 \pm 0.05$. The product of the reactivity ratios is equal to 1.0 within experimental error. This result suggests that butadiene and vinylferrocene undergo 'ideal copolymerization' and that there will be a totally random sequence

of units in the copolymer. This observation is supported by the relationship between the copolymer compositions and their glass transition temperatures.

The Q and e values obtained for vinylferrocene agree with those reported by Aso et al.⁸¹ The e value is negative in accordance with the electron releasing properties of the ferrocene nucleus. Thus, the positive e value reported by Pittman et al.³⁴ appears to be in error.

Copolymers of butadiene and vinylferrocene contain a paramagnetic species. ESR spectroscopy indicates that the species is an Fe (III) high spin complex similar to that found in polyvinylferrocene. The concentration of the paramagnetic species increases as the mole fraction of vinylferrocene in the copolymer increases.

It appears that intramolecular, electron transfer termination of growing polymer chains (or 'intraelectran' termination for short), is quite general in radical polymerizations of vinylferrocene. For example, this unusual termination reaction occurs in homopolymerization, and copolymerization with butadiene. Solvent effects do not appear to be important since it occurs in benzene, chloroform and 1,4 dioxan.

Whether or not 'intraelectran' termination of radical polymerizations is a feature general to all unsubstituted metallocene derivatives will only be ascertained by further studies.

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APPENDIX 1

Abbreviations used in this Thesis.

AIBN	2,2'- azobisisobutyronitrile
TCNE	tetracyanoethylene
DDQ	dichlorodicyanoquinone
PVF	polyvinylferrocene
Et	ethyl
acac	acetylacetonate
GPC	gel permeation chromatography
In	initiator
PVC	poly(vinyl chloride)
THF	tetrahydrofuran
M	monomer
S	solvent
FMA	ferrocenylmethyl acrylate
FMMA	ferrocenylmethyl methacrylate
UV	ultraviolet
NMR	nuclear magnetic resonance
ESR	electron spin resonance
VPO	vapour pressure osmometry
DSC	differential scanning calorimetry
Fc	monosubstituted ferrocenyl group ($C_{10}H_9Fe$)
PVA	poly(vinyl acetate)
DMF	dimethylformamide
IR	infrared
ACVA	4,4'-azobis(4-cyanovaleric acid).
DMSO	dimethylsulphoxide

THE KINETICS OF FREE RADICAL POLYMERIZATION OF VINYLFERROCENE

Introduction

Vinylferrocene has been shown (1-4) to form homopolymers and copolymers quite readily. Only one kinetic study has been reported (5) which suggested that vinylferrocene polymerized according to established vinyl polymerization mechanisms (6). However, a recent kinetic study conducted in these laboratories on the homopolymerization of this monomer has indicated that vinylferrocene does not follow normal vinyl polymerization mechanisms. Thus the initial rate of polymerization at low conversions was found to be dependent on the initial monomer concentration, $[M]_0$, to a power 1.12 and on the initial initiator concentration, $[In]_0$, to a power 1.11.

This result suggests that the termination reaction is both monomolecular and intramolecular. A kinetic scheme is proposed which satisfies the experimental data. Implicit in this scheme is the suggestion that the polymer contains unpaired electrons. The presence of unpaired electrons in polyvinylferrocene has been indicated by nmr and Mössbauer spectroscopy and confirmed by esr spectroscopy.

It is considered that the termination reaction involves direct participation, possibly with solvent interaction, of the ferrocene nucleus. In this reaction an electron is transferred from the iron atom to the growing polymer chain radical and the chain radical becomes deactivated. The resultant paramagnetic species produced in the polymer molecule is considered, on the basis of spectral evidence, to be a transition metal complex in which the iron is formally in the Fe(III) state.

Experimental

Vinylferrocene was purified by successive sublimations at 30°C and 0.1 mm Hg (mpt 52.5 to 53.5°C). Gas chromatography (Pye Unicam 101, carbowax column at 150°C) confirmed a pure sample. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized three times from AnalaR methanol (mpt 101°C to 102°C with decomposition). AnalaR benzene was refluxed over phosphorus pentoxide for six hours and then distilled from fresh phosphorus pentoxide and the middle fraction collected. Rates of polymerization were determined by dilatometry (7) after degassing the reactants by three freeze-thaw cycles at 10^{-4} mm Hg. The density and apparent density of the monomer and polymer were determined by the method of Matheson et al. (8) modified to a small scale. Polymerizations were allowed to proceed to ca. 5% conversion and then the reaction was stopped by precipitation into methanol containing a trace of

TABLE I
Homopolymerization of Vinylferrocene in Benzene Initiated by AIBN

T°C ±0.01	[M] ₀ mole dm ⁻³	[In] ₀ × 10 ² mole dm ⁻³	Conversion %	Rp × 10 ⁵ mole dm ⁻³ s ⁻¹	$\left\{ \frac{R_p \times 10^4}{[M]_0^{1.12} [In]_0^{1.11}} \right\}$	$\bar{M}_n^*$
60	4	0.4	0.6	0.54	5.1	5,900
60	4	1.0	1.8	1.62	5.4	—
60	4	1.0	1.8	1.67	5.6	5,600
60	4	1.8	3.1	2.90	5.0	6,800
60	4	2.0	3.2	3.21	5.1	7,900
60	1	1.0	1.1	0.42	6.0	—
60	2	1.0	1.6	0.78	5.9	2,700
60	3	1.0	1.9	1.34	6.4	5,800
60	4	1.0	1.8	1.71	5.9	6,300
60	4	0.4	0.9	0.58	5.7	—
70	4	0.4	2.0	3.35	—	3,400
75	4	0.4	3.8	5.87	—	6,900
80	4	0.4	5.8	9.54	—	6,600

*Number average molecular weight determined in benzene solution at 37°C by vapor pressure osmometry.

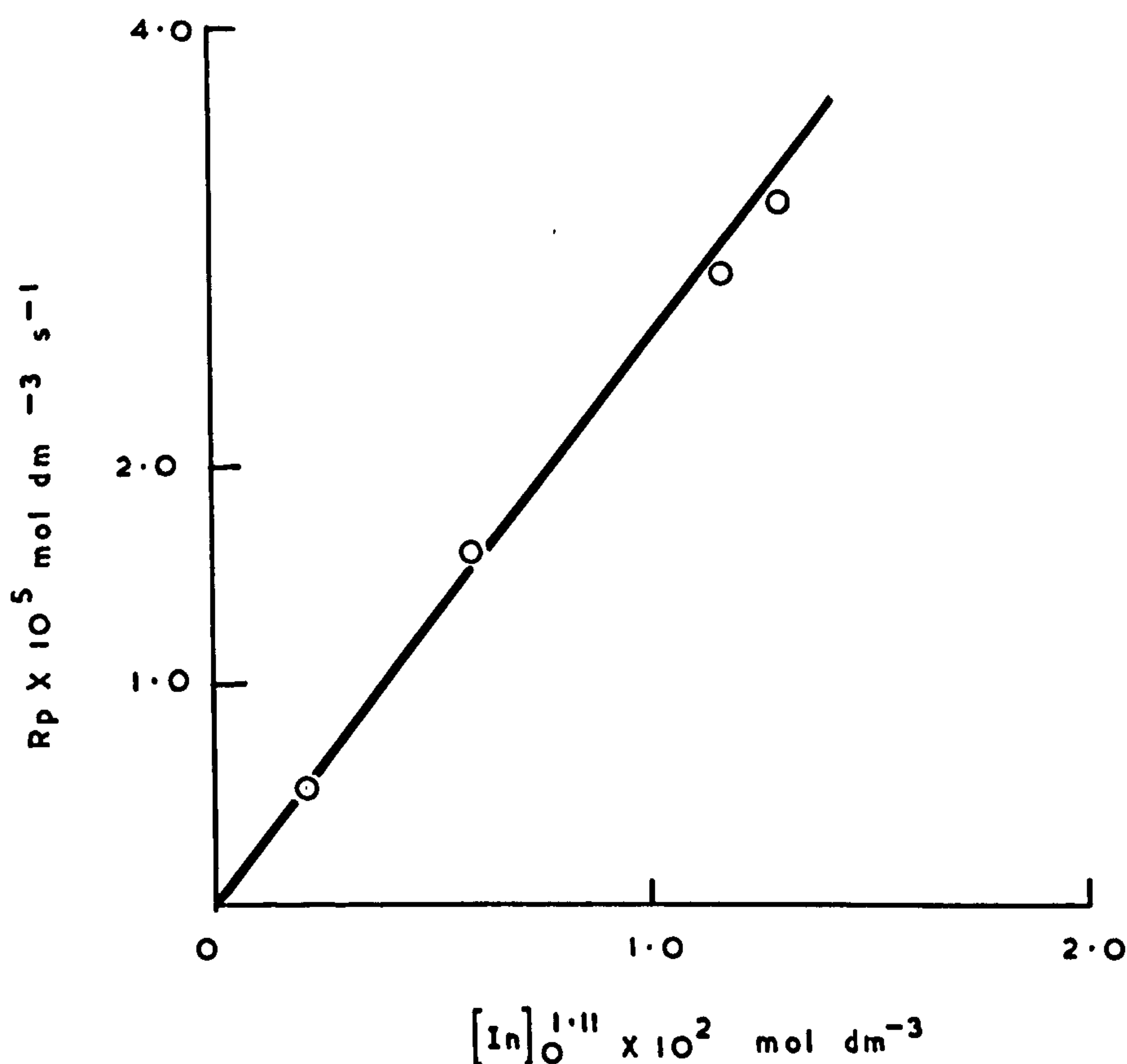


Fig. 1. Initial rate of polymerization of vinyl ferrocene in benzene at 60°C as a function of $[In]_0^{1.11}$, at constant $[M]_0$. $[M]_0 = 4.00 \text{ mole dm}^{-3}$.

hydroquinone. The polymer was redissolved in benzene, precipitated into methanol, and collected on a sintered glass crucible and dried to constant weight at 60°C and 0.1 mm Hg.

Results and Discussion

Representative results of the kinetic experiments are summarized in Table I. Logarithmic plots, using the least squares method of the initial rate of polymerization against initial monomer and initiator concentrations, gave straight lines with slopes equal to 1.12 and 1.11 respectively. The rate expression is therefore of the following form:—

$$R_p = k[M]_0^{1.12} [In]_0^{1.11} \quad (1)$$

where $k = 5.6 \times 10^{-4}$ when R_p is expressed in $\text{mole dm}^{-3} \text{ s}^{-1}$ and $[M]_0$, $[In]_0$

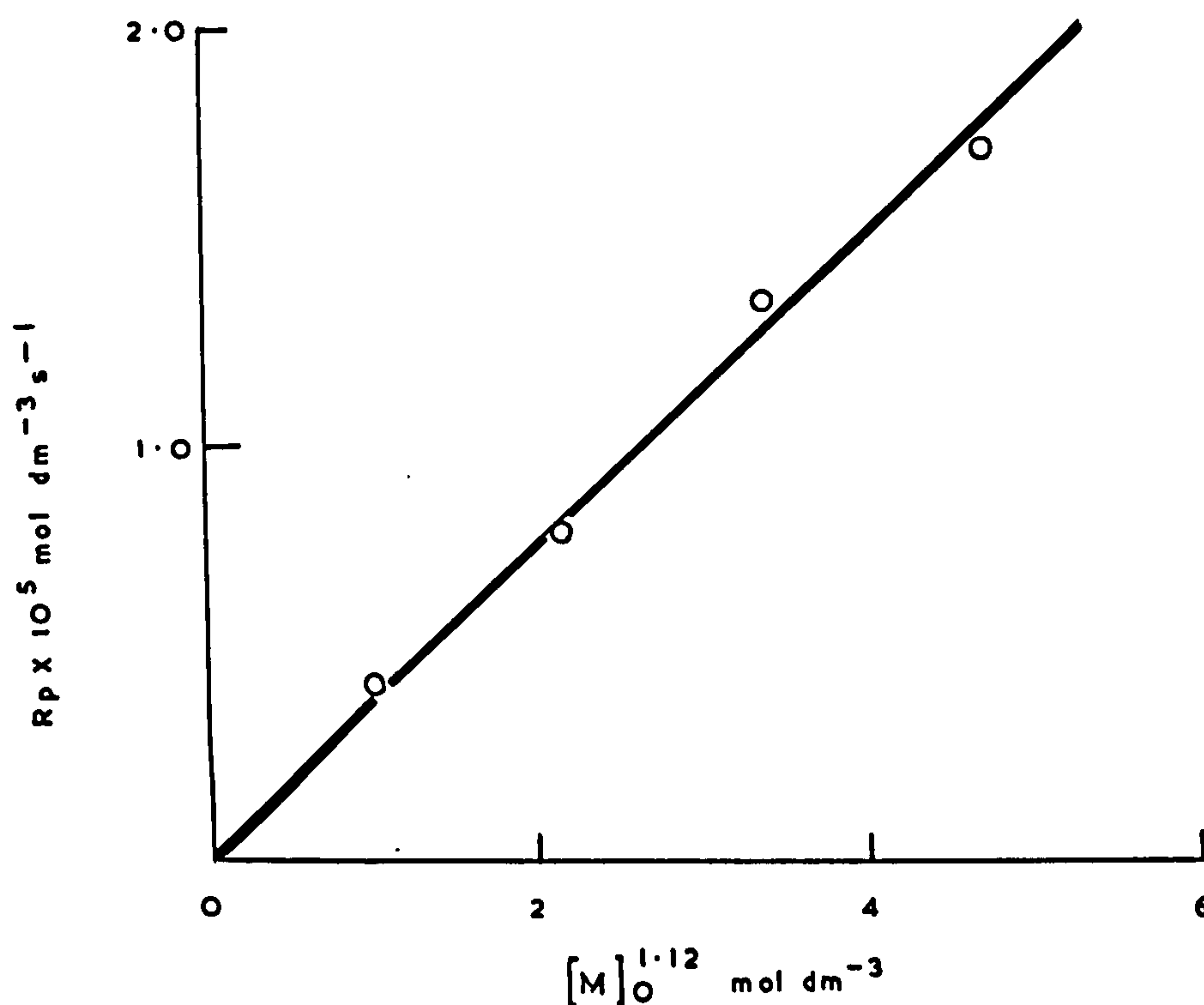
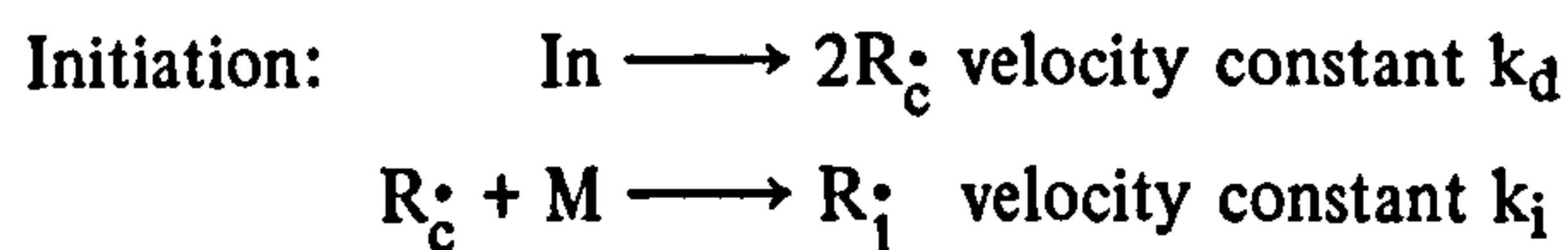


Fig. 2. Initial rate of polymerization of vinyl ferrocene in benzene at 60°C as a function of $[M]_0^{1.12}$ at constant $[In]_0$. $[In]_0 = 1.0 \times 10^{-2} \text{ mole dm}^{-3}$.

in mole dm^{-3} . Plots of R_p against $[M]_0^{1.12}$ and $[In]_0^{1.11}$ are shown in Figures 1 and 2 respectively. The overall activation energy for the polymerization between 60°C and 80°C was found to be 139.7 kJ mole^{-1} .

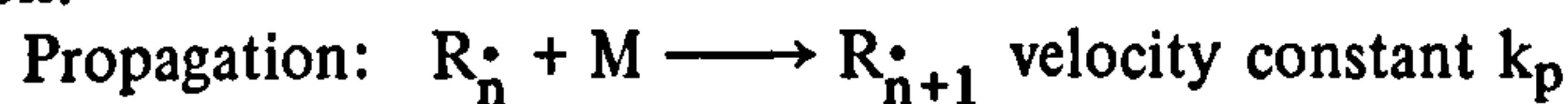
The dependence of the rate on the initiator concentration to a power of approximately 1.0 indicates that the predominant termination step is monomolecular. Normally the termination step in vinyl polymerizations is bimolecular and involves a mutual reaction between two polymer chain radicals (6). Furthermore, the overall form of the rate expression suggests that the termination reaction is intramolecular and does not involve hydrogen abstraction from monomer as in the case of allylic polymerizations (9).

The rate expression can be explained if the termination reaction involves only one growing polymer radical and the product of this reaction is inactive. In accordance with accepted practice (6), the following kinetic scheme can be suggested:



$$\text{Rate of initiation: } I = 2k_d f [\text{In}] \quad (2)$$

where f is the initiator efficiency and $[\text{In}]$ represents the initiator concentration.



$$\text{Rate of monomer removal} = -d[M]/dt = k_p [M] [R^\bullet] \quad (3)$$

where $[R^\bullet] = \sum_{i=1}^{i=\infty} [R_i^\bullet]$ = total concentration of polymer radicals.

Termination: $R^\bullet \longrightarrow$ inactive species, velocity constant k_t . Making the steady state approximation,

$$[R^\bullet] = \{2k_d f [\text{In}] / k_t\} \quad (4)$$

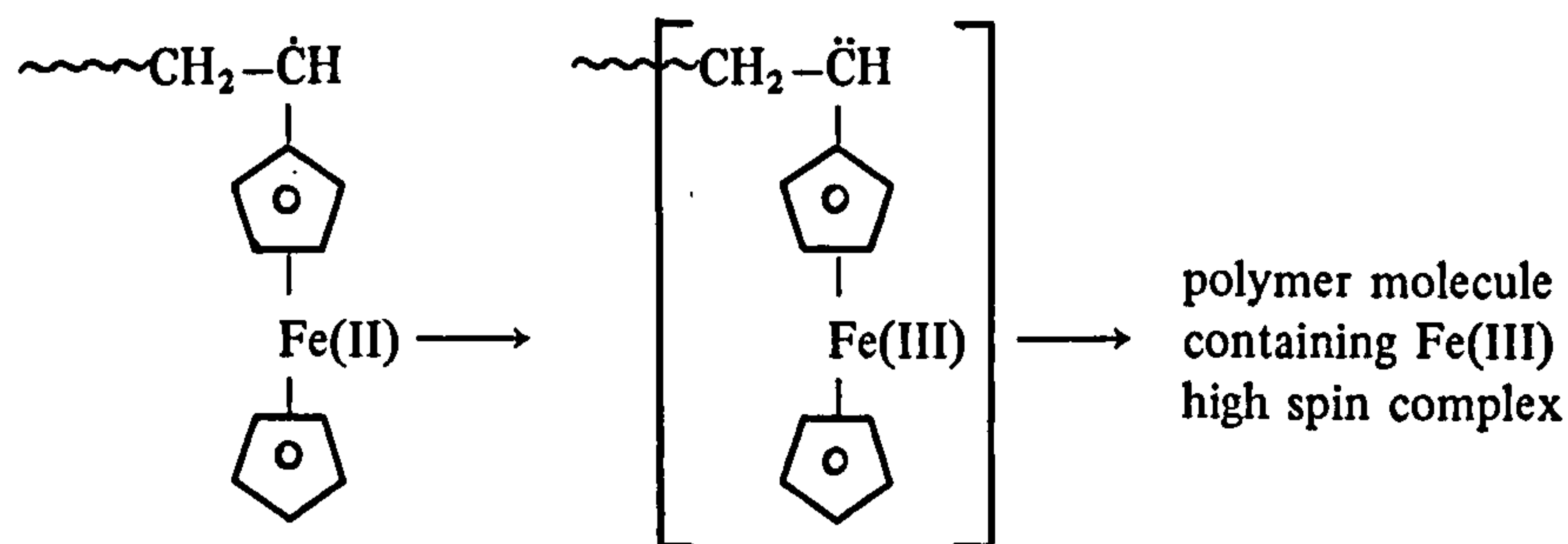
whence the rate of polymerization =

$$R_p = -d[M]/dt = k [M] [\text{In}] \quad (5)$$

where k is a composite constant equal to $\{2k_d f k_p / k_t\}$

This scheme is in reasonable agreement with the experimental results summarized in eq. (1). The relatively high activation energy is also in agreement with this kinetic scheme.

Two characteristic features of metallocenes are their ready oxidation to cationic species by loss of one or more electrons from the metal atom (10) and direct participation of the metal atom in many reactions (11). It seems probable, therefore, that the termination step involves an electron transfer from the iron atom to the polymer chain radical which deactivates the radical and leaves an unpaired electron in the ferrocene nucleus. The ferrocene nucleus which loses an electron in the termination reaction does not retain its d^5 low spin configuration, and evidence presented below suggests that rearrangement occurs to form a polymer molecule containing an Fe(III) high spin complex. A tentative reaction could be depicted:



Thus, the proposed mechanism for the termination step implies that each polymer molecule produced in this reaction contains unpaired electrons. This

observation is supported by spectral studies. The nuclear magnetic resonance (nmr) spectra showed pronounced paramagnetic broadening which was independent of temperature. Paramagnetic broadening of the nmr spectra of addition polymers containing ferrocene has recently been reported (12) and the effect was still present after the addition of ascorbic acid. This suggests that the ferricenium cation was not present. The Mössbauer spectra of polymer samples contained a significant third peak at a small positive velocity (0.17 mm/s) which was not present in the monomer. The peak is not consistent with the ferricenium cation, but appears more likely to be an ionically bound complex involving Fe(III) high spin. This observation is supported by the temperature dependence of this peak which is reduced at low temperatures. Peaks due to covalently bonded iron tend to increase with decreasing temperature. The area of the third peak in the Mössbauer spectra varies between 3% to 14% of the total area and depends on the molecular weight of the polymer and on the extent of conversion of monomer to polymer. The electron spin resonance (esr) spectra confirmed the presence of a substantial concentration of a paramagnetic component in the polymer molecules. A single broad line was observed from solutions in benzene and from the solid polymer. The width varied from 425 gauss in benzene solution to 600 gauss in the solid state at room temperature. At liquid nitrogen temperature the solid produced a line width of 850 gauss. The 'g' value obtained for the centre of the peak was 2.06. The measured spin concentration was necessarily imprecise as it was obtained by comparison of the rather broad peaks with the narrow line from chromium in magnesium oxide. However the recorded value of 10^{19} spins/gram is consistent with the concept of one paramagnetic species per molecule (a value of 8.5×10^{18} spins/gram would correspond to one spin per molecule for a number average molecular weight of ca. 7000). The spectra are consistent with Fe(III) in a high spin configuration which support the Mössbauer results.

Since ferrocene and its compounds are generally regarded as being stable to atmospheric oxidation (13), it is unlikely that oxidation of ferrocene nuclei in polyvinylferrocene is the cause of the spectral results. If oxidation takes place upon storage, then the esr signals should increase with time. This has not been observed. Likewise, oxidation during the polymer isolation is unlikely because Mössbauer studies indicate that the percent of paramagnetic species varies systematically with the degree of polymerization of the polymer examined.

Thus the spectral observations are in agreement with the kinetic analysis. On the basis of spectral evidence it is considered that after the initial electron transfer reaction which terminates the growing polymer chain, a polymer molecule is produced which contains a metal complex of iron in a Fe(III) high spin configuration.

Further studies are in progress to elucidate the precise mechanism operating in the termination step and to characterize the paramagnetic species and its position in the polymer.

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R O C K E T P R O P U L S I O N E S T A B L I S H M E N T
W E S T C O T T

Technical Report No. 7

March 1973

THE KINETICS OF THE FREE RADICAL POLYMERIZATION
OF VINYLFERROCENE

by

G.F. Hayes

SUMMARY

The kinetics of the free radical polymerization of vinylferrocene in benzene at 60°C has been studied by dilatometry. The initial rate of polymerization is dependent on the monomer concentration to a power of 1.12 and on the initiator concentration to a power of 1.11

$$R_p = k [M]^{1.12} [In]^{1.11}$$

An analysis of the kinetic results indicates that vinylferrocene does not follow normal vinyl polymerization mechanisms. The rate expression has been explained by the hypothesis that the growing polymer radical is terminated by a monomolecular and intramolecular reaction. The proposed scheme is supported by the overall activation energy of the polymerization and by ultraviolet and nuclear magnetic resonance spectroscopy. Results predicted by the kinetic scheme have been confirmed by Mössbauer and electron spin resonance spectroscopy. The validity of the scheme is thus supported. It is suggested that the polymerization is terminated by an electron transfer reaction from the iron atom to the chain radical. This reaction deactivates the growing polymer chain and produces a terminal unit which is paramagnetic. The paramagnetic species appears to be an ionically-bound complex of iron (III) in a high spin configuration. This type of termination reaction has not been previously observed in vinyl polymerizations.

The unusual termination reaction may clarify some results from previous investigations concerned with utilizing the properties of the ferrocene nucleus in conventional addition polymers.

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1 INTRODUCTION

There has been considerable interest in the synthesis and properties of ferrocene-containing polymers¹⁻⁴ because of the many desirable features of the ferrocene nucleus. These include radiation stability^{5,6}, thermal stability⁷, catalytic activity^{8,9} and interesting magnetic and electrical properties¹⁰. Much research has been directed towards condensation polymers^{1,11} containing the ferrocene nucleus as an integral part of the polymer backbone. From many aspects and in particular when thermal stability is important, these structures offer appreciably more potential than can be visualized for polymers containing pendent ferrocene units. However, for specialized applications in rocket motor technology, conventional addition polymers containing pendent ferrocene nuclei are of more interest, offering a convenient means of combining the inherent tractability of the addition polymer with specific properties of the ferrocene nucleus. Commensurate with the scientific and technological importance of addition polymers derived from vinyl-type monomers, the most thoroughly examined polymers containing pendent ferrocene nuclei have been obtained from vinylferrocene.

Vinylferrocene was first synthesized in 1955 by Arimoto and Haven who also demonstrated its ready polymerization characteristics¹². Since then several investigators¹³⁻¹⁶ have reported polymers based on vinylferrocene. The only kinetic study reported¹⁷ concluded that vinylferrocene followed normal vinyl polymerization mechanisms, and emphasized its similarity to styrene. The molecular weights reported in this study and in others^{13,14} are low compared with those of other vinyl polymers. Other studies¹⁸ tentatively concluded that vinylferrocene may function as a transfer agent or as a chain terminator.

The Rocket Propulsion Establishment is currently investigating^{19,20} the properties of copolymers of vinylferrocene. Because of the lack of concise kinetic knowledge and the anomalously low molecular weights of polymers obtained from vinylferrocene, an examination of the kinetics of the homopolymerization was considered necessary, to elucidate the mechanisms involved in the homopolymerization, before the copolymerization programme was begun. This report describes a kinetic analysis of the homopolymerization of vinylferrocene in benzene solution.

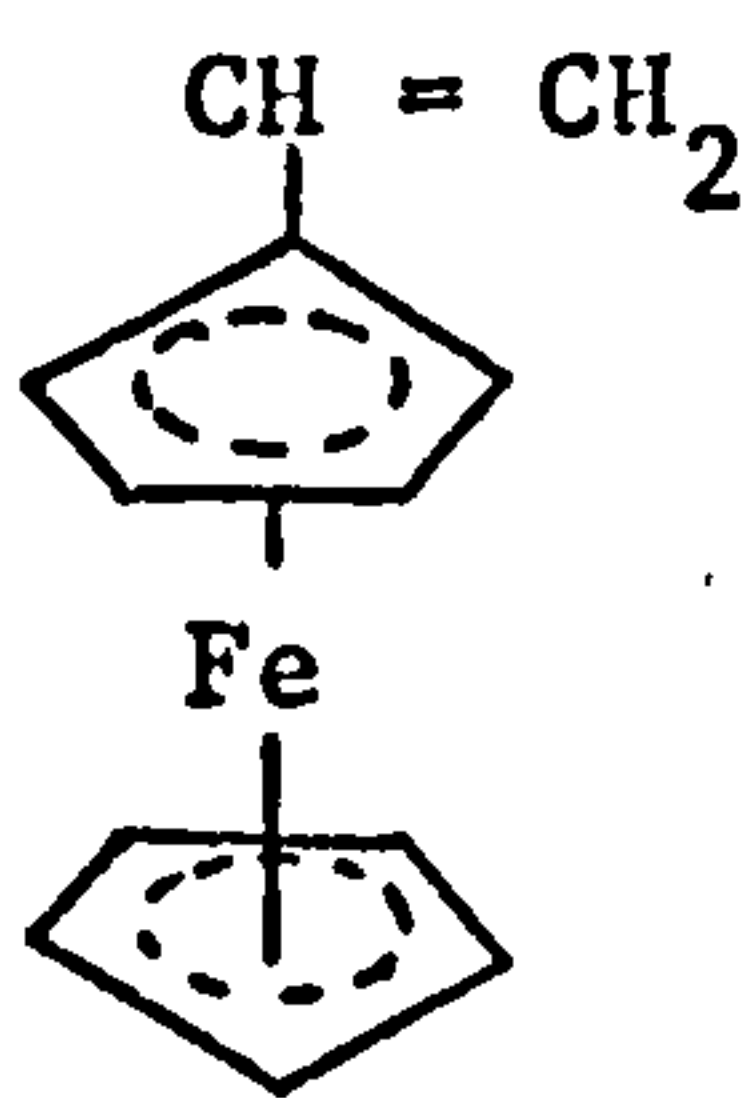
2 EXPERIMENTAL

2.1 Materials

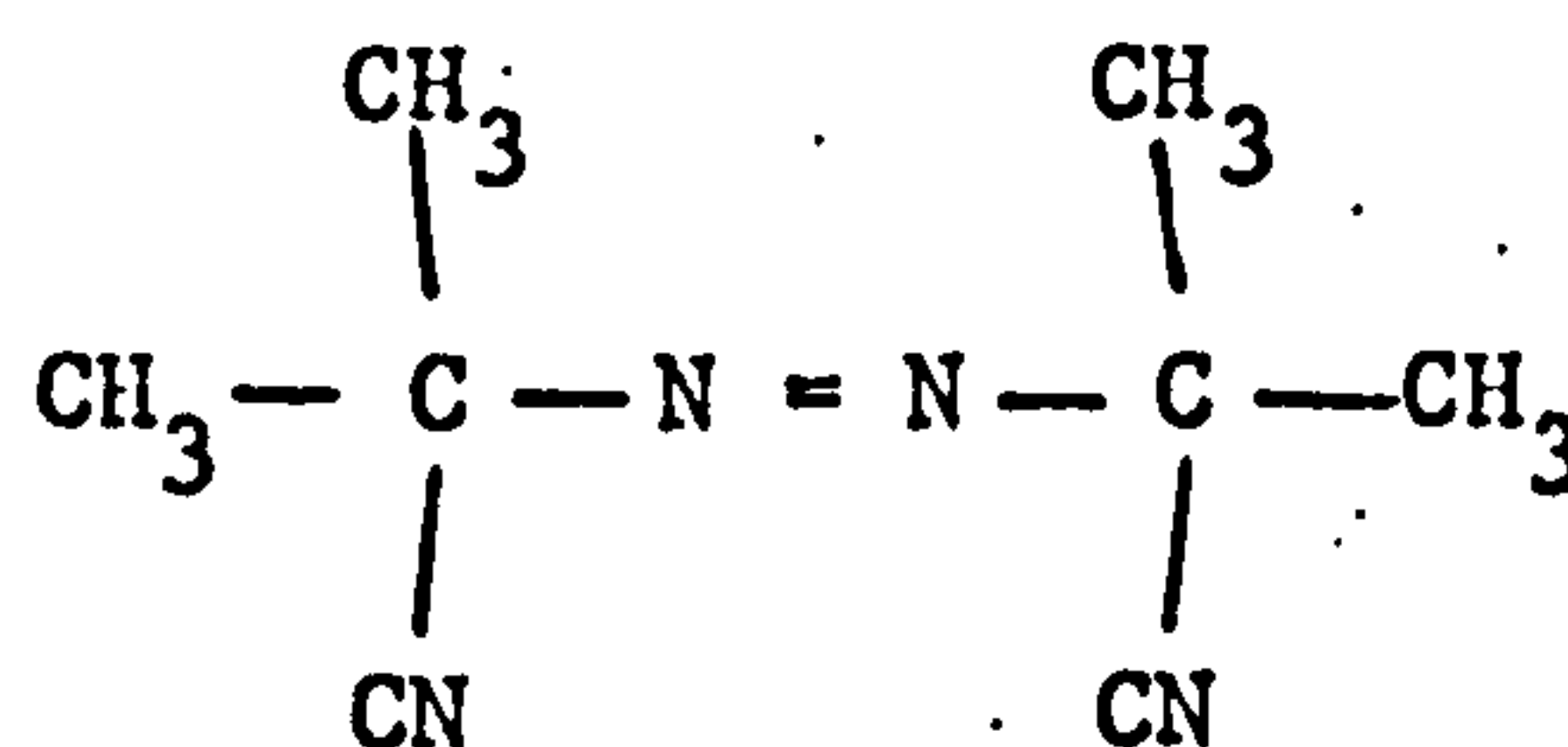
Vinylferrocene (1) was obtained from the Research Organic/Inorganic Chemical

TEXT BOUND INTO THE SPINE

Corporation, California, and purified by successive sublimations at 30°C and 0.1 mm Hg. Samples (mp 52.5 to 53.5°C) were stored at -25°C in sealed flasks until required. Gas chromatographic analysis (Pye Unicam 101 Chromatograph, carbowax column at 150°C) indicated a pure compound. AnalaR benzene was refluxed over phosphorus pentoxide for six hours and then distilled from fresh P₂O₅ at reduced pressure. The first and last portions were discarded and the middle fraction collected and stored in sealed flasks at room temperature in darkness. 2,2'-azobisisobutyronitrile (2) was used to initiate polymerization.



vinylferrocene (1)



2,2'-azobisisobutyronitrile (2)

It was recrystallized three times from AnalaR methanol (mp 101 to 102°C with decomposition) and stored in sealed flasks under oxygen-free nitrogen at -25°C.

2.2 Dilatometers

Dilatometers consisted of Pyrex bulbs attached to lengths of 1.0 mm precision bore tubing (Veridia). The capillary length was approximately 120 mm and the bulbs varied in volume from 1 to 5 cm³. Tubes for filling the dilatometers had a volume of approximately 40 cm³ and each incorporated a side arm and a neck fitted with a B19 socket for attachment to the manifold of a high vacuum line. The dilatometers were attached to the side arms of the filling-tubes and constrictions made in the arms and necks as shown in Fig. 1.

2.3 Dilatometric procedure

A solution of initiator in AnalaR benzene was measured from a micro-burette and allowed to drain through a drawn out capillary so as to lay evenly on the bottoms of the filling-tubes. The benzene was immediately and carefully evaporated at room temperature under reduced pressure, leaving the required amount of initiator as a fine deposit on the bottoms of the filling-tubes. Several tubes prepared in this manner were stored under oxygen-free nitrogen at -25°C until required. Vinylferrocene was then weighed into the tubes, benzene added, the tubes attached to a high vacuum line and the contents degassed by

three freeze-thaw cycles at 10^{-4} mm Hg. The filling-tubes were separated from the vacuum line while still pumping, by sealing the constrictions in the necks. The contents of the tubes were warmed to room temperature. The tubes were then shaken to ensure a homogeneous solution, and tilted to allow the required amount of solution to run into the attached dilatometers. The solutions in the bulbs of the dilatometers and those remaining in the filling-tubes were simultaneously frozen in liquid nitrogen and the dilatometers separated from the fillers by sealing at the constrictions in the side-arms. The dilatometers were then placed in a water bath at $60^{\circ}\text{C} \pm 0.01^{\circ}$ and the change in height of the meniscus measured with a cathetometer accurate to 0.01 mm. Other temperatures were used to examine the effect of temperature on the rate of polymerization.

2.3.1 Determination of densities of vinylferrocene and polyvinylferrocene

Dilatometry provides a reliable and extremely accurate method for observing the kinetics of vinyl polymerization. It is based on the change in density which occurs when the olefinic double bond is saturated. Because the density of the polymer is greater than that of the monomer a contraction in volume takes place during the polymerization reaction. It has been well established that there is a linear relationship between the percentage volume contraction and the percentage conversion²¹. The rate of polymerization may be deduced from a plot of the percentage conversion against time. To obtain an accurate measurement of the rate of polymerization the densities of the monomer and of the polymer at the polymerization temperature must be known. Furthermore, because monomer and polymer volumes may not be additive in solution, the 'apparent densities' of the monomer and polymer in the solvent employed for the polymerization reaction must be determined²².

The variation in the density of vinylferrocene with temperature was determined by standard dilatometric techniques. The density of polyvinylferrocene was determined by three methods; displacement, density gradient column and weighing a known volume. The first two methods presented difficulties and some scatter was found in the experimental results. The third method was easily carried out and produced consistent results. A sample of the polymer was placed in a die (13 mm Specac, London) and degassed. Pressure was applied at room temperature in stages up to 27.6 MN/m^2 (4000 psi). Under these conditions the polymer fused to give a compressed disc similar to the potassium bromide discs used for infrared spectroscopy. The disc was weighed and its thickness and diameter measured with a comparator (Sigma Instruments Ltd) accurate to ± 0.0025 mm. From these measurements a value for its density was obtained.

2.3.2 Determination of apparent densities of vinylferrocene and polyvinylferrocene in benzene

The method used to determine the apparent densities of vinylferrocene and polyvinylferrocene in benzene was based on that of Matheson²². It was reduced to a smaller scale because of the relatively small amounts of polymer available. A solution of monomer or polymer in benzene was introduced into a calibrated dilatometer from a syringe fitted with a fine needle. The volume of the solution was then measured at various temperatures. The apparent densities were obtained from the expression:

$$\text{apparent density of solute} = \frac{\text{mass of solute}}{\text{volume of solution} - \text{volume of solvent}}$$

2.4 Isolation of polymers

The polymerization was allowed to proceed to approximately 5 percentage conversion. The reaction was then stopped by pouring the contents of the dilatometer into 500 cm³ of methanol containing a trace of hydroquinone. The precipitated polymer was filtered out, re-dissolved in benzene, re-precipitated into methanol, collected in a sintered crucible (porosity No. 4) and dried to a constant weight at 70°C and 0.1 mm Hg.

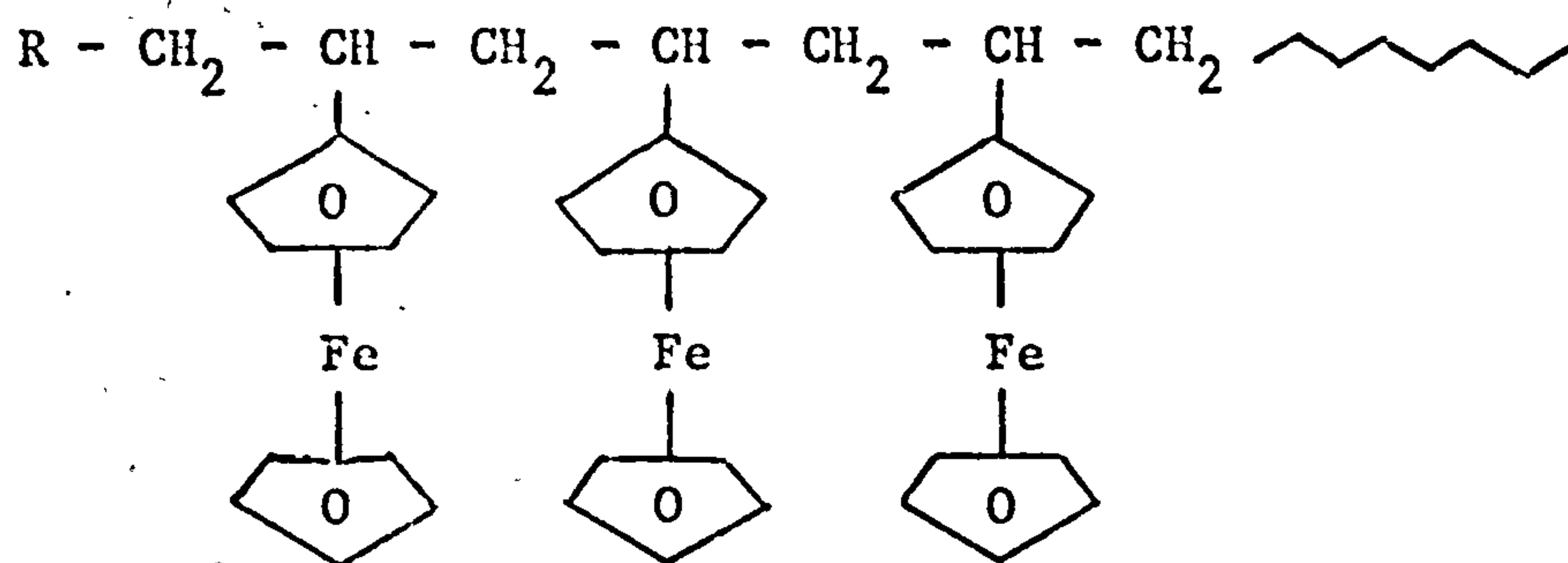
2.5 Characterization of polymers

The polymers were characterized by elemental analysis. Number average molecular weights were determined at 37°C in benzene with a vapour pressure osmometer (Perkin Elmer 115). Molecular weight distribution was examined by gel permeation chromatography. Infrared spectra were obtained on a Perkin Elmer 157G spectrophotometer. Ultraviolet visible and near infrared spectra were recorded on a Pye Unicam SP700. Nuclear magnetic resonance spectra were examined in ortho-dichlorobenzene on a Perkin Elmer R10 60 MHz spectrometer. Mössbauer spectra were obtained by the Physico-Chemical Measurement Unit, AERE, Harwell. Electron spin resonance was carried out at the Analytical Research and Development Unit, AERE, Harwell.

3 RESULTS

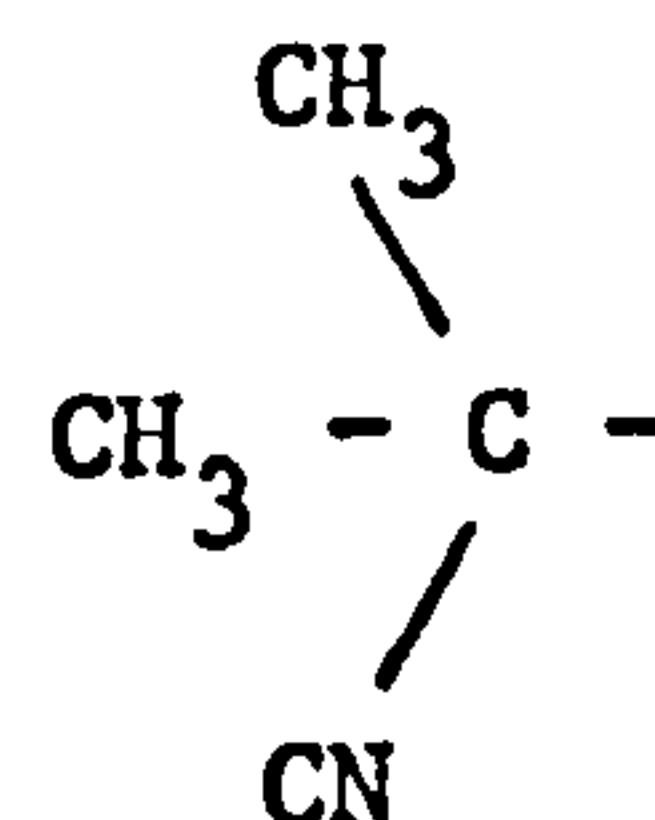
The values of the density and apparent density of vinylferrocene and polyvinylferrocene are recorded in Table 1. The effect of temperature on the density of the polymer was minimal over the temperature range of the experiments. The elemental analysis (C 66.9, H 5.7, Fe 27.4) is in accord with a linear polymer depicted in (3) although the carbon/iron mass ratio is slightly low,

(expected for $(C_{12}H_{12}Fe)_n$ 2.58, found 2.44).



polyvinylferrocene (3)

R = an initiator fragment:



The results of the kinetic experiments are recorded in Tables 2, 3 and 4. The percentage conversion was limited to about 5 to permit simplifying assumptions concerning radical reactivity (see Appendix). A representative plot of percentage conversion against time, given in Fig. 2, emphasizes the linearity of the slope at the conversions employed. Logarithmic plots of the initial rate of polymerization against monomer and initiator concentration produced straight lines with slopes obtained by the method of least squares equal to 1.12 and 1.11 respectively. The rate expression is therefore of the form:

$$R_p = k [M]^{1.12} [In]^{1.11} \quad (1)$$

Plots of initial rate of polymerization against monomer concentration to a power of 1.12, and of initiator concentration to a power of 1.11 are recorded in Figs. 3 and 4 respectively. A plot of log initial rate against $1/K$ is given in Fig. 5 and from the gradient of the linear relationship obtained using the method of least squares the overall activation energy for the polymerization was calculated to be $139.7 \text{ kJ mol}^{-1}$ ($33.4 \text{ Kcal mol}^{-1}$).

4 ANALYSIS OF RESULTS

4.1 Kinetic analysis of the polymerization of vinylferrocene

Aspects of the theory of vinyl polymerizations initiated by free radicals are given in the Appendix. A rate dependence upon initiator concentration to a power approximating to 1.0 suggests that the predominant termination reaction is monomolecular. Monomolecular termination is not observed in most vinyl

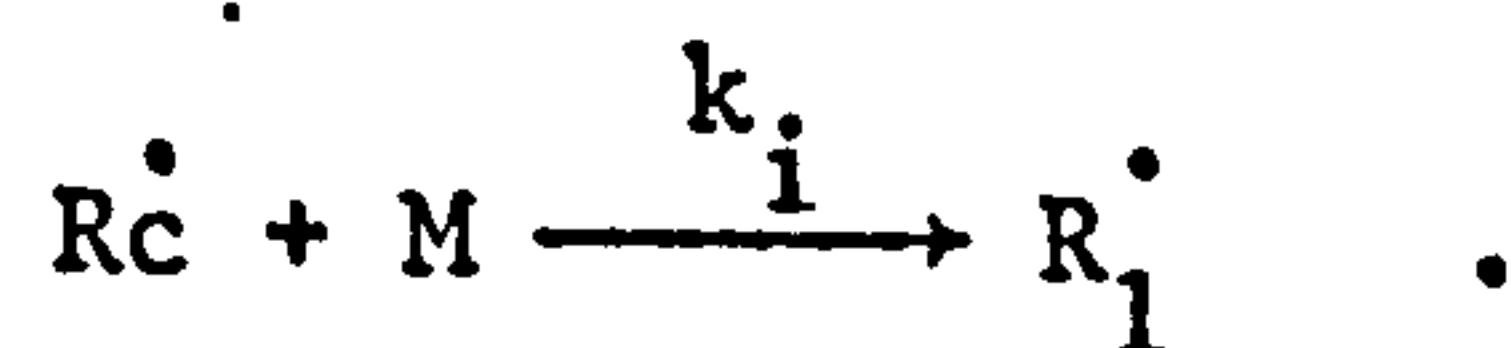
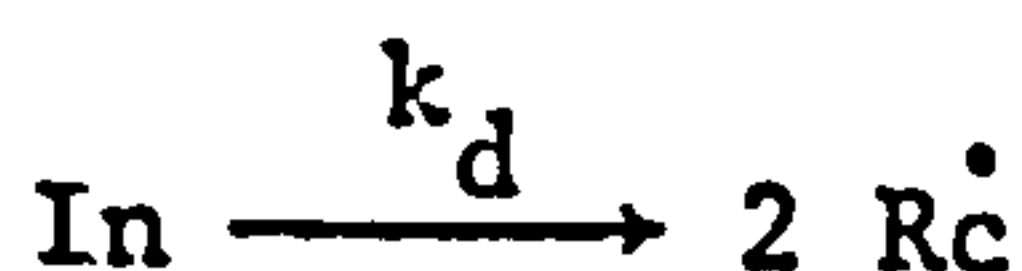
polymerizations^{23,24}. Normally, the termination step in vinyl polymerizations occurs by mutual reaction between two growing polymer chain radicals and is therefore bimolecular. Also the growing polymer chain radical does not terminate by abstraction of hydrogen from another monomer molecule as in the case of allylic polymerizations²⁵. In allylic polymerizations the rate is dependent on the initiator concentration and consequently the termination reaction is monomolecular. However, the rate is independent of the monomer concentration and the termination step is intermolecular. In the present study the appearance of monomer concentration in the rate expression implies that the termination reaction is intramolecular.

The rate expression is readily explained by the proposition that:

- (i) the termination step involves only one polymer chain radical;
- (ii) the products of this reaction are inactive (will not initiate further polymerization reactions).

The scheme detailed in the Appendix leads to the following result.

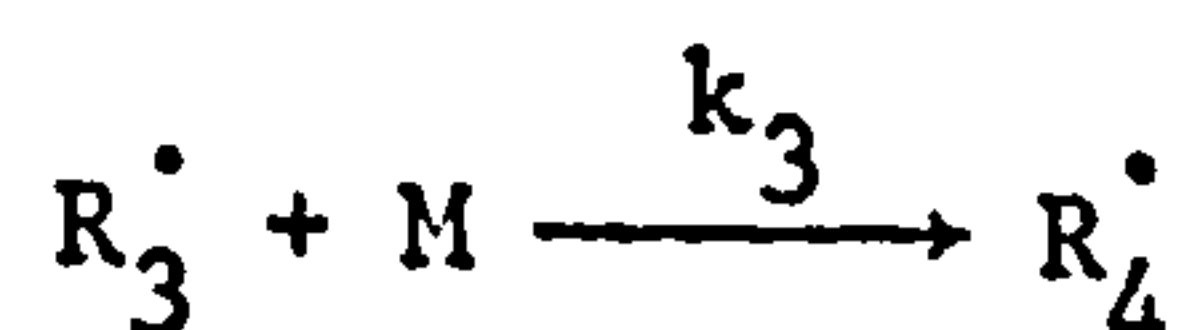
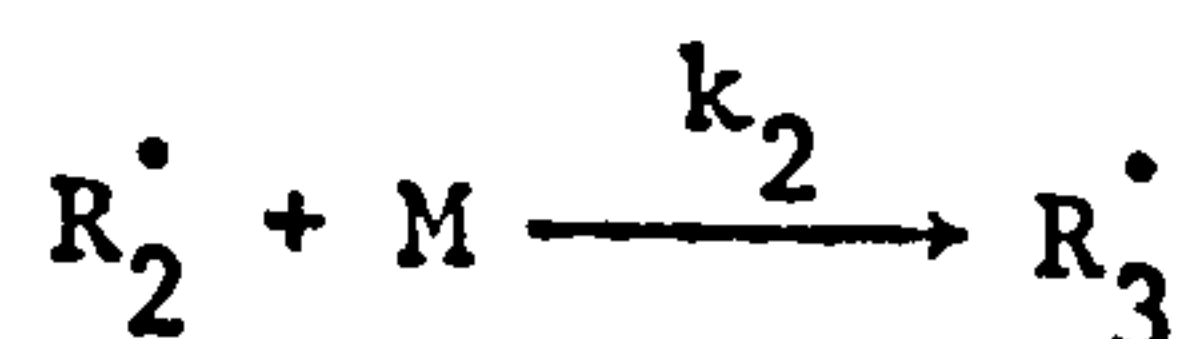
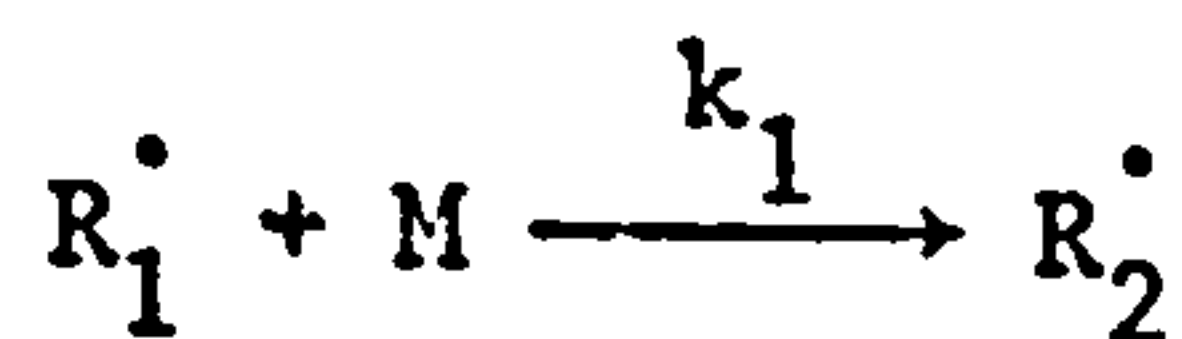
Initiation



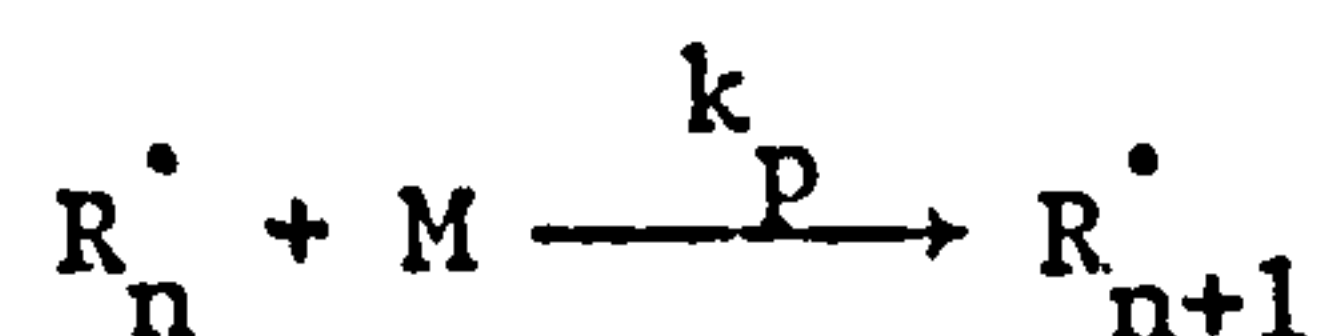
$$\text{Rate of initiation} = \frac{d[\text{R}^\bullet]}{dt} = 2 k_d f[\text{In}] \quad (2)$$

where $[\text{R}^\bullet]$ is the concentration of all chain radicals irrespective of their size, i.e. including $\text{R}_1^\bullet$; $[\text{In}]$ is the concentration of initiator; k_d is its rate constant for decomposition into radicals $\text{Rc}^\bullet$, f is the fraction of these radicals which initiates chains; M indicates molecules of monomer.

Propagation



and because the radical reactivity depends only on the end unit and is therefore the same in each case, the above steps may be written



with a common rate constant for all the propagating steps. The rate of monomer removal is then:

$$-\frac{d[M]}{dt} = k_p [M][R^\bullet] \quad (3)$$

where $[M]$ is the concentration of monomer. The rate of monomer removal may be equated with the rate of polymerization so that:

$$\text{rate of polymerization } R_p = -\frac{d[M]}{dt} = k_p [M][R^\bullet] \quad (4)$$

Termination The termination step in the polymerization of vinylferrocene differs from the normal bimolecular reaction described in the Appendix. It may be represented by:



$$\text{rate of termination} = -\frac{d[R^\bullet]}{dt} = k_t [R^\bullet] \quad (5)$$

Assuming the steady state approximation

$$\frac{d[R^\bullet]}{dt} = -\frac{d[R^\bullet]}{dt} = 0 \quad ,$$

from equations (2) and (5)

$$[R^\bullet] = \frac{2k_d f [In]}{k_t}$$

and substituting for $[R^*]$ in equation (4)

$$R_p = \frac{2k_d f k_p}{k_t} [M][In] \quad (7)$$

or
$$R_p = k[M][In] \quad (8)$$

where $k = \frac{2k_d f k_p}{k_t}$. This scheme therefore agrees with the experimental results shown in equation (1).

4.2 Overall activation energy for the polymerization of vinylferrocene

For normal vinyl polymerizations the general expression for the overall rate of polymerization and the individual rate constants for initiation, propagation and termination has the following form:

$$R_p = k_p [M] \left(\frac{k_d f [In]}{k_t} \right)^{0.5} \quad (9)$$

The overall rate of polymerization and the rate constants are related to the activation energies and may be expressed in the usual form:

$$R_p = A_o \exp(-E_o/RT); \quad k_p = A_p \exp(-E_p/RT);$$

$$k_d = A_d \exp(-E_d/RT); \quad k_t = A_t \exp(-E_t/RT);$$

where A and E are the pre-exponential factors and activation energies for the respective reactions and o, p, d and t indicate overall rate, propagation, initiation and termination. By substituting the Arrhenius expressions for each of the rate constants in equation (9) we can obtain, at constant f, [In] and [M]

$$-E_o/RT \ln A_o = \ln \{ A_p (A_d/A_t)^{0.5} \} - \{ E_p + (E_d - E_t)/2 \}/RT \quad (10)$$

Hence the overall activation energy for the polymerization which was obtained

from the slope of a plot of the logarithm of the rate against $1/T$ is related to the individual activation energies as follows

$$E_o = E_p + \frac{1}{2} (E_d - E_t) \quad (11)$$

The value of E_d is approximately $125.5 \text{ kJ mol}^{-1}$ * whilst the value of E_t for the recombination of two radicals may be regarded as zero. Substituting the value for E_o found experimentally ($139.7 \text{ kJ mol}^{-1}$) for the homopolymerization of vinylferrocene gives a value of 77 kJ mol^{-1} for the activation energy of the propagation reaction. This value is more than double those obtained for most vinyl monomers and exceeds the activation energy (62.8 kJ mol^{-1}) expected for rapid radical reactions²⁶. This result indicates that the relationship expressed in equation (9) is not correct for the polymerization of vinylferrocene.

However, the relationship between the rate of polymerization and the individual velocity coefficients for the polymerization of vinylferrocene is

$$R_p = \frac{k_p [M]^{1.12} k_d f [In]^{1.11}}{k_t} \quad (12)$$

and at constant $[M]$, $[In]$ and f and substituting as before we obtain:

$$E_o = E_p + E_d - E_t \quad (13)$$

Substituting the experimental value of E_o gives the activation energy for the propagation step as 14.2 kJ mol^{-1} , which is lower than the expected value.

However, the value for E_t is taken as zero. Although this is true for recombination of small radicals in the gas phase, the recombination of polymer radicals has finite values (those for vinyl acetate, styrene and methyl methacrylate being 13.5 , 8.0 , 5.0 kJ mol^{-1} respectively). The monomolecular reaction of the polyvinylferrocene radical would be expected to have an activation energy larger than radical combination, so that the value of E_t could be as high as 15 kJ mol^{-1} and hence the value of E_p is increased to a more usual value, $E_p \approx 29 \text{ kJ mol}^{-1}$. The overall activation energy is therefore also consistent with the kinetic analysis.

*4.184 Joule = 1 calorie

4.3 Spectral analysis of polyvinylferrocene

4.3.1 Infrared and ultraviolet spectra

A typical infrared spectrum of polyvinylferrocene is shown in Fig. 6. Characteristic ferrocene absorptions occur at 1411 cm^{-1} , 1109 cm^{-1} , 1003 cm^{-1} and 818 cm^{-1} . The aliphatic unsaturated stretching frequency at 1633 cm^{-1} is absent as expected. Absorptions at 2930 cm^{-1} and 2858 cm^{-1} are not present in the monomer and correspond to stretching frequencies of the aliphatic polymer backbone. All the polymer spectra contain two medium absorptions at 920 cm^{-1} and 885 cm^{-1} .

The ultraviolet spectra showed two main absorptions at 442 nm and 325 nm with $\epsilon = 1330$ and 5050 respectively. The spectrum of the monomer showed one peak at 446 nm, $\epsilon = 2450$ and a shoulder at 333 nm $\epsilon = 5000$ (ϵ is the molar decadic extinction coefficient expressed in $\text{m}^2\text{ mol}^{-1}$). Polyvinylferrocene prepared by cationic polymerization¹⁴ shows only one absorption at 442 nm.

4.3.2 Nuclear magnetic resonance spectra (nmr)

The nmr spectra of the polymer samples showed pronounced paramagnetic broadening of all the peaks, over a range of temperatures up to 150°C . There is still much uncertainty concerning paramagnetism in ferrocene-containing polymers¹. Russian papers have reported paramagnetism in polyferrocenylenes. Subsequent work^{27,28}, however, has shown that the observed magnetophysical phenomenon was due to trace paramagnetic impurities (e.g. ferricenium groups) and that the polymers were diamagnetic. A recent study²⁹ on addition polymers containing pendent ferrocene nuclei reported paramagnetic broadening of the nmr spectra. This effect was still present after the addition of ascorbic acid. Because ascorbic acid reduces the ferricenium cation the observed effect may be intrinsic to the polymer molecule and not caused by oxidised impurities. The observed line broadening with polyvinylferrocene may also be due to rigidity in the polymer structure inhibiting free movement of the polymer molecules.

4.3.3 Mössbauer spectra

The Mössbauer spectra of polyvinylferrocene and of vinylferrocene are shown in Fig. 7 and 8 respectively. The monomer spectrum shows two peaks characteristic of iron in the ferrocene nucleus. There are three peaks in the spectrum of the polymer. Two, at -0.73 and at 1.63 mm/s (with reference to iron metal), are due to iron in the ferrocene nucleus. The third, appearing at a small positive velocity, 0.17 mm/s , is not consistent with iron in the ferricenium cation. This peak is probably due to iron (III) in a high spin configuration (5 unpaired

electrons) and becomes obscured at low temperatures owing to increased absorption of the main peaks. This effect suggests that the extra peak is due to iron in an ionically-bound complex. Covalently bound iron usually shows increased absorptions at low temperatures. The area of the third peak varies between 3 per cent to 14 per cent of the total area dependent on the molecular weight of the polymer.

4.3.4 Electron spin resonance spectra (esr)

A typical spectrum of polyvinylferrocene is recorded in Fig. 9. The strong signal shows that the polymer contains a paramagnetic species which is not present in vinylferrocene. A single line was observed from solutions and from small quantities of solid polymer. At room temperature the line width varied from 425 gauss in benzene solution to 600 gauss in the solid polymer. At 77 K the line width in the solid polymer was 850 gauss. The 'g' value obtained for the centre of the peak was 2.06. The measured spin concentration was necessarily approximate as it was obtained by comparison of the rather broad peaks with the narrow line from chromium in magnesium oxide. The recorded value was about 10^{19} spins/gram. The spin value indicates a substantial concentration of a paramagnetic species. The g-value and line widths are typical of ferric iron in a high spin configuration. Because the ferricenium cation does not give an esr signal, the spectrum is unlikely to be due to this species.

5 DISCUSSION OR RESULTS

5.1 General discussion

The kinetic experiments have shown that the initial rate of polymerization is proportional to the monomer and initiator concentrations to power 1.12 and 1.11 respectively.

No rate expression of this form was obtained by Baldwin and Johnson who concluded that vinylferrocene obeyed normal vinyl polymerization kinetics with $R_p = k[M][In]^{0.5}$. However, a log plot of their values³⁰ for rate against initiator concentration produces a line, the slope of which is 1.15.

A rate dependence to powers approximating to 1.0 implies that the termination reaction is both monomolecular and intramolecular. The growing polymer chain radical is therefore deactivated by some reaction with a molecule or atom in the same polymer chain. The molecular weights of the polymers vary between 3000 and 8000 and the molecular weight of vinylferrocene is 211.97. Thus, the degree of polymerization ($\overline{DP}$) lies approximately between 10 and 40. These values are unusually low for vinyl polymers. Polystyrene prepared under similar experimental conditions normally shows $\overline{DP} = 10^2$ to 10^4 . The unusual

polymerization kinetics are supported by the overall activation energy for the polymerization reaction. The activation energy is much higher than for normal vinyl polymerizations. When the value obtained is substituted into the rate relationships for normal vinyl polymerizations the activation energy for the propagation reaction is untenable but is in accord with the observed kinetics for vinylferrocene.

The following observations may be made from the kinetics. A monomolecular termination reaction should produce a terminal monomer unit differing from interchain vinylferrocene units. Moreover, with so relatively few monomer units in the polymer chain, the terminal unit should be readily evident. An intramolecular reaction between an odd electron and a molecule must produce another odd electron species and therefore the polymer molecule may contain unpaired electrons. Both these observations have been confirmed by spectral studies.

The ultraviolet spectrum of the polymer shows an absorption which is not present in the monomer or in polyvinylferrocene produced by cationic polymerization. This peak indicates the presence of a species which differs from vinylferrocene units in the polymer chain. The Mössbauer spectra demonstrate unequivocally the presence of iron in an environment other than that of the ferrocene nucleus. Normal free radical polymerization should produce a chain containing only pendent ferrocene nuclei. The Mössbauer results therefore support the kinetic observations. A relationship between molecular weight and concentration of a species other than vinylferrocene also agrees with the kinetic predictions.

The presence of unpaired electrons in the polymer was indicated by nmr spectroscopy, the spectra of polymer samples showing paramagnetic broadening of all the peaks. The presence of unpaired electrons in polyvinylferrocene has been confirmed by esr spectroscopy. The kinetics indicate that each polymer chain deactivates itself and therefore each polymer molecule could contain a paramagnetic species. The recorded spin value of 10^{19} spins/gram agrees well with this concept. A value of 8.5×10^{18} spins/gram corresponds to 1 spin per molecule for a molecular weight of approximately 7000. The spectral analyses of polyvinylferrocene therefore confirm and support the kinetic analysis of the polymerization reaction.

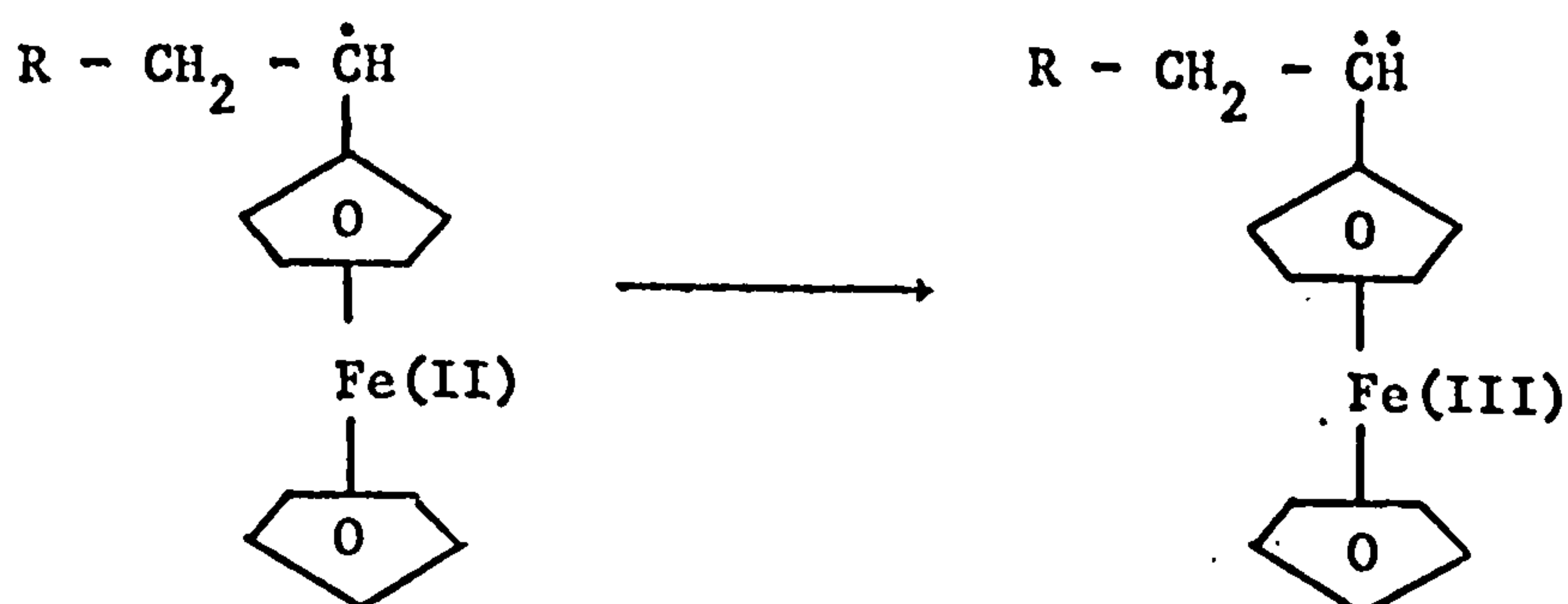
The esr and Mössbauer spectra indicate that the species present in the polymer is an ionic complex of iron (III) in a high spin configuration. The results are unlikely to be due to ferric iron impurities in the system. The gross contamination which would produce the observed high concentration of

paramagnetic species is precluded by the experimental technique. Furthermore, Mössbauer studies indicate that the percentage of this species varies systematically with molecular weight. Oxidation of the monomer during the polymerization reaction could produce an iron (III) compound which would influence the kinetics. This may, however, be disregarded because all the polymerizations were conducted in oxygen-free conditions, under which oxidation of ferrocene derivatives has not been observed. Oxidation of the monomer and polymer during storage is also unlikely. If oxidation occurs during storage the esr signals should increase with time. This has not been observed. Treatment of benzene solutions with ammonium thiocyanate which is a test for ferric ions did not give positive results. The sensitivity of this test confirms the absence of ferric iron. The presence of paramagnetic impurities is also disproved because the polymer shows no conduction properties. Conduction has been observed only with ferrocene polymers in the presence of oxidised impurities³¹.

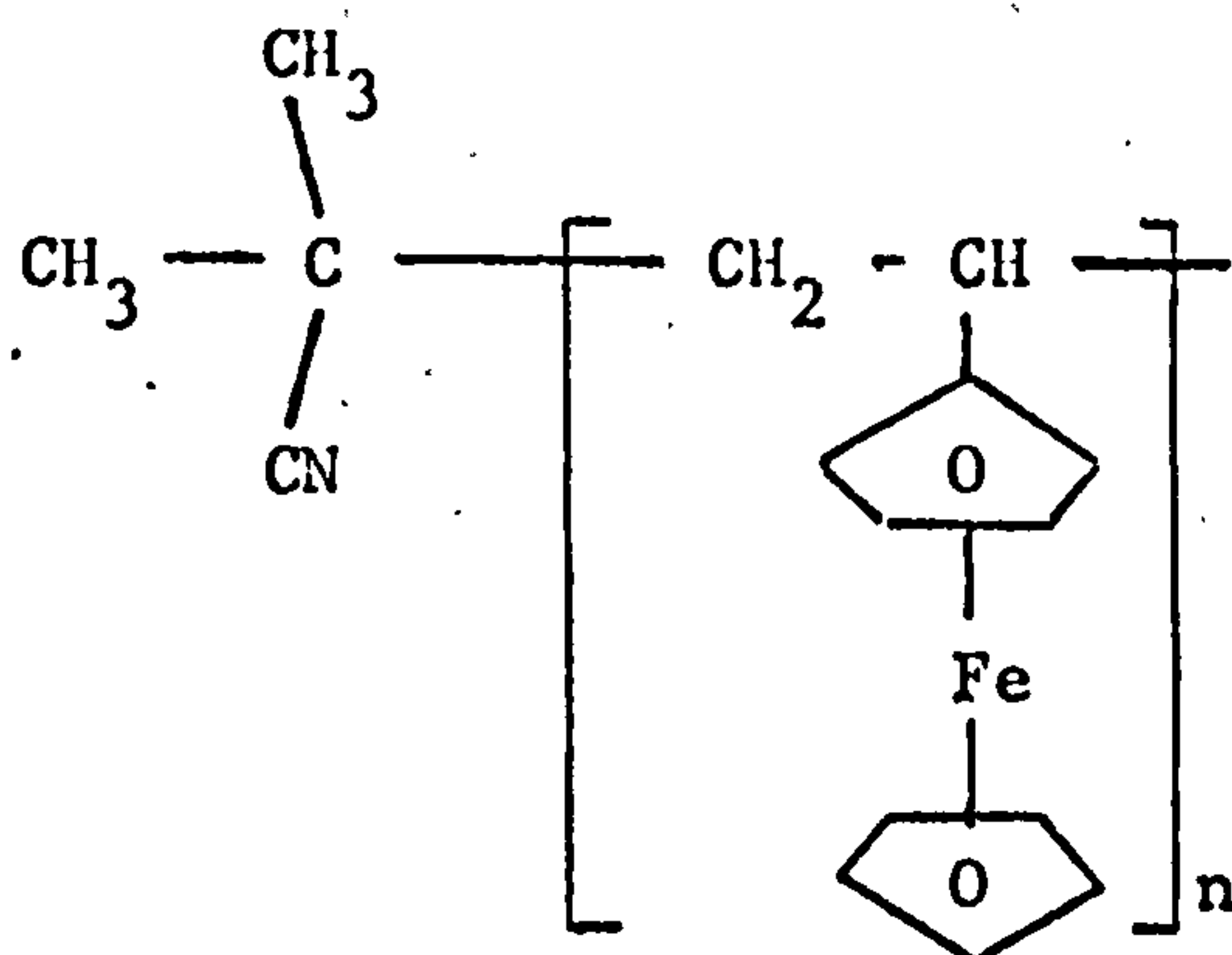
5.2 Termination reaction in vinylferrocene polymerizations

5.2.1 Possible mechanisms

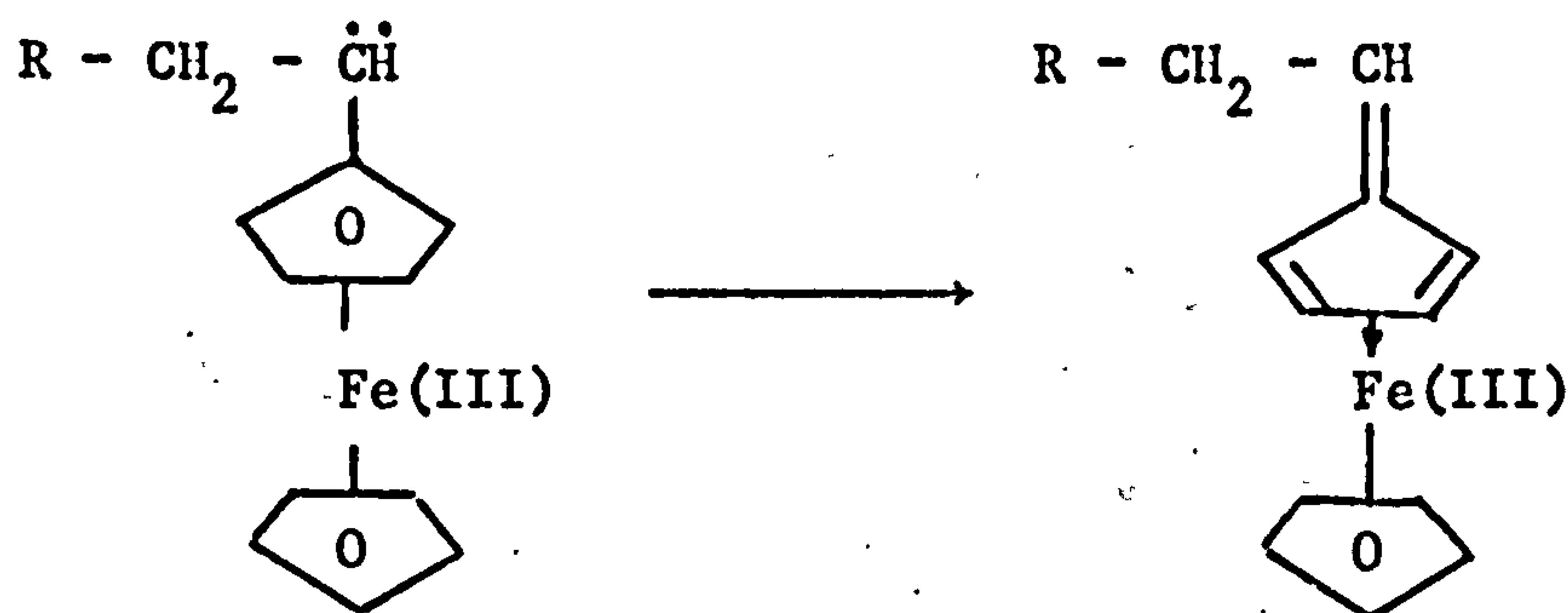
The olefin group in vinylferrocene undergoes many reactions not observed in other mono substituted ethylenes^{32,33}. These suggest that normal vinyl polymerization reactions might not occur. Characteristic features of all metallocenes are their ready oxidation to a cationic species by loss of one or more electrons from the metal atom³⁴, and the direct participation of the metal atom in many reactions³⁵. Spectral analysis of polyvinylferrocene indicates that the species produced in the termination reaction is an ionically-bound complex of iron (III). To obtain iron (III) an electron must be removed from the iron atom in the ferrocene nucleus. It seems probable, therefore, that the termination reaction occurring in the polymerization of vinylferrocene involves an electron transfer from the iron atom. An electron transfer to the polymer chain radical would deactivate the chain radical. The iron atom may be formally regarded³⁶ as being in the ferrous state and the above reaction is shown as:



where R =

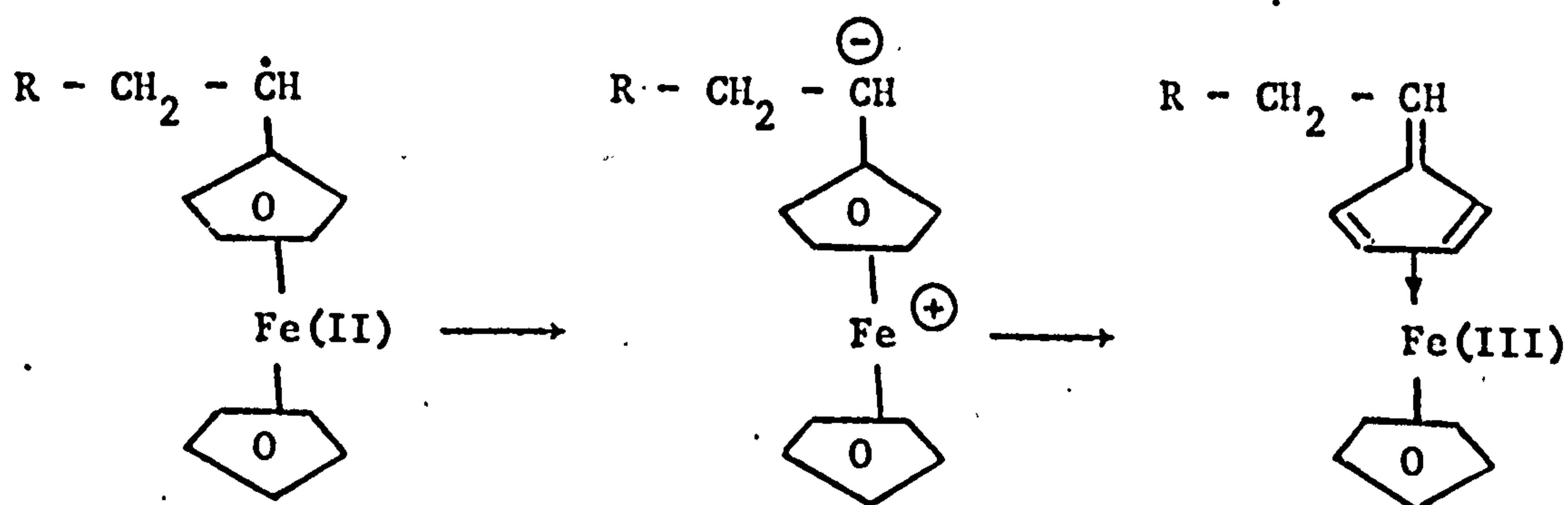


The paired electrons on the terminal carbon atom could form a double bond with the cyclopentadienyl ring. This would cause a redistribution of the π electrons in the ring and a simultaneous alteration in the bonding between the ring and iron atom to give Fe(III) in a high spin configuration.

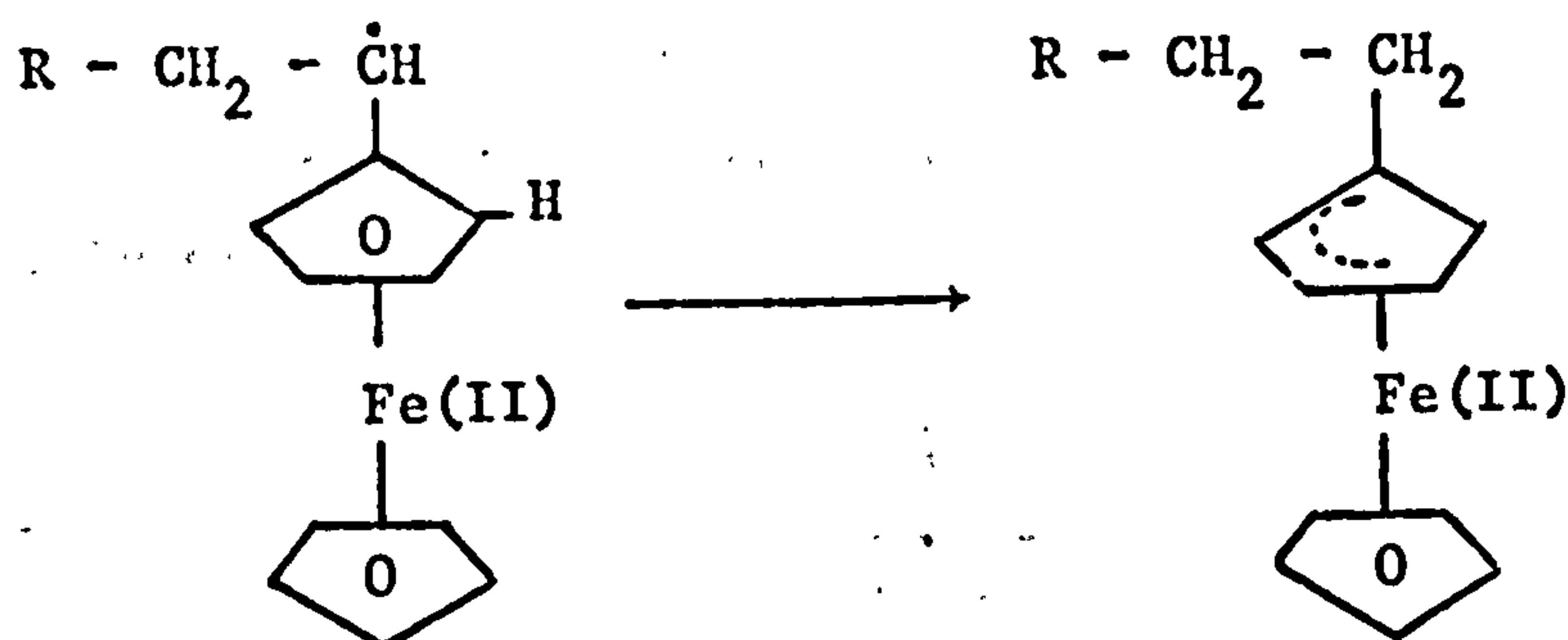


This mechanism would explain the lack of evidence for the presence of a ferrocenium cation. The species formed is not that normally associated with loss of one electron from the iron atom. The unsubstituted ring may or may not be affected in this reaction, although the elemental analysis indicates that it is probably lost.

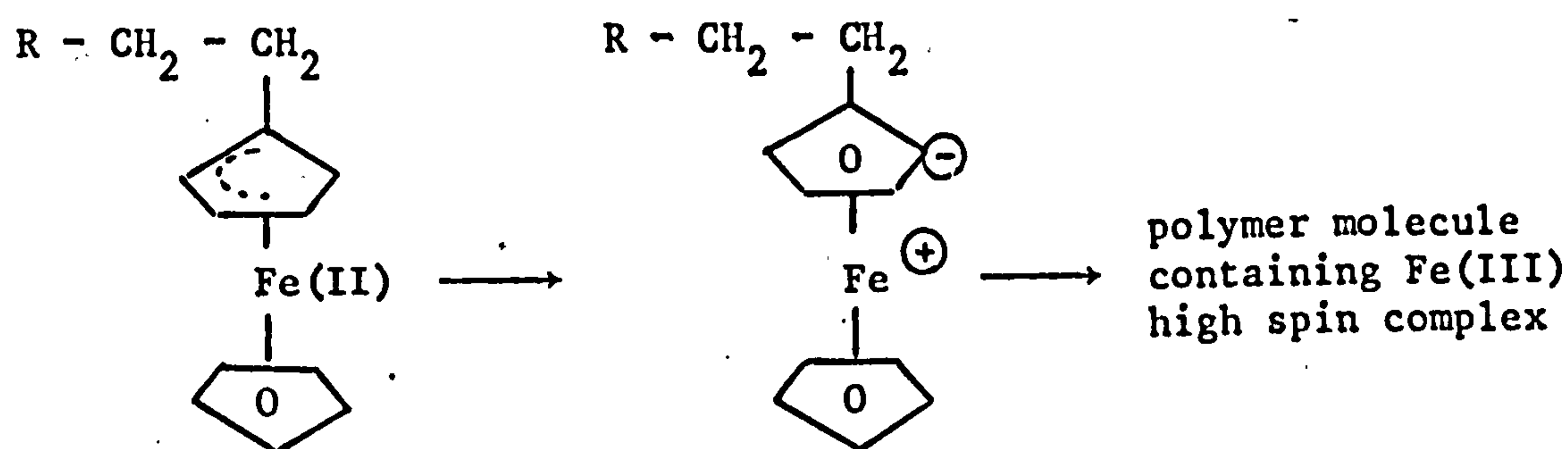
A ferrocenium cation is probably formed initially and a charge transfer complex is present in a transition state, the final ferric high spin configuration being obtained when the polymer is precipitated into methanol. The overall action may therefore be represented as:



An intramolecular hydrogen abstraction reaction also agrees with the kinetic results. Hydrogen abstraction from the ferrocene ring is well documented³⁷. Although these reactions occur at high temperatures the ferrocene ring is expected to be as susceptible to hydrogen abstraction as is benzene³⁸. Hydrogen abstraction would effectively terminate the growing polymer chain radical:



Electron transfer from the iron atom would complete the reaction



5.2.2 Practical effects of the termination reaction

The unusual monomolecular and intramolecular termination step in the polymerization of vinylferrocene will effect the functionality of functionally terminated copolymers. Normal termination of vinyl polymerizations involving bimolecular combination of two growing chain radicals produces a polymer molecule with an initiator fragment at each end of the molecule. If the initiator contains a functional group the molecule is difunctional. Copolymers of vinylferrocene have two possible reactions when the growing polymer chain ends in a vinylferrocene unit:

- (i) addition of another monomer molecule to continue propagation;
- (ii) chain termination.

Chain termination results in a monofunctional molecule which effectively reduces the functionality of the resultant copolymer to below two. Many other factors influence functionality and exact predictions are not possible.

It has been confirmed that vinylferrocene acts as a chain terminator. It will therefore limit molecular weight. This effect is not as detrimental to its usage as may at first appear. When low molecular weight liquid prepolymers are required (for example as propellant binders) it will be a useful comonomer. The molecular weights of the homopolymer prepared in solution are relatively low. However, the kinetics indicate that bulk polymerization will produce higher molecular weight. The degree of polymerization $\overline{DP}$ is a measure of the molecular weight, and is related by the following equation to the rate of polymerization and to the rate of polymer formation:

$$\overline{DP} = \frac{\text{rate of polymerization}}{\text{rate of polymer formation}} = \frac{R_p}{\frac{d[P]}{dt}} \quad (14)$$

The rate of polymer formation is equal to the rate of the termination step only (equation (5)), and $R_p = k_p [M][R^\bullet]$ (equation (4))

$$\therefore \overline{DP} = \frac{k_p [M][R^\bullet]}{k_t [R^\bullet]} \text{ at constant temperatures} \quad (15)$$

The degree of polymerization is therefore directly proportional to the monomer concentration, and polymerization of vinylferrocene in the absence of solvent produces a high molecular weight³⁹.

The species produced in the termination reaction is obviously unreactive in further polymerization reactions. The presence of a paramagnetic species may have an important effect on the quenching properties of the ferrocene nuclei in the polymer. Catalytic effects may also be altered by the presence of a ferric iron species. Further studies will aim to develop methods of altering the termination reaction. Incorporation of electron withdrawing groups into the unsubstituted ferrocene ring will reduce the ease of electron transfer from the iron atom. Solvent and steric effects in the termination reaction may be similarly controlled.

6 CONCLUSIONS

A kinetic study of the free radical polymerization of vinylferrocene in benzene has been completed. The initial rate of polymerization was found to depend on the monomer concentration to a power of 1.12 and on the initiator

concentration to a power of 1.11; $R_p = k[M]^{1.12} [In]^{1.11}$. This result refutes previously published data. (Analysis of these data³⁰, however, supports the conclusions reached in this report.)

An analysis of the kinetic results has indicated that vinylferrocene does not polymerize by normal vinyl polymerization mechanisms. It is suggested that vinylferrocene is subject to a unique termination step which has hitherto not been observed in radical-initiated vinyl polymerizations.

A suggested kinetic scheme which satisfies the experimental data postulates that the mechanism for the termination reaction is monomolecular and intramolecular. These kinetic observations are supported by the activation energy for the polymerization reaction and by ultraviolet and nuclear magnetic resonance spectroscopy. Furthermore, the results predicted by the kinetic analysis have been confirmed by Mössbauer and electron spin resonance spectroscopy.

The species produced in the termination reaction is paramagnetic. On the basis of spectral evidence it appears to be an ionically bound complex of iron (III) in a $3d^5$ high spin configuration.

Possible mechanisms for the termination step have been discussed. These involve direct participation of the iron atom. It seems probable that the chain radical is deactivated by an electron transferred from the iron atom. This produces a polymer molecule containing unpaired electrons in the terminal unit.

Vinylferrocene polymerizes easily and is a useful monomer for preparing linear addition polymers containing pendent ferrocene nuclei. The unusual termination reaction observed does not preclude its use in specialized polymers for rocket motor applications.

7 RECOMMENDATIONS FOR FUTURE WORK

More detailed studies of the homopolymerization of vinylferrocene are required to elucidate the precise mechanism of the termination reaction.

An attempt should be made to characterize the paramagnetic species present in polyvinylferrocene.

Copolymerization of vinylferrocene and butadiene has produced potentially useful materials. This work should continue.

Acknowledgements

I am deeply indebted to Dr. M.H. George of the Chemistry Department, Imperial College of Science and Technology for his constant help and assistance during the course of this experimental study.

I would like to thank Mr. J.R. McLean of the Rocket Propulsion Establishment for performing iron analysis and obtaining uv spectra of the polymers. My thanks to Mr. R.W. Thackray of RPE for statistical analysis of the results. I am grateful to colleagues at the Explosives Research and Development Establishment, particularly Dr. A.V. Cunliffe for carrying out nmr spectroscopy and Dr. R.J. Simpkins and Mr. E.J. Gallacher for gel permeation chromatography. I am also grateful to Dr. B.W. Dale and Dr. R.K. Webster of the Atomic Energy Research Establishment for helpful discussions on Mössbauer and esr spectroscopy.

TABLE 1

Density and apparent density in benzene of vinylferrocene
and polyvinylferrocene

Temperature, °C	Vinylferrocene		Polyvinylferrocene	
	Density	Apparent density (40% in benzene)	Density	Apparent density (5% in benzene)
21	-	1.300	1.404	-
40	1.279	1.284	-	1.400
50	1.268	1.276	-	1.400
60	1.258	1.268	-	1.403
70	1.249	1.262	-	1.417
75	1.243	1.259	-	1.430

TABLE 2

Rate of polymerization of vinylferrocene at 60°C with constant
monomer concentration $[M] = 4.0 \text{ mol dm}^{-3}$

$10^2 \times [In]$ mol dm^{-3}	$R_p \times 10^5$ $\text{mol dm}^{-3} \text{ s}^{-1}$	Conversion per cent	$\overline{M}_n$	$\frac{R_p \times 10^4}{[M]^{1.12} [In]^{1.11}}$
0.4	0.54	0.58	-	5.1
1.0	1.67	1.9	6500	5.6
1.0	1.62	1.75	5600	5.4
1.8	2.90	3.10	6800	5.0
2.0	3.20	3.2	7900	5.1

$\overline{M}_n$ = number average molecular weight

TABLE 3

Rate of polymerization of vinylferrocene at 60°C with constant initiator concentration $[In] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$

$[M]$ mol dm^{-3}	$R_p \times 10^5$ $\text{mol dm}^{-3} \text{ s}^{-1}$	Conversion per cent	$\overline{M}_n$	$\frac{R_p \times 10^4}{[M]^{1.12} [In]^{1.11}}$
1	0.42	1.1	-	6.0
2	0.78	1.6	2700	5.9
3	1.34	1.9	5800	6.4
4	1.71	1.8	6000	5.9

$\overline{M}_n$ = number average molecular weight

TABLE 4

Effect of temperature on the rate of polymerization of vinylferrocene at constant monomer and initiator concentration
 $[M] = 4.0 \text{ mol dm}^{-3}$; $[In] = 0.4 \times 10^{-2} \text{ mol dm}^{-3}$

Temperature °C	$R_p \times 10^5$ $\text{mol dm}^{-3} \text{ s}^{-1}$	Conversion per cent	$\overline{M}_n$
60	0.58	0.9	5400
70	3.35	2.0	3000
75	5.90	3.8	7800
78	9.54	5.8	6500

$\overline{M}_n$ = number average molecular weight

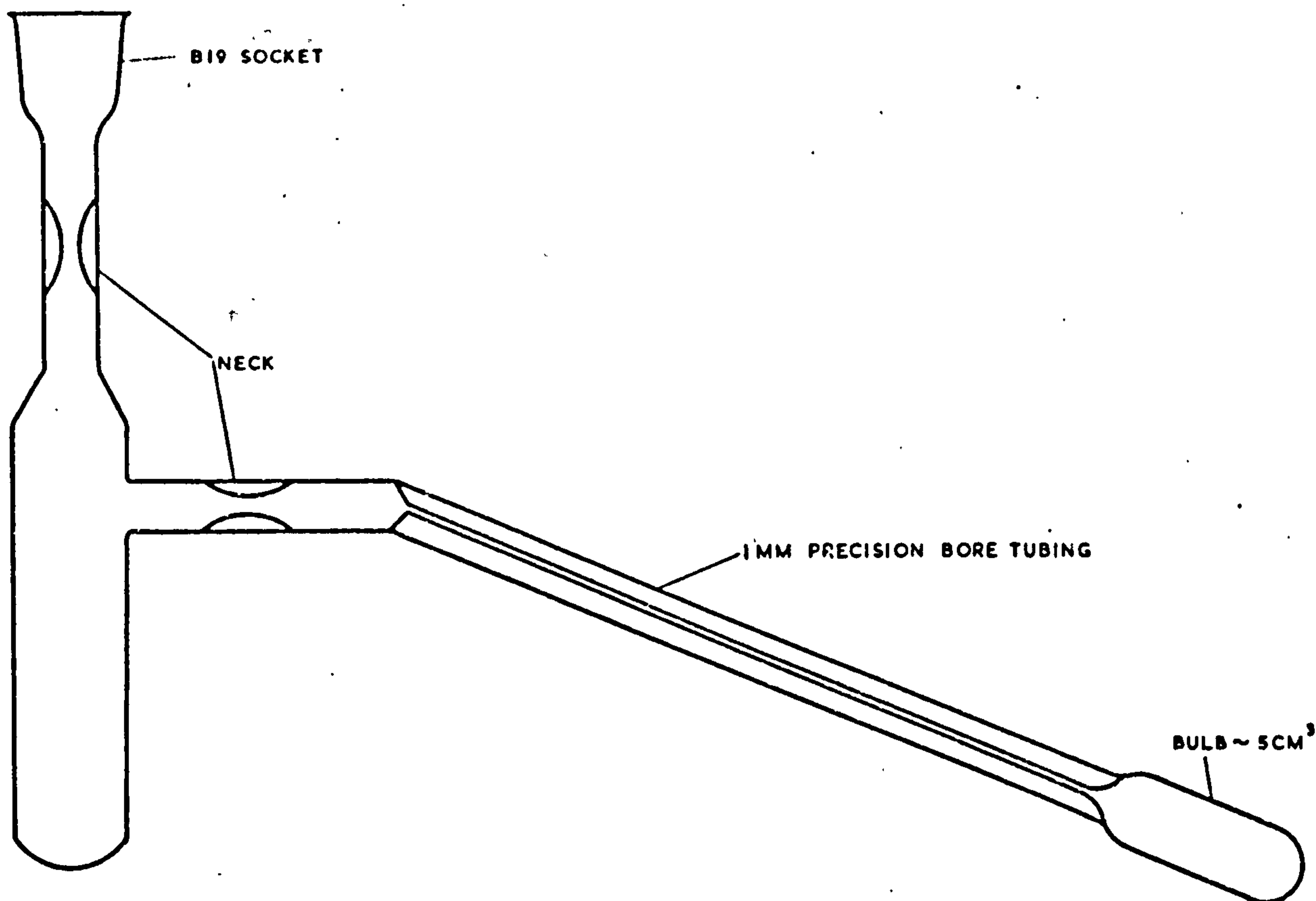


FIG. 1 DILATOMETER FILLER WITH ATTACHED DILATOMETER

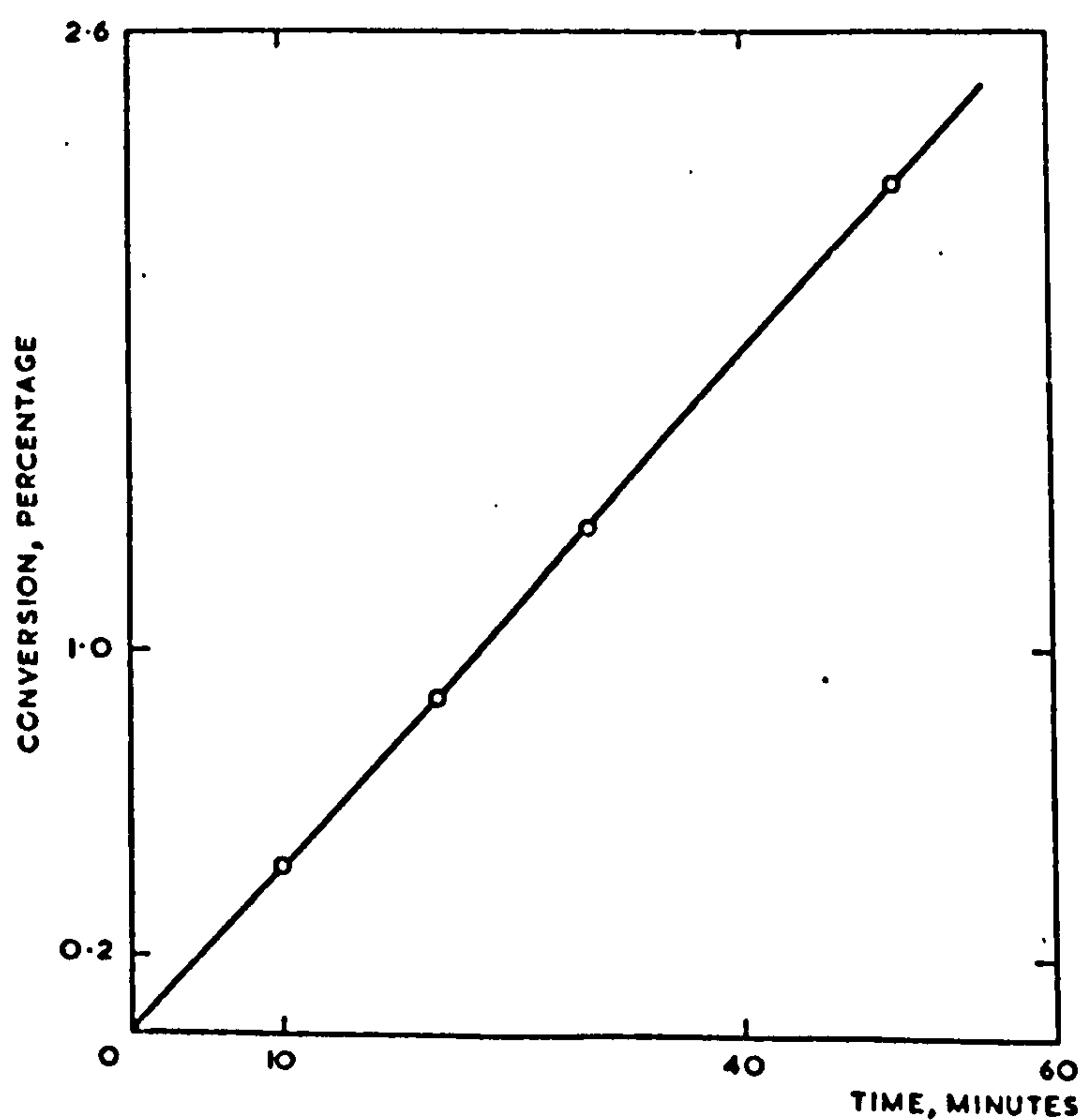


FIG. 2 POLYMERIZATION OF VINYLFERROCENE IN BENZENE, PERCENTAGE CONVERSION AGAINST TIME

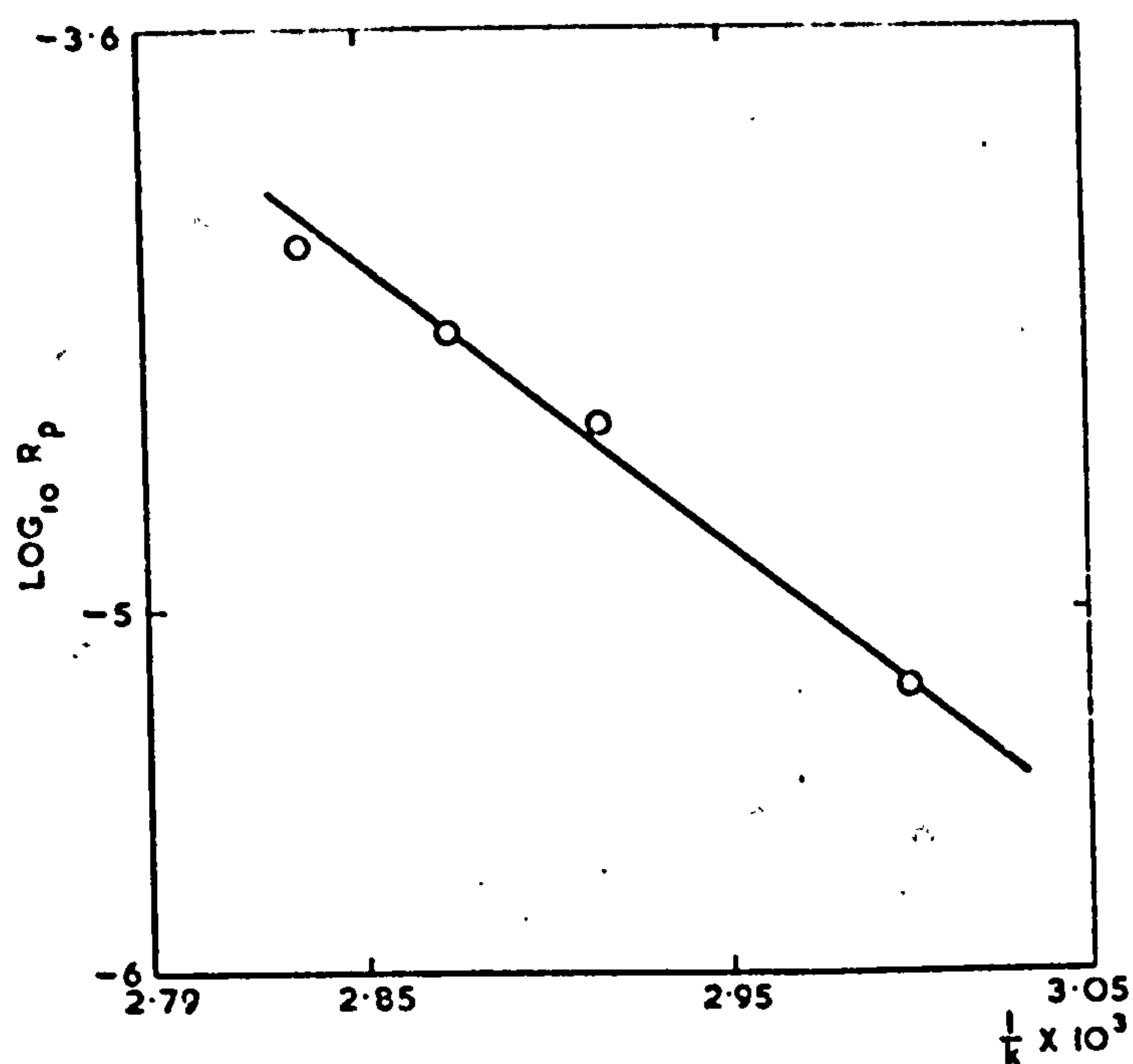


FIG. 5 LOG_{10} RATE OF POLYMERIZATION
AGAINST RECIPROCAL OF TEMPERATURE.
 $[m]_0 = 4.0 \text{ mol dm}^{-3}$ $[In]_0 = 0.4 \times 10^{-2} \text{ mol dm}^{-3}$

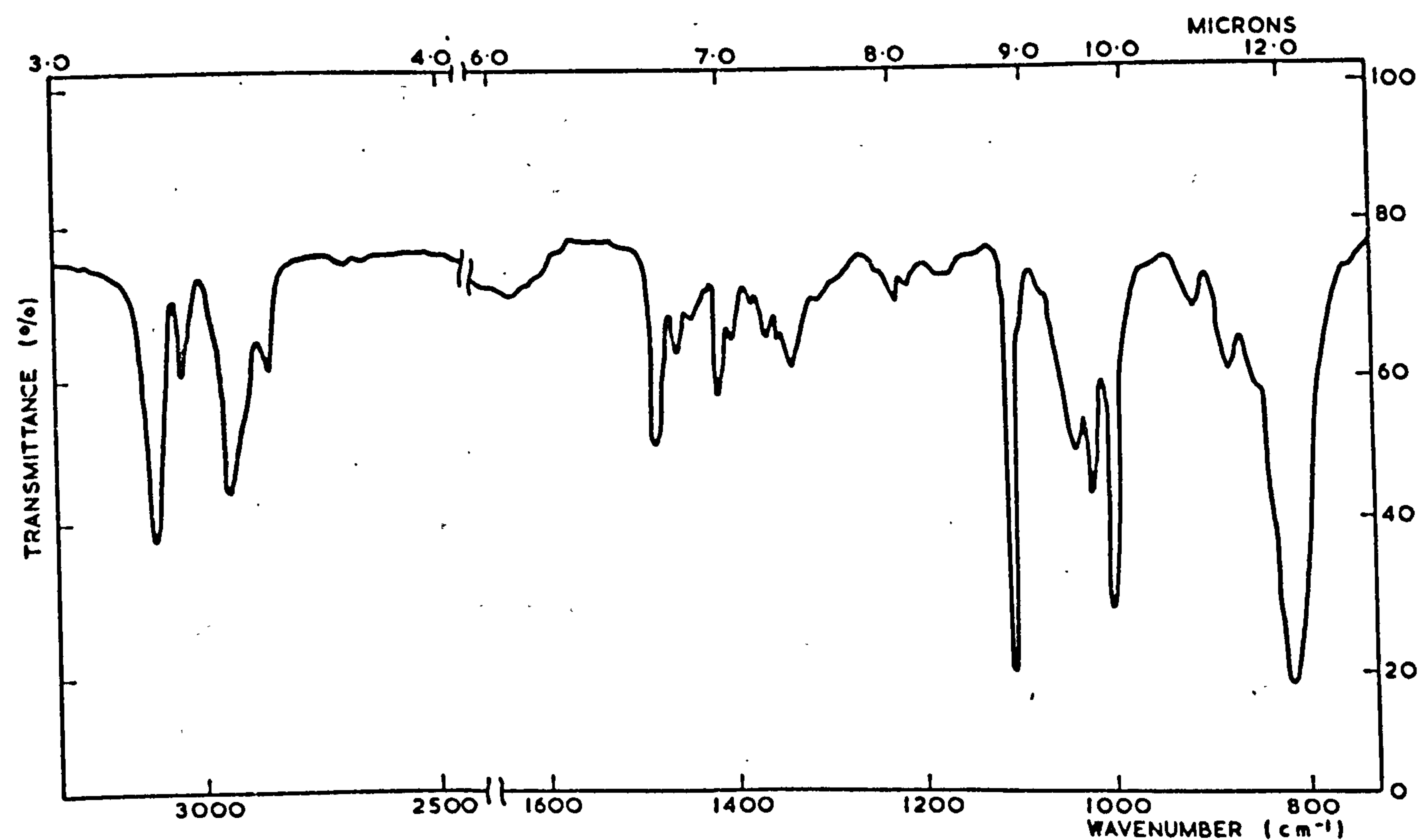


FIG. 6 INFRARED SPECTRUM OF POLYVINYLFERROCENE FILM

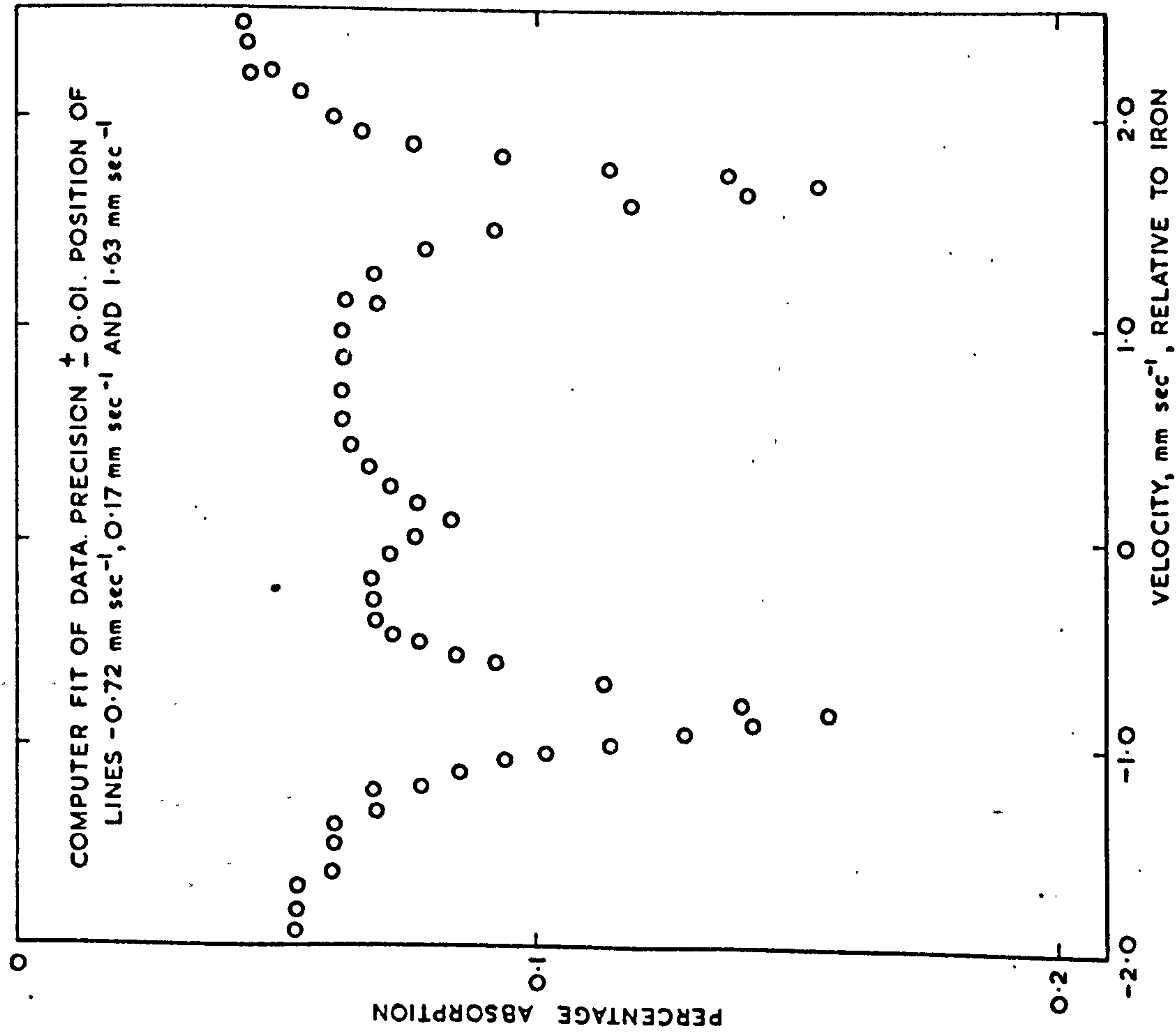
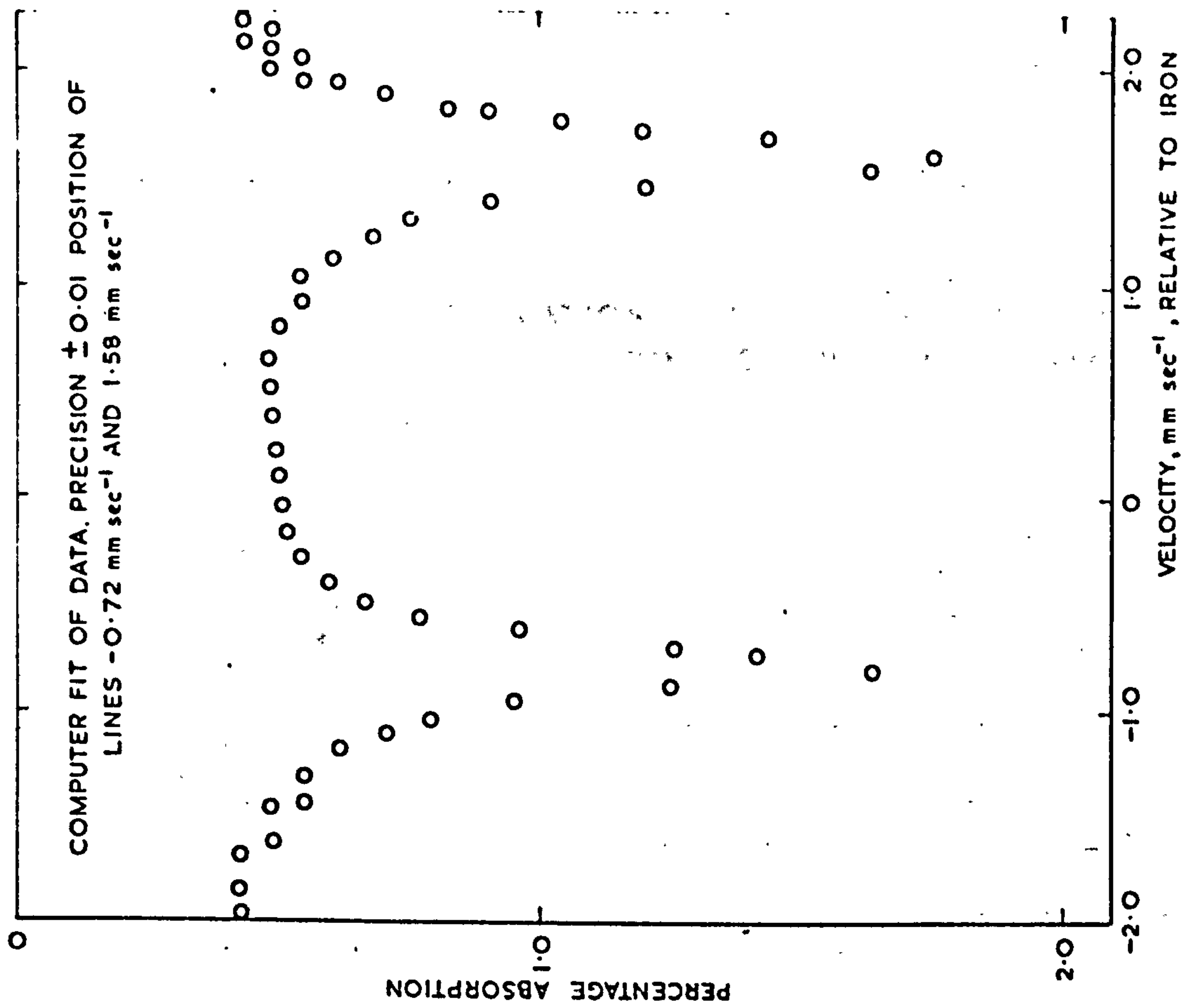


FIG 7 MÖSSBAUER SPECTRUM OF POLYVINYLFERROCENE AT 300 K FIG. 8 MÖSSBAUER SPECTRUM OF VINYLFERROCENE AT 300 K

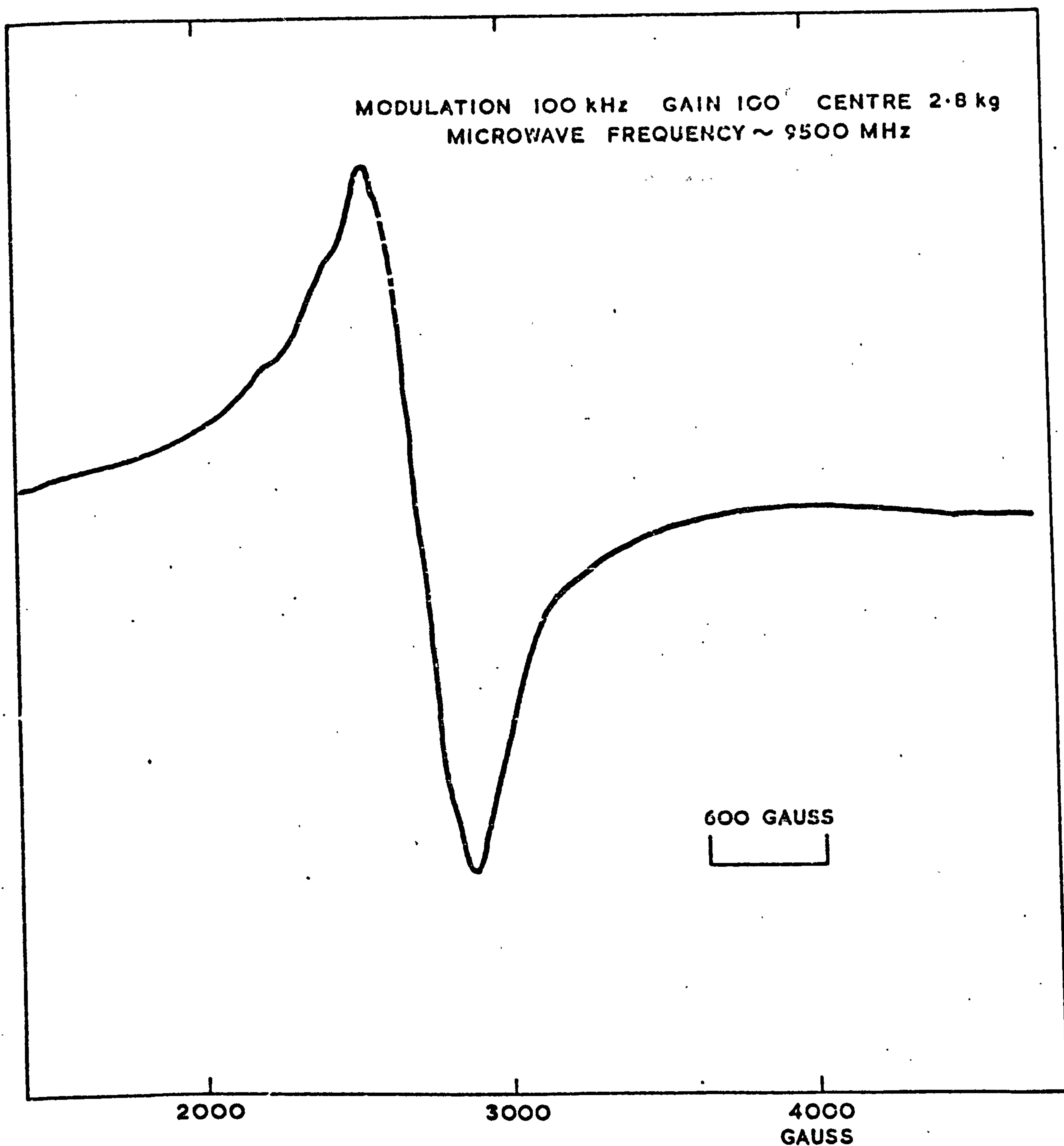


FIG. 9 ELECTRON SPIN RESONANCE SPECTRUM OF
POLYVINYLFERROCENE SOLID SAMPLE AT 298K

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IPC Science and Technology Press Ltd,
IPC House, 32 High Street, Guildford, Surrey, GU1 3EW, England

Polymerization of vinylferrocene in chloroform

Introduction

The polymerization of vinyl monomers by metallocenes^{1,2}, metal carbonyls³ and metal acetylacetonates⁴ in the presence of halogenated and oxygenated solvents is generally accepted to occur by a free radical mechanism. The radicals which initiate the polymerization reaction are generated as a result of an electron transfer reaction between the metal nucleus (Met) and the solvent and the reaction can be depicted as:



Vinylferrocene^{5,6} like its parent compound ferrocene⁷, is decomposed in halogenated solvents, the decomposition

probably being induced by an initial electron transfer process with resulting formation of free radicals. Since vinylferrocene is readily polymerized by free radicals⁸⁻¹² this monomer may initiate its own polymerization in solvents which promote electron transfer reactions. Vinyl ferrocene does not polymerize at 60°C, in the absence of added initiator, in solvents such as benzene and toluene, which do not react with the ferrocene nucleus to produce free radicals. Accordingly, the polymerization of vinylferrocene in chloroform at 60°C has been studied and been found to proceed in the absence of any added free radical initiator.

Experimental

Vinylferrocene was purified by sublimation at 30°C and 0.1 mmHg (m.p. 52.5–53.5°C, lit. value¹³ 52–53.5°C). Gas chromatography (Pye Unicam 101, Carbowax column at 150°C), confirmed the purity of the monomer. Analar chloroform was dried over Linde molecular sieves (3A) and distilled under reduced pressure prior to use. Polymerizations were carried out in sealed glass vessels, after degassing the reactants by three successive freeze–pump–thaw cycles at 10^{−4} mmHg. Other reactions were also attempted after simply passing oxygen-free nitrogen over the frozen reactants before sealing the vessels. The reactants were heated for seven days at 60°C and then precipitated into Analar methanol. Polymers were only obtained from experiments conducted *in vacuo*. The polymers were redissolved in chloroform, precipitated into methanol, collected on a sintered glass crucible (porosity 3) washed with methanol and dried to constant weight at 30°C and 0.1 mmHg. After precipitation and filtration of the polymer the filtrate was evaporated and yielded only negligible amounts of unreacted vinylferrocene.

The polymers were characterized by elemental analysis, infra-red (i.r.) and ultra-violet (u.v.) spectroscopy. Number-average molecular weights were determined by vapour pressure osmometry in benzene and the molecular weight distribution was examined by gel permeation chromatography.

Table 1 Homopolymerization of vinylferrocene in chloroform and benzene at 60°C

Initial monomer concentration (mol/dm ³)	Solvent	Initiator ^a concentration × 10 ³ (mol/dm ³)	Conversion (%)	Iron (%)	Chlorine (%)	$\bar{M}_n^b$
1	CHCl ₃	—	30	23.1, 23.4	0.84	1 140
4	CHCl ₃	—	77	24.0, 24.1	0.54	1 200
4c	CHCl ₃	—	0	—	0.08	—
4c	CHCl ₃	—	0	—	0.10	—
1	benzene	1.0d	15	26.2, 26.1	0.01	5 800
4	benzene	1.0	2	26.4, 26.3	—	5 600
4	benzene	1.0	25	25.2, 25.4	—	12 800

^a 2,2'-Azobisisobutyronitrile used to initiate polymerization in benzene

^b Number-average molecular weight determined by vapour pressure osmometry in benzene at 37°C

^c Nitrogen passed over frozen reactants before sealing. Small amounts of oxygen therefore remain in the reaction vessels

^d Polymerization did not occur in benzene solution at 60°C in the absence of added AIBN

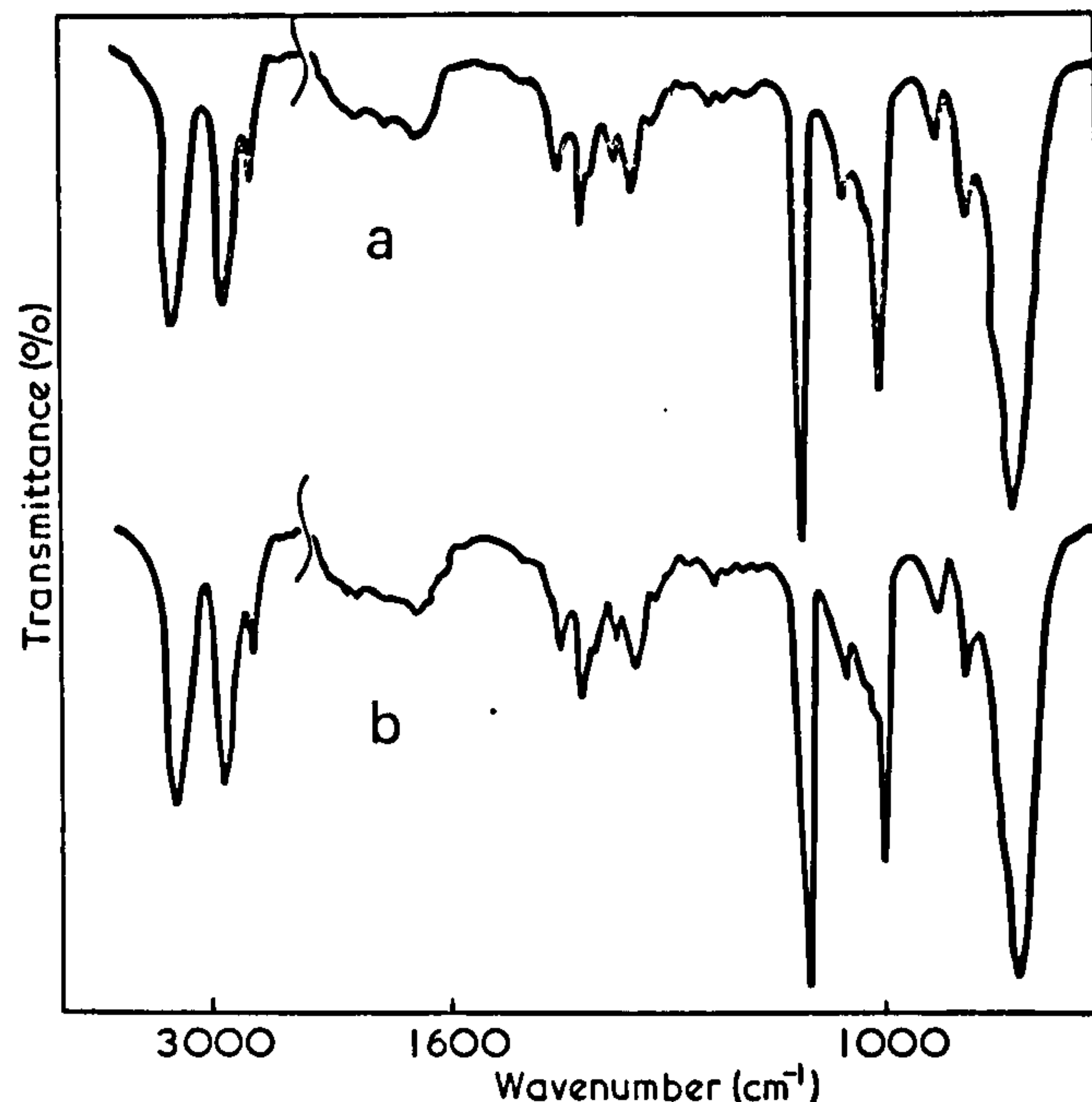


Figure 1 Infra-red spectra of polyvinylferrocene; films cast from benzene. (a) Prepared at 60°C in benzene with 1.0 × 10^{−3} mol/dm³ AIBN; (b) prepared at 60°C in chloroform, no added initiator

To investigate the presence of chlorine in the polymers prepared in chloroform, they were irradiated for 1 min in the pneumatic tube facility of the HERALD reactor (AWRE, Aldermaston, at a thermal neutron flux of 4 × 10¹² neutron cm^{−2} s^{−1}. The 37.5 min ³⁸Cl activity was measured using a high resolution Ge(Li) detector.

Results and Discussion

The results of the polymerization of vinylferrocene in chloroform are recorded in *Table 1*, together with those of polymerizations initiated by 2,2'-azobisisobutyronitrile (AIBN) in benzene. Polyvinylferrocene obtained from reactions in chloroform with the initial monomer concentration [M]₀ = 4.0 mol/dm³ were yellow powders whereas those obtained from reactions with [M]₀ = 1.0 mol/dm³ were coloured green. The green polymer showed an absorption at 635 nm, characteristic of the ferricenium species, which indicated that the polymer contained oxidized ferrocene units¹⁴. These could be reduced with ascorbic acid to give a yellow polymer which did not contain this longwave absorption.

Polymerization did not occur in the presence of oxygen and the monomer was decomposed to a brown ionic solid.

The purified polymers obtained from chloroform had identical i.r. spectra to those obtained by free radical initiation in benzene, which suggests that a similar mechanism is operative in both polymerizations. Some typical spectra are shown in *Figure 1*.

The u.v. and visible spectrum of polyvinylferrocene prepared in chloroform is the same as that of polyvinylferrocene obtained by free radical initiation in benzene. Typical absorption maxima and extinction coefficients are recorded in *Table 2*. The characteristic ferrocene absorptions near 330 nm and 450 nm appear in both. The lower extinction coefficients for the repeat unit of the polymers obtained from chloroform are in accord with their lower iron contents.

All the polymer samples show a similar electron spin resonance signal which consists of a broad line of width ~ 600 G and a g value equal to 2.06. This signal has been ascribed to the presence of a high spin Fe(III) complex in polyvinylferrocene prepared by radical initiation in benzene¹². It has been suggested that the complex is formed as a result of a termination reaction which involves an electron transfer from the ferrocene nucleus to the growing polymer chain radical. The presence of a paramagnetic species in polyvinylferrocene prepared in chloroform suggests that a similar free radical mechanism is also operative in this polymerization.

In agreement with results of other workers^{11,14,15} all the polymers have low molecular weights and the molecular weight distributions are broad and often appear binodal. These results suggest that transfer reactions are significant in radical polymerizations of vinylferrocene. In accordance with this suggestion the transfer constant to monomer has been estimated to be $\sim 8 \times 10^{-3}$ for vinylferrocene polymerized by free radicals in benzene¹⁶. In this system transfer to solvent was found to be negligible.

The very low molecular weights of polyvinylferrocene prepared in chloroform suggest that transfer to this solvent is more important. This is to be expected because of the high transfer activity of the monomer¹⁶ and chloroform¹⁷ in radical polymerizations.

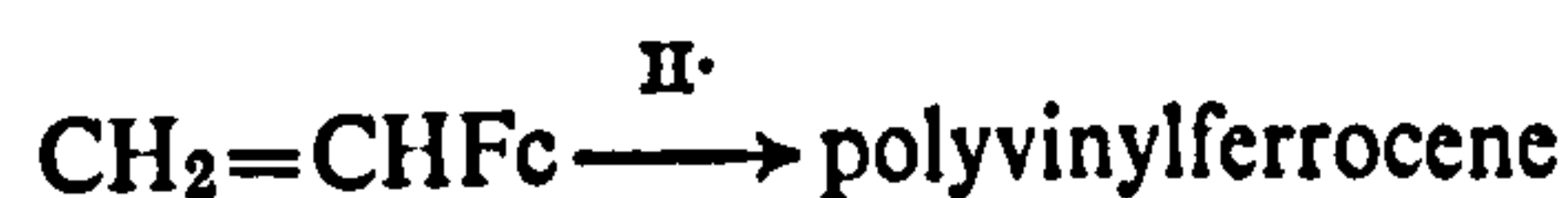
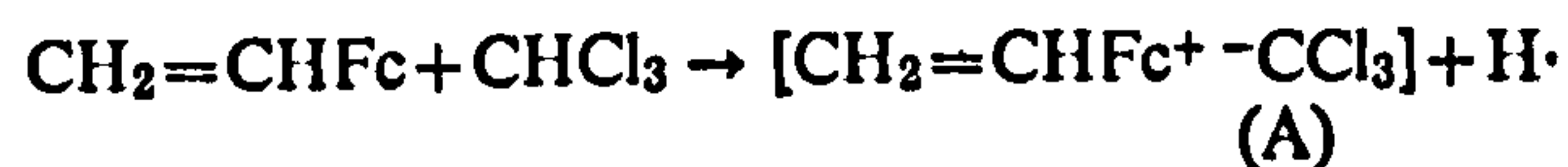
The presence of chlorine in polyvinylferrocene prepared in chloroform was confirmed by neutron activation

analysis. A typical graph of the γ spectrum is shown in Figure 2. The two major ^{38}Cl peaks are well defined. ^{56}Mn and ^{24}Na peaks are also present in the polymers.

From the above discussion it seems apparent that the polymerization of vinylferrocene in chloroform has occurred by a free radical mechanism. Radical polymerization of suitable olefinic ferrocene derivatives in halogenated solvents is not unexpected since the ferrocene nucleus is oxidized in these solvents with the resulting formation of free radicals. The effects of oxygen on the polymerization reaction further supports a radical mechanism for the polymerization reaction.

The chlorine content in the polymers is too low for initiation by a radical species containing chlorine. For example even one chlorine atom per chain would result in a chlorine content of $\sim 3\%$ w/w in a polymer of molecular weight 1200. When the high transfer activity of the system is considered it seems more probable that chlorine is introduced into the polymers as a result of transfer reactions. This view is supported by the higher chlorine contents in polyvinylferrocene prepared in a high concentration of chloroform.

If chlorine is not present in the initiating radical it suggests that the polymerization has been initiated by a hydrogen radical. Since chloroform is readily decomposed to give a stable $-\text{CCl}_3$ anion¹⁸ and ferrocene is readily oxidized in chloroform⁵⁻⁷, the following reaction scheme can be suggested to account for the polymerization of vinylferrocene in chloroform:



where Fc denotes the ferrocenyl group $\text{C}_{10}\text{H}_9\text{Fe}$.

The presence of the ferricenium species, A, in the polymerization reaction is supported by the fact that the colour of the reactants changed from dark red to green. The ferricenium species is very reactive towards free radicals, undergoing ring substitution^{19,20}, and will therefore act as a radical scavenger. However, radical addition to the olefinic double bond must still occur, presumably because of the lower activation energy for this reaction compared with ring substitution, although substitution reactions cannot be precluded.

Although a green polymer was obtained in reactions with a high mole fraction of chloroform, it is unlikely that species (A) has been polymerized. It is more probable that the green colour has resulted because of oxidation of the polyvinylferrocene formed initially. Thus, yellow solutions of polyvinylferrocene in carbon tetrachloride have been observed to turn green and precipitate a green ionic species¹⁵. Similar results have been found in chloroform in the present study.

A recent kinetic study of the radical initiated polymerization of vinylferrocene in benzene has shown that the termination step is monomolecular¹². Thus, the rate of polymerization at 60°C in benzene is related to the mean monomer and initiator concentration by the expression $R_p = k[\bar{M}]^{1.1}[\bar{I}_n]^{1.1}$ where k is a composite constant.

Self-initiation in solvents which promote electron transfer from the nucleus seems to be another unusual feature of this monomer.

Table 2 Ultra-violet spectra of polyvinylferrocene in chloroform

Initial monomer concentration (mol/dm ³)	λ_{max} (nm)	ϵ (dm ³ mol ⁻¹ cm ⁻¹)
1.0a	330; 450	54; 81
4.0a	330; 450	55; 71
1.0b	330; 446	88; 99
2.0b	330; 446	86; 96

a Polymerized in chloroform; no added initiator
b Polymerized in benzene with 1.0×10^{-3} mol/dm³ AIBN

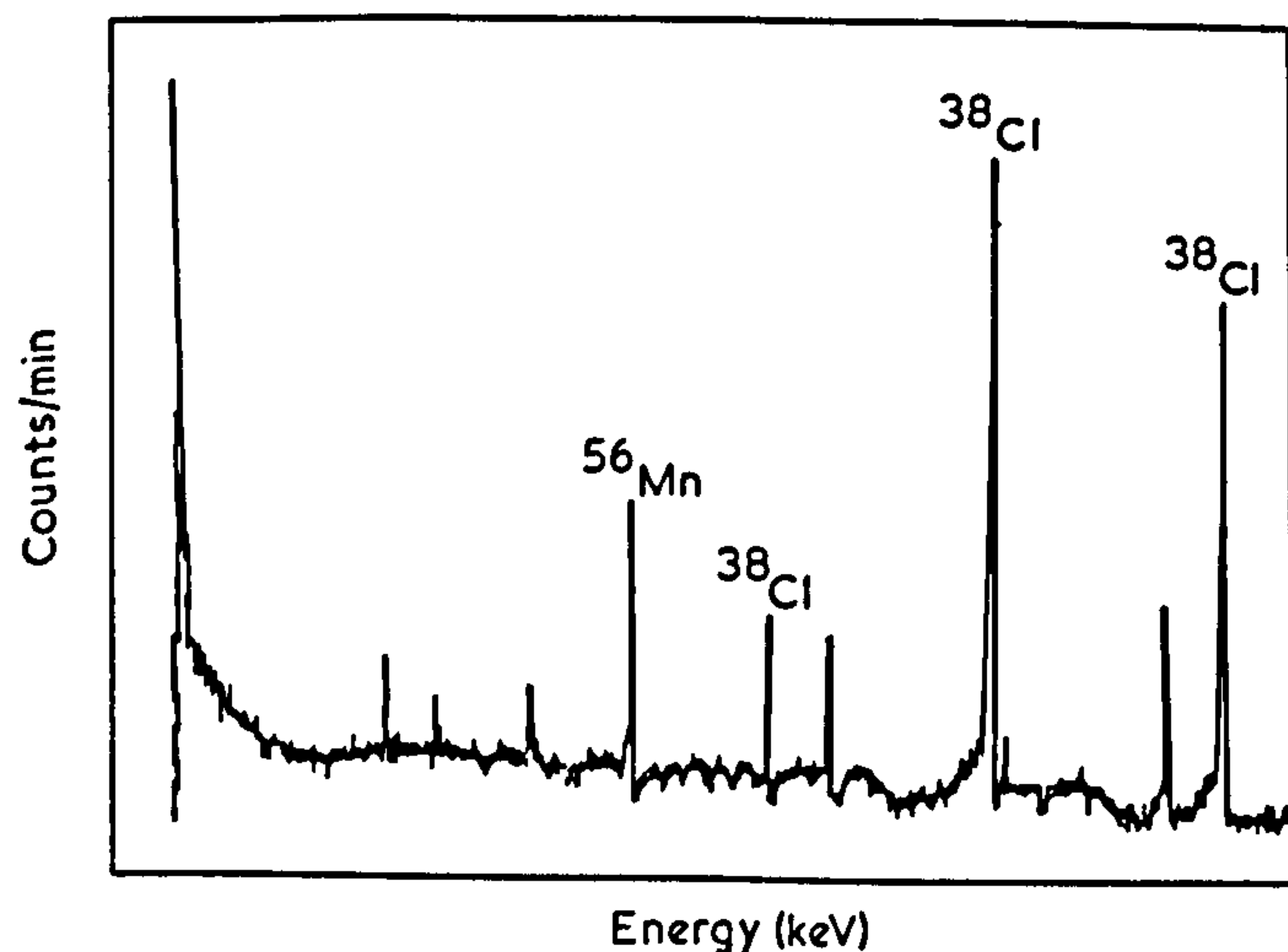


Figure 2 γ spectrum of polyvinylferrocene after irradiation for 1 min in the HERALD reactor. Polymer sample prepared at 60°C in chloroform, no added initiator

More detailed kinetic studies of the polymerization of vinylferrocene in a range of solvents are in progress to elucidate the precise mechanisms operating in the polymerization reactions of vinylferrocene.

Acknowledgement

We are grateful to G. C. Goode, Atomic Weapons Research Establishment, Aldermaston, for carrying out activation analysis of polyvinylferrocene.

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(Received 7 February 1974)

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