

STUDIES OF SOME FERROCENE-CONTAINING POLYMERIZATION SYSTEMS.

by

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To Geraldine,
with love.

Abstract

Evidence for ferrocene-olefin and ferrocene-aromatic interactions has been presented. The bulk and benzene solution thermal polymerization of styrene, both in the absence and presence of 2,2'-azobisisobutyronitrile (AIBN), has been studied at 60°C in the presence of ferrocene derivatives. Simple kinetic schemes for bulk polymerization were inapplicable and enhanced propagation may proceed through styrene interacting with the ferrocene derivative. In the presence of vinylferrocene and ethylferrocene, retardation was also observed. However, the solution polymerization of styrene in the presence of vinylferrocene proceeded normally and a chain transfer constant for vinylferrocene in this polymerization was determined.

The kinetics of the bulk polymerization of styrene at 60°C in the presence of cyclohexanone and ferrocene have been studied and increased polymerization rates were noted. This effect was attributed to the formation of initiating radicals from cyclohexanone and ferrocene. The chain transfer constant for cyclohexanone in styrene polymerization was evaluated.

The kinetics of the AIBN-initiated homopolymerization of vinylferrocene in dioxane have been investigated at 60°C and were found to be normal. Various kinetic parameters have been evaluated. The thermal behaviour of polyvinylferrocene has been studied as a function of molecular weight. Two transitions were observed, the second being assigned as the glass transition. The first transition may be due to rotation of the unsubstituted cyclopentadiene rings.

Vinylferrocene has been free-radically copolymerized with styrene and vinyl acetate at 60°C. Relative reactivity ratios

have been determined for both of these copolymerizations and Q and e values have been calculated for vinylferrocene. Limiting viscosity numbers in toluene at 30°C and glass transition temperatures have been determined for the styrene-vinylferrocene copolymers.

The homopolymerization of vinylferrocene, and copolymerization with styrene, by anionic and Ziegler-Natta catalysts, and with manganese(III) acetylacetonate as initiator, have been investigated.

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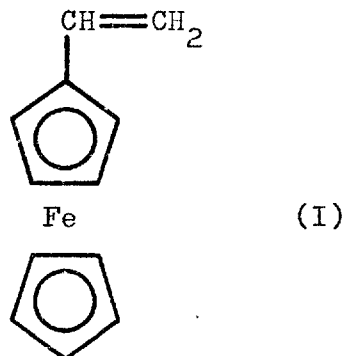
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I Introduction.

Since the synthesis and polymerization¹ of the first, and simplest, olefinic ferrocene compound, vinylferrocene (I), a



variety of ferrocene-containing vinyl monomers have been prepared and polymerized. Some of these studies have been specifically designed to obtain ferrocene-containing polymer for an assessment of a potential application as a redox agent^{2,3} or a semiconductor⁴. Other studies have been more generally motivated by the potential properties of ferrocene-containing polymers, because of the known advantageous properties of many simple ferrocene derivatives, particularly their stability toward ultraviolet light, which enables them to be highly effective stabilizers toward photodegradation^{5,6}. However, few of these studies have been detailed, either with respect to the polymerization or with respect to the polymer formed.

Vinylferrocene is the most extensively studied vinylic ferrocene-containing monomer but, although the free-radical homopolymerization of this monomer has been recorded quite frequently^{1,2,7-15}, it is only recently that a full kinetic study of the solution polymerization has been reported¹⁴. Although an earlier brief study⁹ had suggested that the homopolymerization of vinylferrocene in benzene follows a normal kinetic scheme for free-radical vinyl polymerization

(Section II.A), the rate of polymerization being first-order in monomer concentration and half-order in initiator concentration, the more complete later study demonstrated that the rate of polymerization, whilst still being first-order in monomer concentration, is first-order in initiator concentration. A monomolecular termination step involving the polymer radical was suggested to account for the anomalous rate equation. It was further proposed that this step results in the formation of a paramagnetic Fe(III)-containing species. Mössbauer and esr spectral evidence was reported to substantiate the presence of this species in the polymer formed. These proposals are discussed further in section VII.

Polyvinylferrocene formed in solution polymerizations has invariably been of low molecular weight, often having a number average molecular weight, $\bar{M}_n$, of less than 10,000. However, a polymer prepared in a bulk polymerization was reported² to have a $\bar{M}_n$ of 48,600.

Recently, the solution properties of fractionated polyvinylferrocene have been investigated, and the K and a constants of the Mark-Houwink relationship (Section III.B.15) have been evaluated for benzene ($6.64 \times 10^{-4} \text{ 100cm}^3 \text{g}^{-1}$ and 0.48 respectively) and tetrahydrofuran ($7.2 \times 10^{-5} \text{ 100cm}^3 \text{g}^{-1}$ and 0.72 respectively). Theoretically¹⁶, the value of a has limits of unity, when the polymer molecules are extended in solution, and 0.5 at the theta temperature for the system, when the polymer molecules are contracted. The value for a of approximately 0.5 for polyvinylferrocene in benzene at 30°C has led to the suggestion¹⁵ that the theta temperature for this system might not be too far from 30°C. However, the same study classes benzene as a good solvent for polyvinylferrocene, which is not compatible

with a system close to its theta temperature.

The glass transition temperature, T_g , which marks the onset of segmental motion in the polymer, has been estimated^{10,11} for polyvinylferrocene by differential scanning calorimetry (DSC). The values obtained were in the region 184°C to 194°C, but were approximate because the DSC traces exhibited broad curves. These values are considerably lower than the reported softening points for polyvinylferrocene of 280-285°C¹ and 280-290°C². However, it is clear that T_g for polyvinylferrocene is much higher than that for polystyrene, which has a T_g in the region of 100°C.

Vinylferrocene has been free-radically copolymerized with a number of the more common vinyl monomers (Table I.1) and relative reactivity ratios (Section II.B) have been determined for many of these copolymerizations (Table I.1). The Alfrey-Price Q and e scheme (Section II.B) has been applied to the majority of those copolymerizations for which relative reactivity ratios have been determined, but it appears¹¹ that vinylferrocene does not fit into this scheme. There has been little investigation of the properties of the copolymers formed in these studies. However, softening points were estimated¹⁷ for styrene-vinylferrocene copolymers with a vinylferrocene content of 5-62 mole-percent. These were found to increase with increasing vinylferrocene content (120-130°C to 200-215°C), as would be expected in view of the glass transition temperatures of the homopolymers.

The cationic polymerization of vinylferrocene at 0°C by a variety of suitable catalysts has been reported²². The polymer yields were high, but the molecular weights of the polymers formed were very low (1,100-3,500). This low molecular weight

probably accounts for the generally low softening points observed, compared with values obtained for free-radically prepared polymers, and also for the variation in these values from 160-170°C ($\bar{M}_n = 1,100$) to 235°C ($\bar{M}_n = 3,500$). The ratio of the absorbances at 995 cm^{-1} and 815 cm^{-1} in the infrared spectrum of the cationically prepared polyvinylferrocene was found to be in good agreement with that for free-radically prepared polymer. Since the absorption at 995 cm^{-1} is exhibited only by ferrocene derivatives which have one of the cyclopentadiene rings unsubstituted and the absorption at 815 cm^{-1} is less sensitive to heteroannular substitution²³, it was suggested²² that cationically and free-radically prepared polyvinylferrocene are of similar structure and therefore that nuclear substitution is unimportant in the cationic polymerization of vinylferrocene. However, although this spectral evidence indicates that heteroannular substitution does not occur, it cannot preclude the possibility of homoannular substitution. If polyvinylferrocene is considered to behave as an alkylferrocene, this latter mode of nuclear substitution would be the preferred mode²³.

The ease with which vinylferrocene undergoes cationic polymerization is to be expected from the known stability of the 1-ferrocenylcarbonium ion²³. It is reflected also in the cationic copolymerization of vinylferrocene and styrene²², since styrene was incorporated into the polymer only when the styrene content of the feed was 80-90 mole-percent, depending on the solvent used. The cationic copolymerization of vinylferrocene (M_1) and vinyl isobutyl ether (M_2) was successful over the entire range of monomer feed composition²². The relative reactivity ratios determined for this copolymerization ($r_1 = 0.1$, $r_2 = 9.7$ at 0°C) illustrate the high reactivity of the vinyl

alkyl ethers toward cationic polymerization.

Vinylferrocene has been homopolymerized²⁴ also by soluble Ziegler catalysts and by a $[-P(C_6H_5)_2]/Ni(acac)_2$ catalyst. The Ziegler catalysts gave moderately high polymer yields after 6 hr at 60°C, but substantial amounts of the polymers were methanol soluble, which suggests low polymer molecular weights. The $[-P(C_6H_5)_2]/Ni(acac)_2$ catalyst gave somewhat higher yields under similar conditions. The polymerization mechanism in the presence of this catalyst was thought to be of an anionic coordinative nature.

Divinylferrocene has been polymerized by free-radical^{25,26}, cationic²⁵⁻²⁷, Ziegler²⁵ and anionic²⁵ techniques, but this polymerization is characterized by cyclization and crosslinking, much of the polymer formed being benzene insoluble.

Two groups of ferrocene-substituted monomers which have been studied almost as extensively as vinylferrocene are the ferrocene-containing acrylates and methacrylates. Ferrocenylmethyl acrylate and methacrylate^{10,28} and 2-ferrocenylethyl acrylate and methacrylate²⁹ all appear to follow a normal kinetic scheme (Section II.A) in their free-radical homopolymerization in benzene, since their rates of polymerization are first-order in monomer concentration and half-order in initiator concentration. 1-ferrocenylethyl acrylate²⁹ decomposes to vinylferrocene in competition with polymerization at 70°C.

Values have been determined^{10,29} for K and a in the Mark-Houwink relationship (Section III.B.15) for these polymers in benzene, but, since the viscosity measurements were made on unfractionated polymer samples and the limiting viscosity numbers were related to $\bar{M}_n$ and $\bar{M}_w$, these values were given as preliminary estimates only.

As with polyvinylferrocene, DSC traces obtained for these polymers exhibited broad curves. However, these were interpreted as indicating glass transition temperatures of 197-210°C, 185-195°C, 157°C and 209°C for poly(ferrocenylmethyl acrylate)¹⁰, poly(ferrocenylmethyl methacrylate)¹⁰, poly(2-ferrocenylethyl acrylate)^{10,29} and poly(2-ferrocenylethyl methacrylate)^{10,29}, respectively. Few other polyacrylates and polymethacrylates have glass transitions at temperatures as high as these.

These four ferrocene-containing acrylic and methacrylic esters have been copolymerized free-radically with a variety of common vinyl monomers. The details of these copolymerizations, including relative reactivity ratios, are summarized in table I.2. Two partial summaries of the free-radical polymerization of these four monomers and vinylferrocene have been published^{12,13}. The relative reactivity ratios for copolymerizations with a common comonomer clearly indicate that 2-ferrocenylethyl acrylate and methacrylate are more reactive monomers than ferrocenylmethyl acrylate and methacrylate. It has been suggested²⁹ that this difference in reactivity is due to steric factors, the bulky ferrocene nucleus being closer to the polymer backbone in the ferrocenylmethyl monomers and polymers. The Alfrey-Price Q and e scheme (Section II.B) has been applied to the ferrocenylmethyl acrylate and methacrylate copolymerizations^{30,31}, but, when a Q-e map was constructed, no satisfactory single values of Q and e were obtained for either monomer. This was attributed, in part, to the rather large confidence limits associated with some of the copolymerizations. Also, steric factors were considered to be intervening, and these are not accommodated in the Q and e scheme.

Limiting viscosity numbers, in tetrahydrofuran, and glass

transition temperatures were obtained³¹ for several of the copolymers of ferrocenylmethyl methacrylate and acrylonitrile, maleic anhydride and N-vinyl-2-pyrrolidone, and also for several ferrocenylmethyl acrylate-maleic anhydride copolymers. However, no systematic study of the variation of polymer properties with copolymer composition has been reported.

1-ferrocenyl-1,3-butadiene has been homopolymerized by free-radical³⁴⁻³⁶ and anionic^{34,35,37} techniques and copolymerized free-radically with styrene^{35,36} and methyl methacrylate³⁵. The azobisisobutyronitrile (AIBN) initiated homopolymerization in toluene at 67°C was reported³⁵ to give only dimer, in high yield. However, a later study³⁶ of this polymerization in benzene at 70°C was successful in preparing homopolymer of low molecular weight ($\bar{M}_n = 1,650$). The softening point of this polymer was given as 140°C. This latter study also included the more complete investigation of the free-radical copolymerization of 1-ferrocenyl-1,3-butadiene (M_2) with styrene (M_1). In agreement with the earlier study³⁵, 1-ferrocenyl-1,3-butadiene was found to be preferentially incorporated into the copolymer. This is reflected in the values obtained³⁶ for the relative reactivity ratios for this copolymerization ($r_2 = 2.47$, $r_1 = 0.76$). The Alfrey-Price Q and e scheme was applied to these values, and Q and e for 1-ferrocenyl-1,3-butadiene were calculated to be 1.56 and -0.8 respectively.

The anionic homopolymerization of 1-ferrocenyl-1,3-butadiene, in toluene at room temperature with n-butyllithium as initiator, has been studied³⁷ over a wide range of monomer:initiator ratios. The polymerizations did not proceed to 100% conversion at high monomer:initiator ratios (greater than 20), and molecular weights were higher than would be expected from the monomer:initiator

ratio. Also, the dispersity indices ($\overline{M}_w/\overline{M}_n$) of the polymers formed were relatively high for anionic polymerizations. These observations were interpreted as indicating that chain transfer had occurred. In view of the known lithiation of ferrocene, it was suggested that transfer occurs to the ferrocene nucleus of the monomer and polymer.

Three alkenoylferrocene monomers have been polymerized. Acryloylferrocene has been homopolymerized by free-radical^{8,38} anionic³⁸ and cationic³⁸ techniques. However, both furylacryloylferrocene⁸ and trans-cinnamoylferrocene^{8,39} failed to form homopolymers when standard free-radical techniques were employed. All three monomers have been successfully copolymerized free-radically; acryloylferrocene with acrylonitrile³⁸, vinyl acetate⁸, styrene⁸ and methyl methacrylate⁸, furylacryloylferrocene⁸ with styrene and methyl methacrylate, and trans-cinnamoylferrocene^{8,39} with a range of comonomers, including dienes.

Isopropenylferrocene also has been reported⁴⁰ as not undergoing homopolymerization in toluene at 100°C in the presence of AIBN as initiator, although it did copolymerize with styrene and methyl methacrylate. This behaviour is similar to that of its benzene analogue, α -methylstyrene. However, diisopropenylferrocene has been homopolymerized⁴¹ by free-radical, cationic and Ziegler-Natta techniques, although the latter method gave only oily oligomer. An attempted anionic homopolymerization⁴¹ failed to produce polymer.

Among the less common ferrocene-containing vinyl monomers are trans- β -ferrocenylacrylonitrile, which has been copolymerized free-radically⁴², and di(1-chlorovinyl)ferrocene, which has been homopolymerized⁴³ by an anionic technique. A range of silicon

and ferrocene substituted vinyl monomers also has been homopolymerized⁴⁴ and copolymerized⁴⁵ by anionic techniques.

The non-vinylic ferrocene-containing monomer ferrocenylacetylene (ethynylferrocene) is of some interest here, because it has been homopolymerized by free-radical^{24,46}, anionic⁴⁷ and Ziegler-Natta^{24,48} techniques and copolymerized by thermal⁴⁹, cationic⁵⁰ and Ziegler-Natta⁵¹ techniques.

An observation which is of importance to studies of the free-radical polymerization of all of these ferrocene-containing vinylic monomers is the ineffectiveness of benzoyl peroxide as an initiator in these systems. This has been reported on several occasions^{9,39}, and has been attributed to a non-radical reaction of benzoyl peroxide with the ferrocene nucleus of the monomer.

The polymerization of ferrocene substituted vinylic monomers represents only one method of preparing ferrocene-containing polymers. More study has been directed toward the preparation of such polymers by condensation methods. These investigations are not of direct relevance to this work, and are reviewed elsewhere⁵².

Table I.1

The free-radical copolymerization of vinylferrocene

Comonomer (M_2)	^a r_1	^a r_1	^b Q_1	^b e_1	Ref.
Styrene	-	-	-	-	1,7,8,9
^c	0.2	4	0.4	-1.3	17
^c	0.08	2.5	0.145	0.47	11
^c	0.097	2.91	-	-	11
Methyl acrylate ^c	0.82	0.63	1.16	1.39	11
Methyl	-	-	-	-	1,7,8,9
methacrylate ^c	0.52	1.22	0.79	1.07	11
Acrylonitrile ^c	0.15	0.16	0.05	0.72	11
Maleic anhydride ^d	0.02	0.21	-	-	18
N-vinyl-2-pyrrolidone ^c	0.66	0.40	-	-	19
Ethyl acrylate	-	-	-	-	9
Butadiene	-	-	-	-	20,21
Chloroprene ^e	-	-	-	-	1,7

^a Relative reactivity ratios.

^b Alfrey-Price Q and e scheme based on $Q = 1.0$ and $e = -0.8$ for styrene.

^c In benzene at 70°C.

^d In a solvent mixture of 75% benzene and 25% ethyl acetate at 70°C.

^e Emulsion polymerization.

Table I.2

Free-radical copolymerizations of ferrocene-containing acrylic and methacrylic esters

Monomer (M_1)	Comonomer (M_2)	^a r_1	^a r_2	Ref.
Ferrocenylmethyl acrylate	^b styrene	0.02	2.3	30
	^b vinyl acetate	1.44	0.46	30
	^b methyl acrylate	0.14	4.46	30
	^b methyl methacrylate	0.08	2.9	30
	^c maleic anhydride	0.61	0.11	31
Ferrocenylmethyl methacrylate	^b styrene	0.03	3.7	30
	^b vinyl acetate	1.52	0.20	30
	^b methyl acrylate	0.08	0.82	30
	^b methyl methacrylate	0.12	3.27	30
	^c maleic anhydride	0.28	0.10	31
	^d acrylonitrile	0.30	0.11	31
	^d N-vinyl-2-pyrrolidone	3.71	0.05	31
2-ferrocenylethyl acrylate	^b styrene	0.41	1.06	32
	^e vinyl acetate	3.4	0.07	32
	^e methyl acrylate	0.76	0.69	32
	η (benzyl acrylate)	-	-	33
	chromium tricarbonyl			
2-ferrocenylethyl methacrylate	^b styrene	0.08	0.58	32
	^e vinyl acetate	8.79	0.06	32
	^e methyl methacrylate	0.20	0.65	32

^a Relative reactivity ratios. ^b In benzene at 70°C.

^c In 1:1 v/v benzene:ethyl acetate at 80°C.

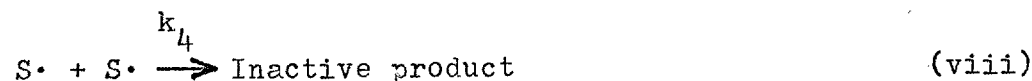
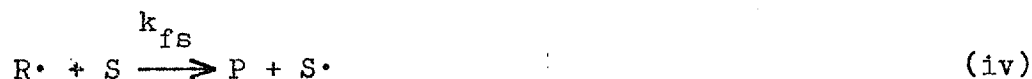
^d In benzene at 80°C. ^e In benzene at 60°C.

II Kinetic aspects of free-radical polymerization

II.A Free-radical homopolymerization

Several thorough treatments of the kinetics of the free-radical homopolymerization of vinyl monomers have been published⁵³. The following scheme is, therefore, only a framework necessary for the treatment and discussion of the results which are to be presented.

The scheme considers the general case of the polymerization of a monomer, M, via polymer radicals, R $\cdot$, in the presence of another chemical species, S, to give polymer, P. Initiating radicals, R $_c$ $\cdot$, are formed at a rate I.



In many polymerizations, steps II.(vii) and II.(viii) are of minor importance and do not influence the polymerization significantly. Furthermore, in any polymerization which yields high polymer, step II.(ii) occurs many times more than steps

II.(i) and II.(v). Thus, the rate of polymerization,

$$R_p = -\frac{d[M]}{dt} = k_p[R\cdot][M] \quad (1)$$

Assuming a steady state concentration of polymer radicals, that is,

$$\frac{d[R\cdot]}{dt} = 0 \quad (2)$$

$$I + k_2[S\cdot][M] = 2k_t[R\cdot]^2 + k_{fs}[R\cdot][S] \quad (3)$$

For a steady state concentration of $S\cdot$, assuming steps II.(vii) and II.(viii) to be negligible,

$$k_{fs}[R\cdot][S\cdot] = k_2[S\cdot][M] \quad (4)$$

and equation II.3 becomes

$$[R\cdot] = (I/2k_t)^{0.5} \quad (5)$$

Hence,

$$R_p = k_p(I/2k_t)^{0.5}[M] \quad (6)$$

In the presence of a free-radical initiator, In , initiating radicals are formed by



Then, the rate of initiation

$$I = 2fk_d[In] \quad (7)$$

where f , the initiator efficiency, is the fraction of radicals which initiate polymerization. The rate of polymerization may be given now by

$$R_p = k_p(fk_d/k_t)^{0.5}[M][In]^{0.5} \quad (8)$$

When the degree of polymerization of the polymer, $\overline{DP}$, is considered, the precise mode of termination, generalised in step II.(vi), becomes important. The general nature of this treatment may be preserved by regarding the rate of formation of polymer by this step to be $k_{ter}[R\cdot]^2$. Then, by definition,

$$\overline{DP} = \frac{k_p [R\cdot] [M]}{k_{ter} [R\cdot]^2 + k_{fm} [R\cdot] [M] + k_{fs} [R\cdot] [S]} \quad (9)$$

or,

$$\frac{1}{\overline{DP}} = \frac{k_{ter} [R\cdot]}{k_p [M]^2} + \frac{k_{fm}}{k_p} + \frac{k_{fs} [S]}{k_p [M]} \quad (10)$$

Combining equations II.1 and II.9 gives

$$\frac{1}{\overline{DP}} = \frac{k_{ter} R_p}{k_p^2 [M]^2} + \frac{k_{fm}}{k_p} + \frac{k_{fs} [S]}{k_p [M]} \quad (11)$$

or, introducing C_m and C_s , the chain transfer to monomer and species S constants respectively, where C_m and C_s are equal to (k_{fm}/k_p) and (k_{fs}/k_p) respectively,

$$\frac{1}{\overline{DP}} = \frac{k_{ter} R_p}{k_p^2 [M]^2} + C_m + C_s \frac{[S]}{[M]} \quad (12)$$

II.B Free-radical copolymerization

In a binary copolymerization, the composition of the copolymer formed is related to the composition of the monomer feed by the copolymer equation. This is based on a consideration^{54,55} of the propagation steps in the copolymerization:



Then,

$$-\frac{d[A]}{dt} = k_{11}[A\cdot][A] + k_{21}[B\cdot][A] \quad (13)$$

and

$$-\frac{d[B]}{dt} = k_{22}[B\cdot][B] + k_{12}[A\cdot][B] \quad (14)$$

Assuming steady state conditions,

$$k_{21}[B\cdot][A] = k_{12}[A\cdot][B] \quad (15)$$

from which

$$k_{11}[A\cdot][A] = \frac{k_{11}k_{21}[B\cdot][A]^2}{k_{12}[B]} \quad (16)$$

Combining equations II.13, II.14, II.15 and II.16 gives

$$\frac{d[A]}{d[B]} = \frac{(k_{11}k_{21}[B\cdot][A]^2/k_{12}[B]) + k_{21}[B\cdot][A]}{k_{22}[B\cdot][B] + k_{12}[A\cdot][B]} \quad (17)$$

and dividing through by $k_{21}[B\cdot][B]$,

$$\frac{d[A]}{d[B]} = \frac{(k_{11}[A]^2/k_{12}[B]^2) + [A]/[B]}{(k_{22}/k_{21}) + [A]/[B]} \quad (18)$$

Defining the relative reactivity ratios, r_1 and r_2 , as

$$r_1 = k_{11}/k_{12} \quad (19)$$

and

$$r_2 = k_{22}/k_{21} \quad (20)$$

and introducing these into a rearranged form of equation II.18 gives

$$\frac{d[A]}{d[B]} = \frac{(r_1[A]/[B]) + 1}{(r_2[B]/[A]) + 1} \quad (21)$$

If the composition of the monomer feed is M_1 mole-percent of A and M_2 mole-percent of B, equation II.21 becomes

$$\frac{d[A]}{d[B]} = \frac{r_1(M_1/M_2) + 1}{r_2(M_2/M_1) + 1} \quad (22)$$

which is the differential form of the copolymer equation. At low conversion, the copolymer composition reflects the relative rates of incorporation of A and B into the polymer, that is

$$\frac{d[A]}{d[B]} = \frac{m_1}{m_2} \quad (23)$$

where m_1 and m_2 are the mole-percent of A and B in the copolymer respectively. Thus,

$$\frac{m_1}{m_2} = \frac{r_1(M_1/M_2) + 1}{r_2(M_2/M_1) + 1} \quad (24)$$

The Fineman-Ross⁵⁶ method provides a simple means of determining r_1 and r_2 if the monomer feed and copolymer compositions are known. Substituting F for M_1/M_2 and f for m_1/m_2 in equation II.24 and rearranging gives

$$(fr_2/F) + f = r_1F + 1 \quad (25)$$

Hence

$$(f - 1)/F = r_1 - r_2(f/F^2) \quad (26)$$

and

$$(F/f)(f - 1) = r_1(F^2/f) - r_2 \quad (27)$$

Thus, plots of $(f - 1)/F$ against f/F^2 are straight lines of gradient $-r_2$ and with r_1 as intercept, and plots of $(F/f)(f - 1)$ against F^2/f have a gradient of r_1 and $-r_2$ as intercept. The

advantage of having the two forms of the basic equation is that, on some occasions, one form gives a better plot than the other.

A knowledge of the relative reactivity ratios for a system permits the prediction of the composition of the copolymer formed from a given monomer feed, or allows the calculation of the composition of the monomer feed required to give a copolymer with a desired composition. The values of r_1 and r_2 obtained for one system may be used also in a semi-quantitative predictive manner in other copolymerizations, by using the Alfrey-Price Q-e scheme⁵⁷. This is based on the assumption that the rate constant for the attack of a radical 1 upon monomer 2 is given by

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \quad (28)$$

where P_1 is the radical reactivity factor, Q_2 is the mean reactivity of monomer 2, and e_1 and e_2 are measures of the polarity of the radical 1 and monomer 2 respectively. The same polarity factor is used for a monomer and its adduct radical, thus

$$k_{11} = P_1 Q_1 \exp(-e_1^2) \quad (29)$$

Then, dividing equation II.29 by equation II.28 gives

$$\frac{k_{11}}{k_{12}} = r_1 = \left(\frac{Q_1}{Q_2} \right) \exp \left\{ -e_1 (e_1 - e_2) \right\} \quad (30)$$

Similarly,

$$\frac{k_{22}}{k_{21}} = r_2 = \left(\frac{Q_2}{Q_1} \right) \exp \left\{ -e_2 (e_2 - e_1) \right\} \quad (31)$$

These relationships may be used to predict values for the relative reactivity ratios for a copolymerization from the Q and e values for the two monomers, which have been determined previously by studies of other systems. Such a use of the Q and e scheme must be undertaken with caution, since the scheme has several limitations, which are discussed elsewhere⁵⁸.

Q and e values for a new monomer may be calculated from experimentally determined relative reactivity ratios for the copolymerization with a monomer with known Q and e values (styrene being particularly useful in this respect, since it is taken as the standard for the system, with $Q = 1.00$ and $e = -0.8$) using equation II.30 or II.31 and

$$r_1 r_2 = \exp\{-(e_1 - e_2)^2\} \quad (32)$$

which derives from equations II.30 and II.31.

III Experimental

III.A Materials

III.A.1 Vinylferrocene

Initially, vinylferrocene was prepared from acetylferrocene via 1-hydroxyethylferrocene. For example, acetylferrocene (Koch-Light), 10 g, and sodium borohydride (BDH), 5.4 g, were dissolved in a 2:1 v/v dimethyl sulphoxide water mixture, 450 cm³, and the solution was stirred for 5 hr at 90°C. The cooled solution was extracted overnight with 60-80 petroleum ether, 150 cm³, in an upward displacement liquid/liquid extractor. The petroleum ether solution was cooled to room temperature, seeded, and then further cooled in an ice-bath. The amber, needle-shaped crystals of 1-hydroxyethylferrocene were filtered off, washed with ice-cold 60-80 petroleum ether and dried in vacuo at room temperature; yield 8.9 g (88%), mp 75.5-76.2°C (Lit. mp 73-75°C¹, 78-80°C⁵⁹). A further 0.8 g (7%) of crude product (mp 71.8-72.8°C) was obtained by evaporating the filtrate to dryness under reduced pressure. Recrystallization of this crude product from 60-80 petroleum ether yielded 0.5 g (4%) of 1-hydroxyethylferrocene (mp 75.6-76.4°C).

Pyrolysis of 1-hydroxyethylferrocene, on an alumina catalyst and under reduced pressure⁶⁰, gave a 50% yield of vinylferrocene, mp 50.5-51.1°C (Lit. mp 46.5-47.5°C⁹, 52-53.5°C⁶¹).

Vinylferrocene, prepared by the above method, supplied commercially (ROC/RIC) or recovered from previous polymerizations, was purified prior to use by recrystallization. A warm (50°C) methanolic solution (7% w/v) was repeatedly filtered through a double thickness of Whatman No. 42 filter paper until the filtrate was clear and no deposit was left on the filter paper. This solution was cooled first to room temperature and then to

-60°C. The solid was collected by filtering through a pre-cooled (solid carbon dioxide) Büchner funnel and washed with chilled methanol. The crystalline mass was dried at the pump while it attained room temperature. Final drying was carried out on a high vacuum line (Section III.B.1, Fig. III.2, outlet 9). After degassing to 10^{-6} mm Hg, the solid, at room temperature, was connected to a trap (T3) cooled by liquid nitrogen. After 24 hr, the solid mass was broken up with a magnetic follower, the trap was cleaned and the drying process repeated. This method gave high purity vinylferrocene, as indicated by the melting point, typically 53.4-54°C, and the absence of induction periods in subsequent polymerizations.

III.A.2 Styrene

The inhibitor present in the styrene (BDH) was removed by shaking three times with 10% w/v aqueous sodium hydroxide solution and three times with distilled water. The styrene was dried, by stirring over powdered calcium hydride overnight, before being fractionally distilled from calcium hydride under reduced pressure. The centre cut was retained and, if necessary, stored in the dark at -20°C for no more than 24 hr before being used.

III.A.3 Vinyl acetate

Vinyl acetate (BDH) was fractionally distilled and 2-2'-azobisisobutyronitrile (AIBN), 0.4 g, was added to the centre cut, 60 cm³. This was partially polymerized in a distillation apparatus by warming gently until the monomer distilled of its own accord. The centre cut was used immediately.

III.A.4 Solvents

Benzene (BDH, AR grade), dioxane (M & B, R grade), tetrahydrofuran (THF, Koch-Light, puriss) and cyclohexane

(Koch-Light, puriss) were stirred over calcium hydride overnight and fractionally distilled from calcium hydride. The centre cuts of the solvents required for free-radical polymerizations were stored in the dark prior to use. Solvents which were required for either Ziegler-Natta or anionic polymerizations were further dried either by stirring over 'living' polystyrene overnight or, where contamination by hexane from the anionic initiator required for this process was undesirable, by stirring over sodium/potassium alloy⁶². Both of these drying procedures were carried out on the high vacuum system and the solvents were used immediately.

n-Hexane (BDH) was dried over n-butyllithium solution on the high vacuum line.

Decahydronaphthalene (Koch-Light) was dried over molecular sieves (Linde, 4A) and purged with dried oxygen-free nitrogen before use.

III.A.5 Ferrocene

Ferrocene (BDH) was purified by sublimation under reduced pressure (0.5 mm Hg, 80°C), mp 175°C, as determined by DSC (Lit. mp 174°C²³).

III.A.6 Ethylferrocene

Ethylferrocene was prepared by catalytic reduction of acetylferrocene⁶³ (Koch-Light). After the chromatographic purification, thorough removal of solvent was ensured by evacuating the product on the high vacuum line until the ethylferrocene began to distil. The infrared spectrum of the purified product exhibited only absorptions due to ethylferrocene. Handling time for the ethylferrocene was kept to a minimum because of its relatively low oxidative stability.

III.A.7 Cyclohexanone

Cyclohexanone (R. N. Emanuel) was purified by the procedure adopted for solvents required for free-radical polymerizations.

III.A.8 2,2'-Azobisisobutyronitrile (AIBN)

2,2'-Azobisisobutyronitrile (R. N. Emanuel) was recrystallized three times from A.R. methanol, dried in vacuo at room temperature and stored in the dark at -20°C (mp $101.8-102.4$ with decomposition).

III.A.9 Manganese(III) acetylacetonate ($\text{Mn}(\text{acac})_3$)

Manganese(III) acetylacetonate (Koch-Light) was recrystallized by adding a benzene solution to n-heptane⁶⁴ and dried in vacuo at room temperature (decomposes at ca. 169°C , by DSC).

III.A.10 n-Butyllithium (n-BuLi)

n-Butyllithium (Koch-Light) was used as supplied (15% n-hexane solution) and at lower concentration, thoroughly dried n-hexane being used as the diluent. The Gilman double titration method⁶⁵ gave the concentrations of active butyllithium as 1.2 mol dm^{-3} and $4.11 \times 10^{-2} \text{ mol dm}^{-3}$.

III.A.11 Cumylpotassium

Cumylpotassium (Orgmet. Inc.) was supplied as a suspension in heptane in the presence of potassium metal. A heptane-free THF solution was prepared, the potassium metal being removed by filtration. The concentration of 'active' cumylpotassium was determined by reacting the solution with butyl bromide, and titrating the potassium bromide liberated with aqueous silver nitrate solution (Section III.B.3). This method gave the concentration as $9.95 \times 10^{-2} \text{ mol dm}^{-3}$. The solution was stored at -20°C for the short period between its preparation and use,

because cumylpotassium reacts slowly with THF.

III.A.12 Titanium(IV) chloride (TiCl_4) and
 Vanadium(V) oxotrichloride (VOCl_3)

Titanium(IV) chloride and vanadium(V) oxotrichloride were diluted, under dried, oxygen-free nitrogen (OFN), by sodium-dried A.R. benzene to give solutions of concentration $0.898 \text{ mol dm}^{-3}$ and $0.883 \text{ mol dm}^{-3}$, respectively. These solutions were stored under OFN in a flask fitted with a spring-loaded stopcock (Fig. III.1.a).

III.A.13 Titanium(III) chloride (TiCl_3) and
 Vanadium(III) chloride (VCl_3)

Titanium(III) chloride (Stauffer AA, $\delta\text{-TiCl}_3 \cdot 1/3\text{AlCl}_3$, ball-milled) and vanadium(III) chloride (ball-milled) were supplied in the form of benzene suspensions, which were stored under OFN in flasks fitted with a spring-loaded stopcock and a stirrer (Fig. III.1.b). The concentration of the TiCl_3 slurry was determined, by titration with cerium(IV) sulphate solution, to be $0.406 \text{ mol dm}^{-3}$ (Section III.B.4). Redox titration of the VCl_3 slurry with potassium permanganate solution gave the concentration as $0.448 \text{ mol dm}^{-3}$ (Section III.B.5).

III.A.14 Triethyl aluminium (AlEt_3) and
 diethyl aluminium chloride (AlEt_2Cl)

Triethyl aluminium and diethyl aluminium chloride were supplied as benzene solutions under OFN (Fig. III.1.a). The 'active' concentrations of these solutions were determined, by ethane liberation, to be $0.938 \text{ mol dm}^{-3}$ and 1.36 mol dm^{-3} , respectively (Section III.B.6).

TiCl_3 , TiCl_4 , VCl_3 , VOCl_3 , AlEt_3 and AlEt_2Cl were kindly supplied by I.C.I. Ltd., Plastics Division, Welwyn Garden City.

III.B Techniques

III.B.1 The high vacuum/inert gas system

This system, depicted in fig.III.2, combined a conventional high vacuum line with a buffered inert gas (dried, oxygen-free nitrogen, OFN) supply. The high vacuum pumping section of the line was capable of evacuating to 10^{-6} mm Hg in a short time, ca. 15 minutes. OFN, dried by a concentrated sulphuric acid (D1)/sodium hydroxide (D2) train, could be delivered at pressures ranging from several cm of mercury to several cm of liquid paraffin, pressure regulation in the latter case being provided by a liquid paraffin bubbler (D3). This OFN supply system, working in conjunction with a rotary vacuum pump, provided an evacuation-OFN purge facility. Silicone H.V. grease was used in sections of the line involved with solvent and monomer transfer and purification (9,16-21,28,29). Normal hydrocarbon based H.V. grease was used throughout the remainder of the high vacuum system. PTFE stopcocks (22-27) were used in the OFN supply system, primarily because their design was compatible with the range of pressures used and permitted easy control of low gas flow rates.

III.B.2 Techniques for handling air-sensitive compounds

All actions involving the anionic initiators, n-butyllithium and cumylpotassium; the Ziegler-Natta catalysts and components, titanium(III) chloride, titanium(IV) chloride, vanadium(III) chloride, vanadium(V) oxotrichloride, triethyl aluminium and diethyl aluminium chloride; and polymerization systems generated by these compounds were carried out under OFN. The pressure in vessels containing these compounds and systems was kept at a level slightly above atmospheric pressure, and thus wherever possible spring-loaded stopcocks were used and all joints were

restrained by elastic retainers. Silicone grease was used on these stopcocks and joints because it is slightly more resistant to stripping by solvent vapours than hydrocarbon-based greases. The problem of stripping was further reduced by using vessels designed to prevent any stripped grease from reaching the contents of the vessel (Fig.III.3.a). Vessels of this pattern were used for storing anionic initiator solutions, monomer solutions and purified solvents for Ziegler-Natta and anionic polymerizations.

Large scale transfer of liquids under OFN was carried out via stainless steel tubing (bore ca. 1 mm) by applying the minimum pressure differential across the tubing for sustained liquid flow.

Transfer of accurately known volumes of liquids and slurries under OFN required the careful use of syringes. A syringe was flushed with OFN and primed with the appropriate purged solvent. The priming served to wet the barrel-plunger joint, thus providing a seal, excess solvent being thoroughly expelled by repeatedly flushing with OFN. In the cases of n-butyllithium, cumylpotassium and the alkyl aluminium solutions, the syringe was purged twice with the solution prior to the final flushing with OFN. The syringe was filled by slowly withdrawing the plunger until the mark on the lower tip of the barrel coincided with the required volume graduation. Then, OFN was drawn into the syringe, thus emptying the contents of the needle into the syringe and preventing loss of liquid during the transfer. Maximum discharge of the liquid or slurry was ensured by flushing the syringe with OFN into the receiving vessel.

The slurries required special techniques to maximise the uniformity of concentration over many withdrawals. The design

of the storage vessels (Fig.III.1.b) was such that a reasonably uniform suspension was created at moderate stirring speeds. Withdrawal of the slurry from a constant depth also increased the uniformity of the samples. In addition, it was necessary to agitate the syringe during the entire transfer procedure to prevent settling of the solid in the syringe barrel.

III.B.3 Cumylpotassium analysis

Butyl bromide was purified by stirring over calcium hydride overnight and fractionally distilling, under reduced pressure, from calcium hydride. 1 cm^3 of the centre cut was transferred to a two-necked flask (100 cm^3), which then was connected to the OFN supply, the other neck being sealed by a rubber septum. The butyl bromide was degassed by three alternate evacuation-OFN purge cycles and an accurately measured volume of cumylpotassium solution, 1 cm^3 , was added via a syringe, under OFN. The fine precipitate of potassium bromide, which formed on the immediate discharge of the red colour of cumylpotassium, was dissolved in distilled water, 5 cm^3 , and titrated with standardized aqueous silver nitrate solution, with fluorescein as indicator. This method was found to have a zero blank. The concentration of the cumylpotassium solution, C_K , was given by

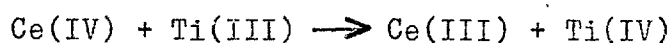
$$C_K = \frac{C_A V_A}{V_K} \quad (1)$$

where V_K was the volume of cumylpotassium solution used and C_A and V_A were the concentration and titration volume of the silver nitrate solution, respectively.

III.B.4 Titanium(III) chloride analysis

Sulphuric acid (1 mol dm^{-3}), 100 cm^3 , was purged out by adding a piece of solid carbon dioxide. An accurately measured volume, 5 cm^3 , of the titanium(III) chloride slurry was

syringed, under OFN, into the sulphuric acid. The syringe was washed three times with purged acetone, the washings being added to the sulphuric acid solution. This solution was titrated with a standardized aqueous cerium(IV) sulphate solution (0.2 mol dm^{-3}), using a 2% w/v solution of diphenylamine in concentrated sulphuric acid as indicator. The purple colour of the solution faded to milky-white just prior to the persistent bright blue endpoint. This titration, which had a zero blank, may be summarized as



Thus, the concentration of the titanium(III) chloride slurry, C_T , was given by

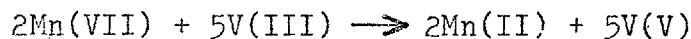
$$C_T = \frac{C_C V_C}{V_T} \quad (2)$$

where V_T was the volume of the titanium(III) chloride used and C_C and V_C were the concentration and titration volume of the cerium(IV) sulphate solution, respectively.

III.B.5 Vanadium(III) chloride analysis

Sulphuric acid (1 mol dm^{-3}), 100 cm^3 , was purged by adding a piece of solid carbon dioxide. An accurately measured volume, 5 cm^3 , of the vanadium(III) chloride slurry was syringed, under OFN, into the sulphuric acid. The syringe was washed three times with purged acetone, the washings being added to the sulphuric acid. This solution was titrated with a standardized aqueous solution of potassium permanganate (0.1 mol dm^{-3}). The purple slurry gave a blue solution in the acid, this colour changing to very pale yellow as the titration was carried out. At this point the solution was heated to 60°C before the titration was continued to the first persistent pink endpoint. This titration, which had a significant blank arising from the oxidation of acetone by potassium permanganate,

may be summarized as



The concentration of the vanadium(III) chloride slurry, C_V , was given, therefore, by

$$C_V = \frac{2C_P V_P}{5V_V} \quad (3)$$

where V_V was the volume of the vanadium(III) chloride slurry used and C_P and V_P were the concentration and titration volume of the potassium permanganate solution, respectively.

III.B.6 Analysis of triethyl aluminium and diethyl aluminium chloride

Sulphuric acid (3 mol dm^{-3}), 20 cm^3 , and benzene, 1 cm^3 , were stirred in a flask (100 cm^3 , long-neck) connected, by gas-tight joints, to a gas burette (Fig. III.3.b). Alkyl aluminium solution, ca. 1 cm^3 , was added in order to saturate the apparatus with ethane. The gas burette was levelled, when the apparatus had returned to ambient temperature. An accurately measured volume, 1 cm^3 , of alkyl aluminium solution was syringed slowly, with stirring, into the acid. As ethane was liberated, the pressure in the apparatus was held close to atmospheric pressure by adjusting the gas burette. After complete addition of the alkyl aluminium solution, the apparatus was allowed to equilibrate to room temperature before the gas burette was levelled. The volume of ethane evolved, room temperature and atmospheric pressure were recorded. Three further additions of alkyl aluminium solution were carried out. The number of moles of ethane produced by 1 dm^3 of alkyl aluminium solution at STP, and thus the concentration of the solution with respect to alkyl groups, C_R , was given by

$$C_R = \frac{V_A V_E 273 \cdot 3 P}{76 T \times 1000} \quad (4)$$

where V_E was the total volume of ethane produced (cm^3), at a temperature T (K) and pressure P (cm Hg), by the total volume of alkyl aluminium solution added, V_A (cm^3). The 'active' alkyl aluminium concentration was, therefore, $C_R/3$ for the triethyl aluminium solution and $C_R/2$ for the diethyl aluminium chloride solution.

III.B.7 Polymer isolation and purification

In general, polymers were isolated and purified by a standard method. The concentration of the polymer solution was adjusted with A.R. toluene to be approximately in the appropriate concentration range for its predicted molecular weight; 4% for M.W. less than 75,000, ca. 2% for M.W. 75,000-500,000 and 0.8% for M.W. greater than 500,000. These values were found to be necessary to obtain polymer of a tractable physical form on precipitation. The diluted polymer solution was passed slowly through a No. 2 glass sinter into a stirred ten-fold excess of methylated spirits. The precipitated polymer was allowed to settle, collected on a No. 4 glass sinter, washed with methylated spirits and dried to constant weight in vacuo at room temperature. These polymers were purified by reprecipitation from A.R. toluene into methylated spirits, following the scheme used for their isolation.

III.B.8 Anionic homopolymerization of vinylferrocene

III.B.8.a n-Butyllithium initiated in cyclohexane solution

Vinylferrocene, 4 g, was degassed to 10^{-3} mm Hg in a two-necked flask, one neck of which was sealed by a rubber septum. Purified cyclohexane, 21 cm^3 , was distilled, under vacuum, onto the vinylferrocene and the vacuum was broken with OFN. The solution was heated, with stirring, to 60°C and n-butyllithium

solution (1.2 mol dm^{-3}), 0.85 cm^3 , was added via a syringe. This solution was stirred for 2 hr at 60°C and then A.R. methanol, 0.5 cm^3 , was added to terminate any activity. Polymer precipitated as the solution cooled and it was necessary to add A.R. toluene, 25 cm^3 , and warm the solution to redissolve this polymer. The polymer was isolated and purified by the standard method (Section III.B.7).

III.B.8.b n-Butyllithium and cumylpotassium initiated in THF

Vinylferrocene, 4 g, was purged, in a storage vessel (Fig. III.3.a), by three evacuation-OFN purge cycles. Purified THF, 37 cm^3 , was syringed onto the vinylferrocene to give a stock solution. A flask, 25 cm^3 , sealed with a rubber septum and equipped with a magnetic follower, was purged, via a side-arm, by three evacuation-OFN purge cycles. Vinylferrocene solution, 5 cm^3 , was syringed into the flask, which then was placed in a bath at the required temperature. After equilibration, anionic initiator solution (n-butyllithium, $4.11 \times 10^{-2} \text{ mol dm}^{-3}$; cumylpotassium, $9.95 \times 10^{-2} \text{ mol dm}^{-3}$), 1 cm^3 , was added and the solution was stirred for 1 hr at the desired polymerization temperature. Any activity was terminated then by pouring the solution, under OFN, onto a rapidly stirred slurry of finely powdered solid carbon dioxide in THF, 5 cm^3 . Any polymer formed was isolated by the standard method (Section III.B.7).

III.B.8.c n-Butyllithium initiated in decahydronaphthalene

The technique described above (Section III.B.8.b) was employed, but in this case the decahydronaphthalene, 4.5 cm^3 , solutions of vinylferrocene, 0.5 g, were prepared in situ.

III.B.9 Anionic random copolymerization of vinylferrocene and styrene

A styrene, 1 g, solution of vinylferrocene, 2 g, was

purged, by three evacuation-OFN purge cycles, in a flask sealed with a rubber septum and equipped with a magnetic follower. Purified cyclohexane was added to give ca. 25 cm^3 of solution. Polymerization was initiated by n-butyllithium solution (1.33 mol dm^{-3}), 0.2 cm^3 , and the solution was stirred at 60°C for 3 hr. Methanol, 0.5 cm^3 , was added to terminate any activity and the polymer was isolated and purified by the standard method (Section III.B.7).

III.B.10 Homopolymerization of vinylferrocene by
 Ziegler-Natta catalysts

These polymerizations were carried out in a vessel of the type shown in fig. III.1.a. The flask was equipped with a magnetic follower and purged by three evacuation-OFN purge cycles. Alkyl aluminium solution, 1 cm^3 , was syringed into the flask and transition metal chloride (0.5 cm^3 of slurry or 0.2 cm^3 of solution) was added. This catalyst was aged by stirring at 60°C for 30 minutes. A benzene solution of vinylferrocene (2.13 mol dm^{-3} solution prepared as in section III.B.8.b), 2.5 cm^3 , was added and the mixture stirred for a further 1 hr. Then the catalyst was deactivated by pouring the mixture directly into a stirred ten-fold excess of methylated spirits and the precipitated polymer was isolated by the standard method (Section III.B.7). Vinylferrocene was polymerized also by TiCl_3 using this method, but omitting the alkyl aluminium and catalyst ageing step.

The polymers obtained from the $\text{TiCl}_3/\text{AlEt}_3$, $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$ and TiCl_3 systems were purified, the standard procedure (Section III.B.7) being adopted for the powdery polymer produced by the $\text{TiCl}_3/\text{AlEt}_3$ system. However, both the $\text{TiCl}_3/\text{AlEt}_2\text{Cl}$ and the TiCl_3 systems yielded, primarily, a gum when the reaction mixture was poured into the methylated spirits. This material was purified,

therefore, by dissolving in THF, filtering the solution and evaporating it to dryness under reduced pressure, with a final drying of the polymer in vacuo at room temperature.

III.B.11 Homopolymerization of styrene and copolymerization of styrene and vinylferrocene with $\text{TiCl}_3/\text{AlEt}_3$ as catalyst

A benzene solution of styrene (1.98 mol dm^{-3} , prepared as in section III.B.8.b) was polymerized by $\text{TiCl}_3/\text{AlEt}_3$ using the method given in the previous section (III.B.10). The isotactic polystyrene was purified by reprecipitation from warm chlorobenzene solution into methylated spirits, using the standard procedure (Section III.B.7).

A solution of vinylferrocene, 1.04 g, in styrene/benzene (1.98 mol dm^{-3}), 2.5 cm^3 , was prepared by the method described in section III.B.8.b and polymerized by the procedure given in the previous section (III.B.10). The polymer obtained was treated repeatedly with A.R. toluene until no further polymer was extracted. The polymer from this solution was isolated by the standard method. The remaining polymer was reprecipitated from warm chlorobenzene solution into methylated spirits by the standard procedure (Section III.B.7).

III.B.12 Free-radical homopolymerizations

Free-radical homopolymerizations were studied by dilatometry and the mean rates of polymerization were obtained by gravimetric determinations. These polymerizations were taken to no more than 10% conversion.

The monomer feed, which was prepared by weight, was thoroughly mixed before being introduced, via a finely drawn funnel, into a dilatometer-filler or polymerization vessel. The latter was a round-bottomed flask (50 cm^3) with a capillary

(9 mm o.d., 3 mm i.d.) neck, which facilitated the sealing off from the high vacuum line. Round-bottomed flasks were preferred to tubes, because the former were not subject to breakage by the thermal expansion of their frozen contents. Dilatometer-fillers were polymerization vessels equipped with a capillary side-arm leading to a calibrated dilatometer. The dilatometers used comprised a length (ca. 15 cm) of precision-bore capillary (0.2 mm i.d.) joined to a cylindrical bulb. The capacity of the bulb used was chosen according to the monomer concentration of the solution to be polymerized and the expected rate of polymerization. The former parameter fixed the amount of monomer present in the dilatometer, and hence the total drop in meniscus height, whilst the latter parameter governed the rate of drop of the meniscus.

The contents of the dilatometer-filler or polymerization vessel were degassed to 10^{-6} mm Hg, by three alternate freeze-thaw cycles, on the high vacuum line. The vessel was sealed off from the line and, in the case of the dilatometer-filler, the solution was transferred to the dilatometer, which then was sealed off from the filler. All polymerization vessels were screened with aluminium foil to prevent photopolymerization.

The polymerizations were carried out in a water bath thermostatted ($\pm 0.02^{\circ}\text{C}$) at the required temperature, and were timed from the moment of immersion of the vessel in the bath. Care was taken to mount the dilatometers vertically and meniscus heights were read, at timed intervals, with a cathetometer fitted with a vernier scale (resolution ± 0.001 cm).

The conclusion of the polymerization was taken to be the time at which the vessel was removed from the bath and cooled to ambient temperature. The vessel was opened, weighed, emptied,

washed (the washings being combined with the polymer solution), dried and reweighed. Dilatometers were emptied by inverting the dilatometer and removing the contents with nitrogen, which was introduced via a stainless steel tube. The dilatometer was washed by forcing A.R. toluene or dioxane, where this was used as solvent in the polymerization, up the stainless steel tube.

Styrene polymers were isolated and purified by the standard method (Section III.B.7). Vinylferrocene polymer were isolated and purified by the standard procedure but with THF as solvent.

The drop in meniscus height in the capillary, radius r , arises from the difference between the density of the monomer, D_m , and the polymer D_p . Thus, for a volume of monomer V_m the change in volume on complete polymerization, ΔV , is given by

$$\Delta V = V_m - (V_m D_m / D_p) \quad (5)$$

For a change in meniscus height from l_0 cm at zero time to l_1 cm after a time t seconds, the change in volume of the solution, Δv is

$$\Delta v = \pi r^2 (l_0 - l_1) \quad (6)$$

Thus,

$$\% \text{polymerization } s^{-1} = \frac{100 \pi r^2 (l_0 - l_1)}{t \{V_m - (V_m D_m / D_p)\}} \quad (7)$$

Gravimetric studies also yield an expression of this type, since

$$\% \text{polymerization } s^{-1} = \frac{100 W_p}{t W_m} \quad (8)$$

where W_p is the weight of polymer formed from W_m g of monomer in t seconds.

The rate of polymerization, R_p , of a monomer of molecular weight MW may be obtained from

$$R_p = \frac{1000 D_m (\% \text{polymerization } s^{-1})}{MW} \text{ mol dm}^{-3} s^{-1} \quad (9)$$

For studies of styrene polymerizations in the dilatometers

described in this section, and using density values of 0.8712 g cm^{-3} and 1.0563 g cm^{-3} for monomer⁶⁶ and polymer⁶⁷ respectively, equation III.7 reduces to

$$\% \text{polymerization s}^{-1} = \frac{17.93}{V_m} \left(\frac{dl}{dt} \right) \quad (10)$$

where (dl/dt) is the rate of fall of meniscus height in cm s^{-1} .

For these studies, equation III.9 therefore becomes

$$R_p = 8.369(\% \text{polymerization s}^{-1}) \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1} \quad (11)$$

III.B.13 Free-radical copolymerizations

Free-radical copolymerizations were carried out in polymerization vessels as described in section III.B.12, and were taken to no more than 10% conversion. 60-80 petroleum ether was used as precipitant in the isolation and purification steps in the vinylferrocene-vinyl acetate copolymerization.

III.B.14 Recovery of unreacted vinylferrocene after polymerizations

Any solution containing an appreciable amount of unreacted vinylferrocene was evaporated to dryness, under reduced pressure, on a rotary evaporator. In order to minimise the amount of vinylferrocene carried over in this procedure, the solution was kept at ambient temperature and the condenser of the evaporator at ca. -5°C . Vinylferrocene recovered by this method was purified before use (Section III.A.1).

III.B.15 Viscometry and molecular weight determination by this method

Polymer limiting viscosity numbers in A.R. toluene were determined using a suspended level dilution viscometer of a modified Ubbelohde pattern (details of Ubbelohde viscometers and a comprehensive treatment of viscometry are given elsewhere⁶⁸). The modification involved the introduction of a short fourth arm (A in fig. III.4.b) close to the opening of

the main inlet arm of the viscometer. It was then possible to fit a filter tube in the main inlet arm of the viscometer and keep it in place throughout the entire determination. This permitted the filtration of measured volumes of solvents and solutions directly into the viscometer, thereby reducing the possibility of dust particles being introduced into the viscometer.

The filter tube and the viscometer were thoroughly cleaned with chromic acid (24 hr), distilled water, A.R. acetone and, finally, A.R. toluene. All solutions and solvents were introduced into the viscometer via the filter tube. The viscometer was connected to the pumping system (Fig. III.4.a) via dust-free flexible tubing and immersed in a constant temperature bath at 30°C ($\pm 0.02^\circ\text{C}$).

A.R. toluene was introduced into the filter tube and forced through the sinter and capillary tube, T (Fig. III.4.b), by nitrogen, using the attachment shown in fig. III.4.c. This attachment was replaced by a screw cap, K, and the solvent was allowed to equilibrate in the viscometer. Tap 3 of the pumping system (Fig. III.4.a) was closed and the three-way tap 2 set to allow only the viscometer access to the atmosphere. Three-way tap 1 was set to connect the rubber bellows, R, with the viscometer and pressure was applied until the liquid level in the capillary arm, C, had entered the second bulb, whereupon the pressure in the viscometer was returned to atmospheric pressure by setting tap 1 to allow only the viscometer access to the atmosphere. The suspended level was obtained immediately by opening tap 3 and the solvent flow time was obtained in the normal manner⁶⁸. This was repeated until three consecutive readings agreed to within 0.1 second. The filter tube was removed, placed in a dust-free tube while the viscometer was

emptied, and then replaced. The entire apparatus was dried by warming with a hot air blower and flushing with nitrogen, via the filter tube.

Polymer solution (generally ca. 1% w/v), 4 cm³, was pipetted into the filter tube and introduced into the viscometer as before. The flow time was obtained by the method described for the solvent. A.R. toluene, 1 cm³, was pipetted into the filter tube and thoroughly discharged into the viscometer. Complete mixing of the solution was ensured by pumping it up the capillary arm several times and passing air from the bellows, via taps 2 and 3, through the solution. The flow time of this solution was determined. Further dilutions (1 cm³, 2 cm³ and 4 cm³) were carried out and flow times were determined for the solutions obtained. The viscometer and filter tube were thoroughly washed with A.R. toluene and dried as before.

Relative, η_r , and specific, η_{sp} , viscosities were calculated from

$$\eta_r = t/t_o \quad (12)$$

and

$$\eta_{sp} = \eta_r - 1 \quad (13)$$

where t_o and t were the flow times for solvent and solution respectively. The limiting viscosity number, $[\eta]$, of the polymer in toluene at 30°C was obtained from the standard double plot of η_{sp}/C and $(\ln \eta_r)/C$ against C , where C was the polymer concentration in g (100 cm³)⁻¹. This plot arose from the relationships⁶⁸

$$\eta_{sp}/C = [\eta] + k_1[\eta]^2C \quad (14)$$

and

$$(\ln \eta_r)/C = [\eta] - k_2[\eta]^2C \quad (15)$$

It therefore gave the limiting viscosity number as the common intercept (Fig. III.5), which was determined by least mean squares

analyses of the data.

For a polydisperse polymer, the viscometric average molecular weight, $\bar{M}_v$, may be calculated from the limiting viscosity number using the Mark-Houwink relationship

$$[\eta] = K\bar{M}_v^a \quad (16)$$

where K and a are constants. Literature values of K and a are available for a wide range of polymers, solvents and temperatures. For polystyrene in toluene at 30°C, this relationship becomes

$$\log_{10} \bar{M}_v = (3.873 + \log_{10} [\eta]) / 0.71 \quad (17)$$

when the appropriate literature values for K and a are inserted⁶⁹.

Number average molecular weights, $\bar{M}_n$, were calculated from the viscometric average molecular weights by the method described by Henrici-Olivé, Olivé and Schulz⁷⁰. This method is based on the relationship between an experimentally determinable parameter Q and the degree of polymerization of the polymer, $\overline{DP}$, the link between the two being provided by the weight fraction of molecules of polymer terminated by a mechanism other than polymer radical combination, y, and the non-uniformity of the polymer, U. Q is defined by

$$Q = \frac{\overline{DP}_n \bar{R}_p k_{tc}}{[\bar{M}]^2 (2 + b) k_p^2} \quad (18)$$

where

$$b = (1 + a)/2 \quad (19)$$

and, for styrene,

$$\overline{DP}_n = \bar{M}_v / 104.1 \quad (20)$$

$\bar{R}_p$ is the mean rate of polymerization of the monomer, M, and k_p and k_{tc} are the velocity constants for propagation and termination by combination of polymer radicals respectively. For polystyrene prepared at 60°C, a literature value⁷¹ of (k_{tc}/k_p^2) of 861 mol s dm⁻³ was used. The non-uniformity of the polymer, U,

is defined by

$$U = (\overline{DP}_w / \overline{DP}) - 1 \quad (21)$$

where $\overline{DP}_w$ is the weight average degree of polymerization. Q is related to y by

$$Q = \frac{(1 - y)(2 + b + 2by - by^2)}{(1 + y)(2 + b)} \quad (22)$$

and U is related to y by

$$U = 0.5 + y(1 - 0.5y) \quad (23)$$

Finally, for the polymers under consideration,

$$\overline{DP} = \overline{DP}_n / (1 + bU) \quad (24)$$

A table of values of bU for given values of Q was constructed (Table III.1) and this facilitated a rapid calculation of $\overline{M}_n$ from $\overline{M}_v$, since for polystyrene

$$\overline{M}_n = 104 \cdot \overline{DP} \quad (25)$$

III.B.16 Molecular weight determinations by membrane osmometry

The osmotic pressure, π , of polymer solutions in A.R. toluene ($3-10 \text{ g dm}^{-3}$) were measured on a Melabs CSM-2 recording osmometer fitted with a Sartorius membrane (11539) and operating at 37°C . The signals generated by low osmotic pressures were amplified by using increased recorder sensitivity.

Initially, the standard plot⁷² of (π/C) against C was constructed, C being the polymer concentration (g dm^{-3}). Where straight lines were obtained, the intercept, $(\pi/C)_{C=0}$, was calculated by least mean squares analysis of the data. The number average molecular weight, $\overline{M}_n$, of the polymer was calculated from

$$\left(\frac{\pi}{C}\right)_{C=0} = \frac{RT}{\overline{M}_n} \quad (26)$$

the value of RT being 3.04×10^4 for toluene at 37°C .

However, the plots for high molecular weight polymers exhibited pronounced curvature. This arose because of an approximation made in the derivation of the plots, which were

based on the relationship¹⁶

$$\frac{\pi}{C} = \left(\frac{\pi}{C} \right)_{C=0} (1 + \Gamma_2 C + 8\Gamma_2^2 C^2) \quad (27)$$

The approximation made was that the term in C^2 was negligible, and this is not applicable at high molecular weights. An alternative approximation¹⁶, that $g = 0.25$, was applied to give

$$\frac{\pi}{C} = \left(\frac{\pi}{C} \right)_{C=0} (1 + \Gamma_2 C + \frac{\Gamma_2^2}{4} C^2) \quad (28)$$

or

$$\frac{\pi}{C} = \left(\frac{\pi}{C} \right)_{C=0} (1 + \frac{\Gamma_2^2}{2} C)^2 \quad (29)$$

and hence

$$\left(\frac{\pi}{C} \right)^{\frac{1}{2}} = \left(\frac{\pi}{C} \right)_{C=0}^{\frac{1}{2}} (1 + \frac{\Gamma_2^2}{2} C) \quad (30)$$

Thus, plots of $(\pi/C)^{\frac{1}{2}}$ against C were constructed for data which gave curved plots of π/C against C . The intercept, $(\pi/C)^{\frac{1}{2}}_{C=0}$, was determined by the least mean squares analysis, and the number average molecular weight was calculated from equation III.26, as before.

III.B.17 Gel Permeation Chromatographic (GPC) analysis of polymers

GPC analysis of polymers was carried out by the Polymer Supply and Characterization Centre of the Rubber And Plastic Research Association, G.B. The author is grateful for the assistance received from this body.

III.B.18 Thermal analysis of polymers

Thermal analysis of polymers was carried out on a Dupont 990 thermal analyser operating in the DSC and DTA modes, the cell being continually flushed by a low flow of oxygen-free nitrogen.

In the case of vinylferrocene homopolymers; eight heating rates between 2 and 50 °C min⁻¹ were used. The transition temperatures at zero heating rate were estimated from a plot of log₁₀(transition temperature) against heating rate⁷³ (for example,

fig. III.8), the intercepts being calculated by least mean squares analysis of the data.

An important polymer transition temperature is the glass transition temperature, T_g , below which there is no segmental motion and the polymer is said to be in its glass state. Above T_g , the polymer exists in its rubbery state, in which segmental motion takes place. The presence of segmental motion causes an increase in the heat capacity of the polymer, and thus the T_g of the polymer is characterized by an endothermic dip in the trace from the thermal analyser. The T_g of a polymer is an important physical property and many detailed accounts of this phenomenon and its detection are available⁷⁴.

III.B.19 Ultraviolet and visible spectroscopy

Ultraviolet and visible spectra were obtained on a Perkin-Elmer 137 UV spectrophotometer, and were calibrated with absorptions given by a holmium oxide glass sample.

III.B.20 Infrared spectroscopy

Infrared spectra were run on a Perkin-Elmer 157G spectrometer, and were calibrated with polystyrene absorptions. The spectra were obtained for solutions (spectroscopic grade carbon tetrachloride and carbon disulphide), mulls (spectroscopic grade nujol and hexachlorobutadiene), and, in the case of polymers, films. Films were cast from an appropriate solvent, allowed to dry under ambient conditions, and then evacuated in a vacuum oven at 60°C, to remove the final traces of solvent.

III.B.21 Nuclear magnetic resonance (nmr) spectroscopy

Thanks are due to Dr. M. Kinns and Mr. S. J. Roberts for running ^1H nmr spectra, either at 100 MHz on a Varian HA 100 spectrometer or at 60 MHz on a Varian A 60 spectrometer, and to Mr. R. B. Jones and Mr. M. Pendlebury for running ^{13}C nmr spectra

on a Varian XL 100 spectrometer, operating at 25.16 MHz.

III.B.22 Electron spin resonance (esr) spectroscopy

X-band esr spectroscopy was carried out on a Varian E-9 spectrometer.

III.B.23 Mössbauer spectroscopy

A Mössbauer spectrum of polyvinylferrocene, prepared by free-radical polymerization in dioxane solution, was obtained by Mr. A. Ghosh and Mr. I. E. G. Morrison using an Inter technique SA40B multichannel analyser with an Elron MDA-13S digital to analogue converter and an Elron MDI Mössbauer drive amplifier. Their assistance is gratefully acknowledged.

Table III.1

Values of Q and bU for polystyrene in toluene at 30°C

Q	bU	Q	bU
0	0.855	0.55	0.6819
0.05	0.8525	0.60	0.6564
0.10	0.8461	0.65	0.6300
0.15	0.8364	0.70	0.6027
0.20	0.8237	0.75	0.5750
0.25	0.8086	0.80	0.5464
0.30	0.7914	0.85	0.5171
0.35	0.7723	0.90	0.4878
0.40	0.7516	0.95	0.4578
0.45	0.7296	1.00	0.4275
0.50	0.7062		

Values of bU for intermediate values of Q can be obtained by interpolation.

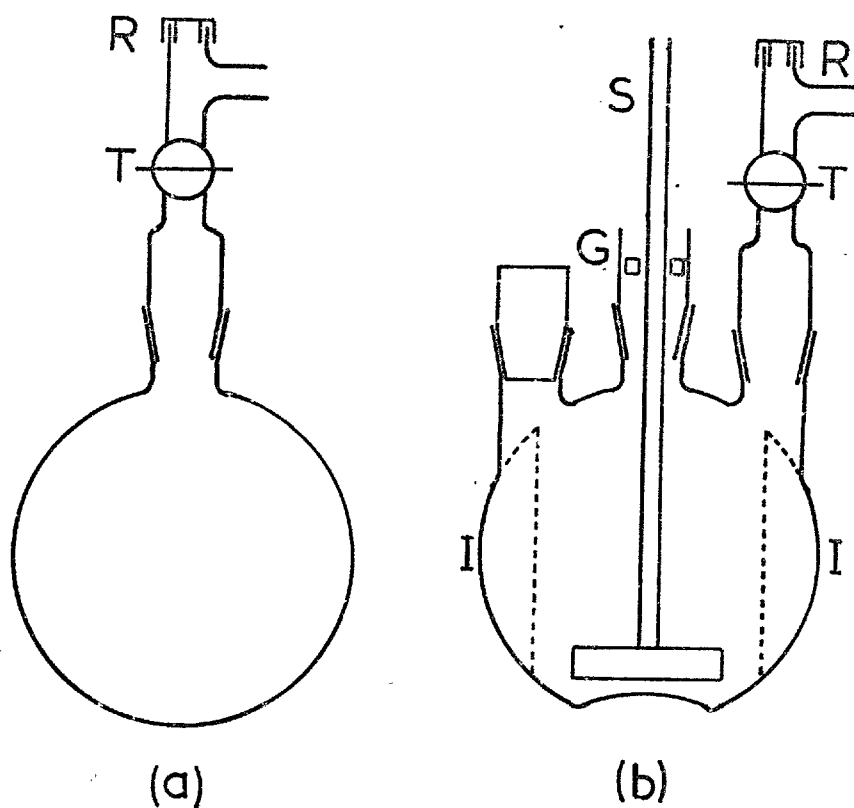


Fig. III.1

Ziegler-Natta catalyst component storage vessels, (a) for solutions (b) for slurries.

Key

- G Stirrer gland, sealed and lubricated with liquid paraffin.
- I Indentations, four of these largely prevented the formation of a vortex on stirring.
- R Rubber septum.
- S Stirrer.
- T Spring-loaded stopcock.

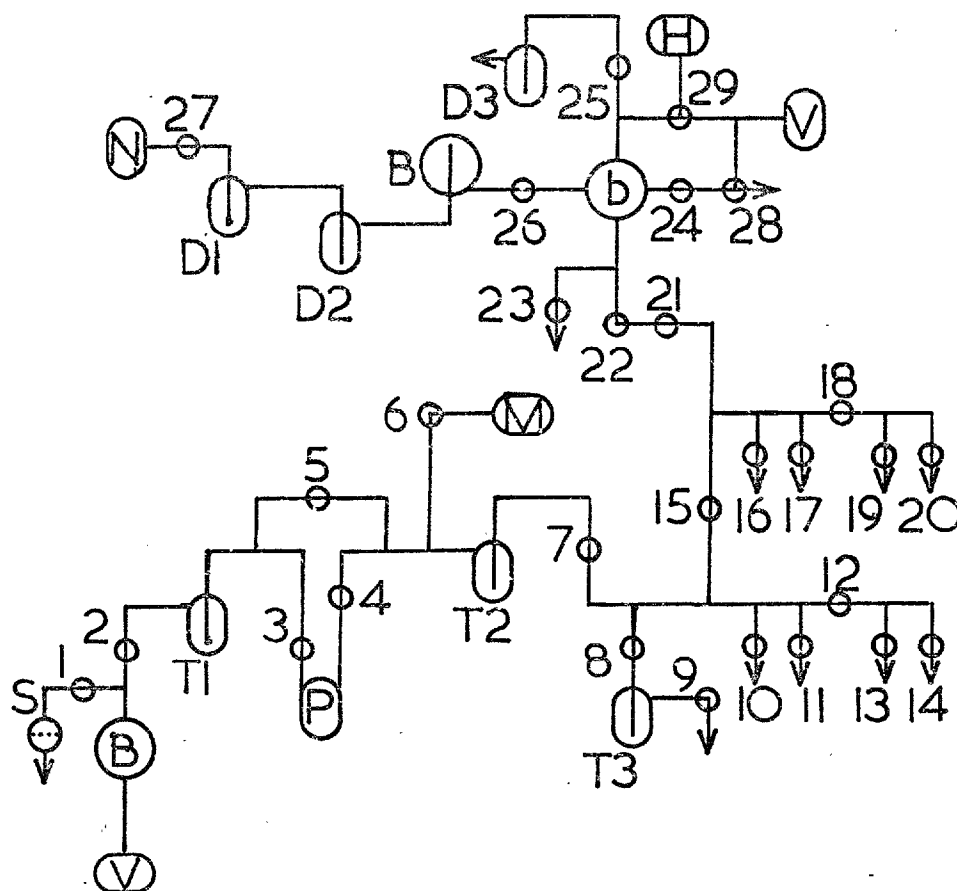


Fig. III.2

High vacuum-OFN supply line.

Key

- b 500 cm³ buffer volume.
- B 5 dm³ bulbs, providing a buffer volume.
- D Dreschel bottle.
- H Mercury manometer (1 mm-100cm Hg).
- M McLeod gauge (10⁻²-10⁻⁶ mm Hg).
- N Oxygen-free nitrogen supply.
- P Mercury diffusion pump.
- S Gas filter (No. 2 sinter).
- T Cold trap.
- V 2-stage rotary vacuum pumps protected by non-return valves.

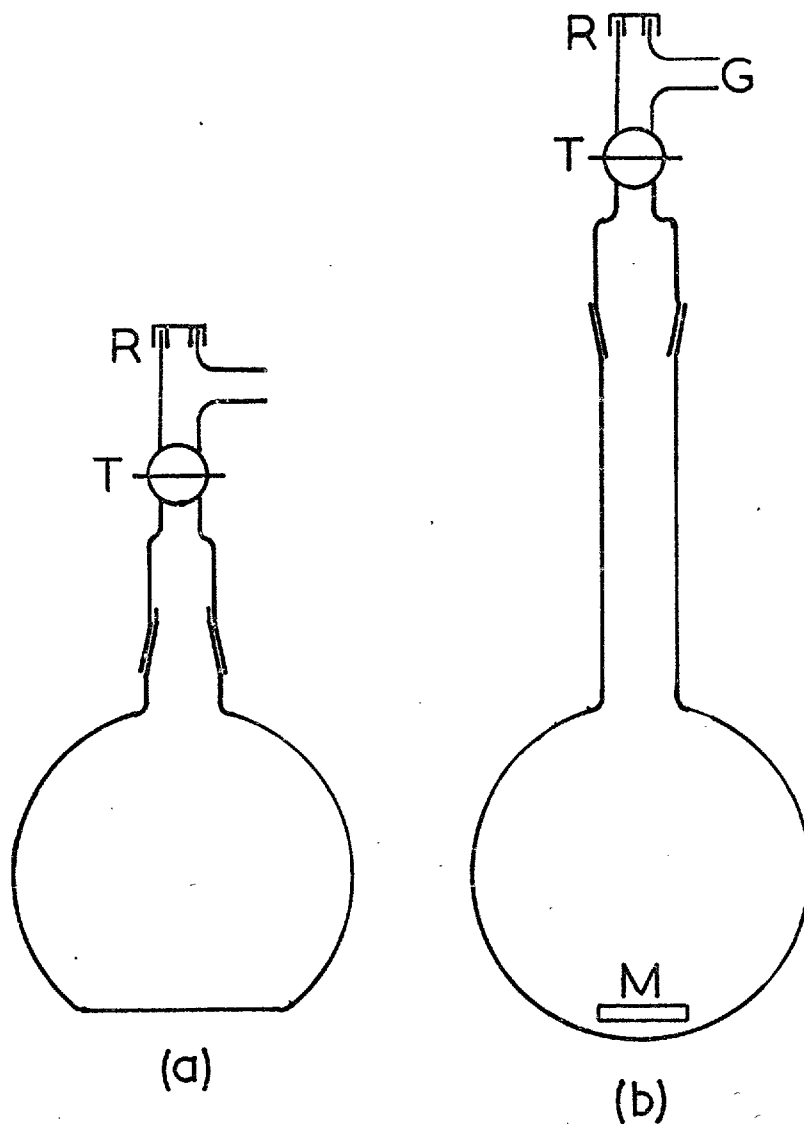


Fig. III.3.a

Storage vessel.

Fig. III.3.b

Aluminium alkyl analysis apparatus.

Key

- G Outlet to gas burette.
- M Magnetic follower.
- R Rubber septum.
- T Spring-loaded stopcock.

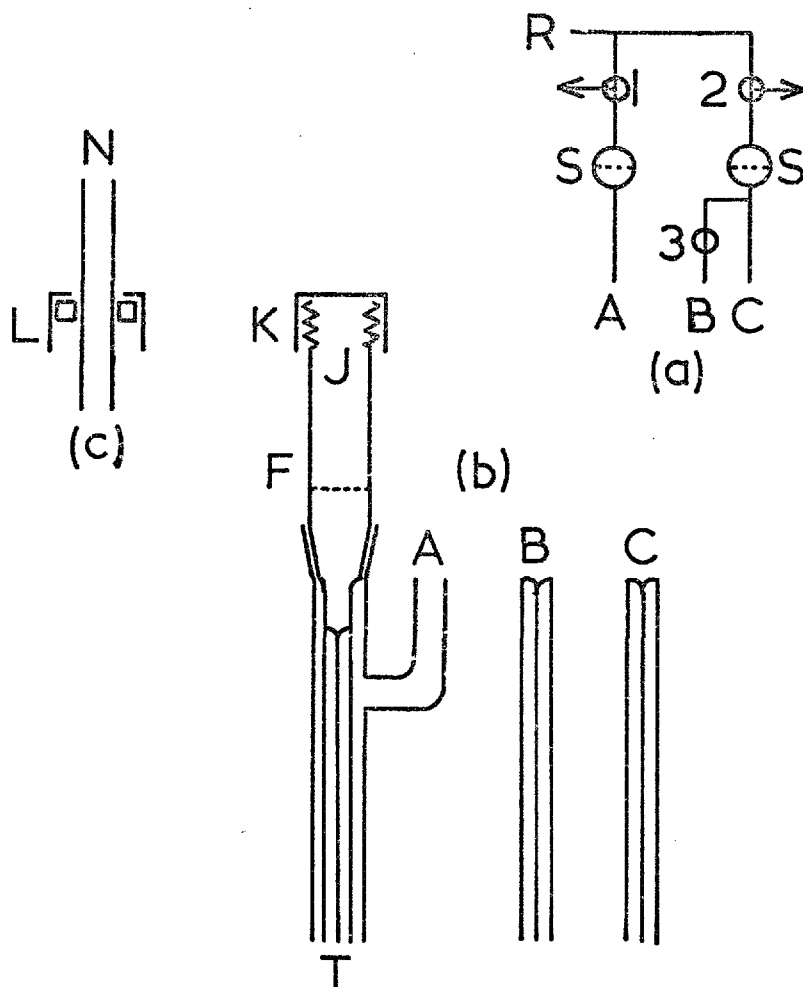


Fig. III.4

Viscometer top fitted with the filtration device, (b) and (c), and viscometer pumping system (a).

Key

- A, B, C Viscometer arms and matching pumping system outlets, the corresponding points are linked with dust-free flexible tubing.
- F Filter tube with No. 3 glass sinter.
- J 'Sovirel' threaded glass joint.
- K 'Sovirel' screw cap.
- L 'Sovirel' sliding joint.
- N Nitrogen supply.
- R Inlet from a rubber bellows.
- S Gas filters with No. 2 sinter.
- T Capillary tube reaching to the bottom of the main viscometer bulb.

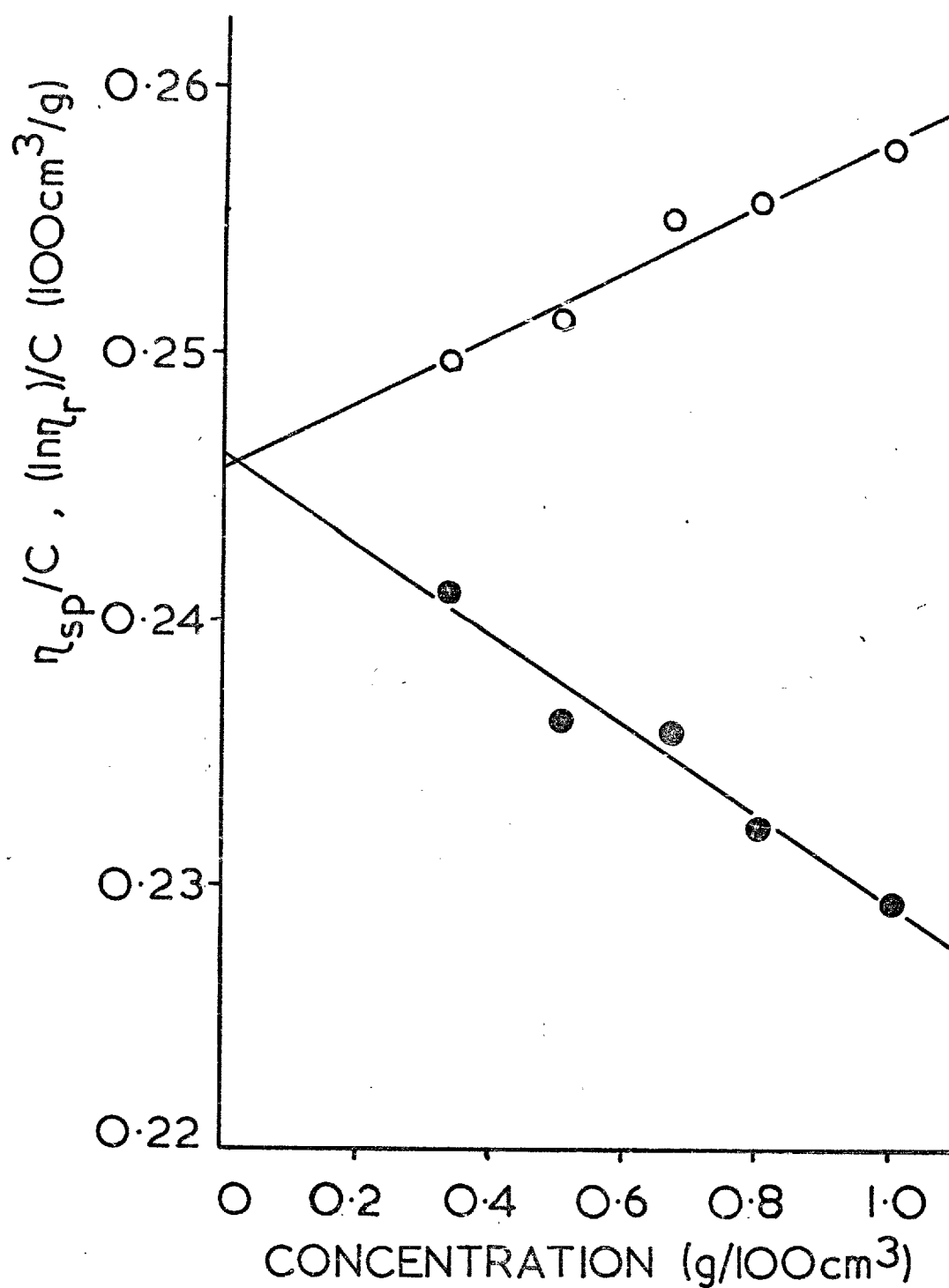


Fig. III.5

A double plot of η_{sp}/C (O) and $(\ln\eta_r)/C$ (●) against concentration for a toluene solution of a vinylferrocene-styrene copolymer (12.2 mole percent vinylferrocene content) at 30°C.

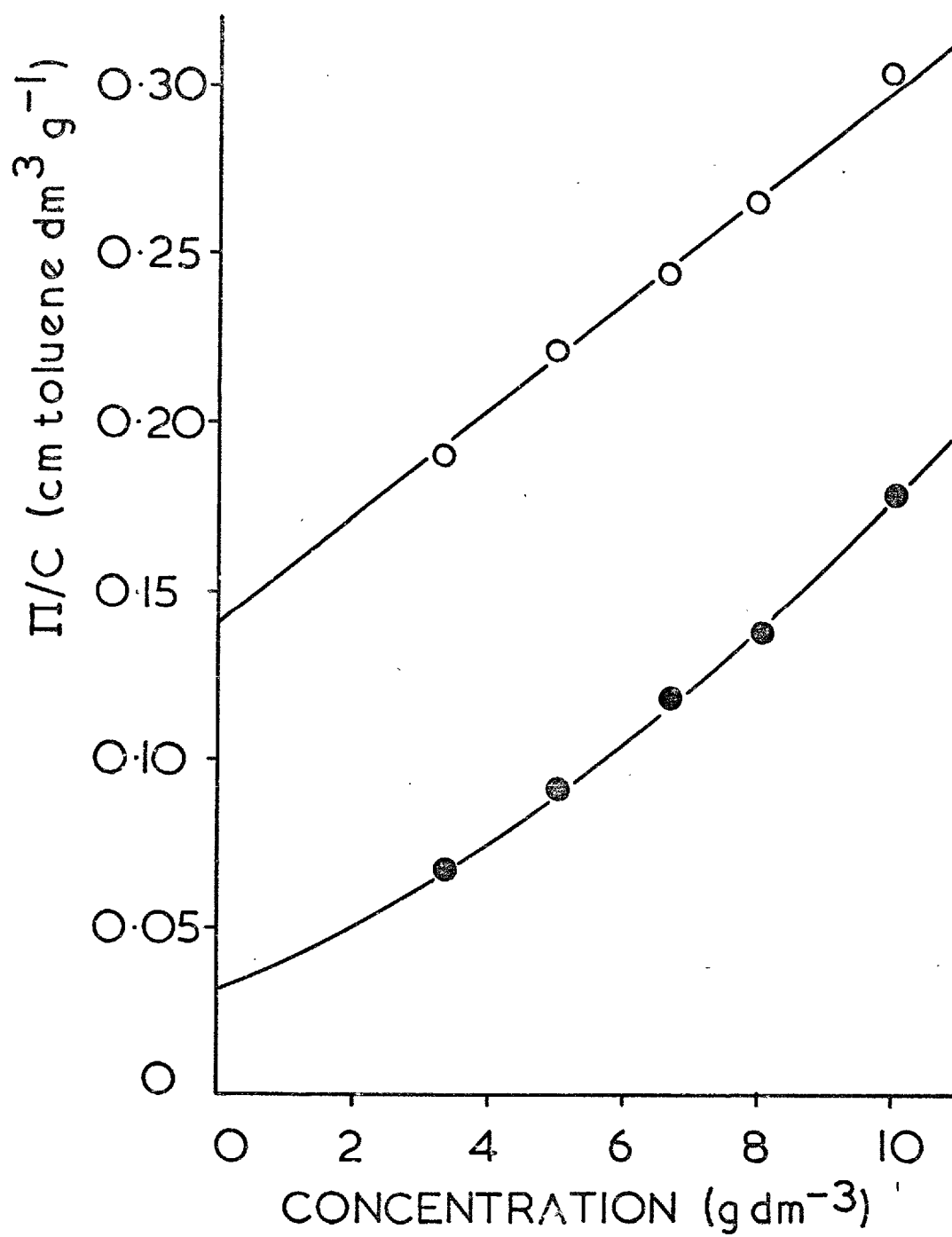


Fig. III.6

Π/C as a function of concentration for toluene solutions of polystyrene, ○ $\bar{M}_n = 217,000$ ● $\bar{M}_n = 947,000$.

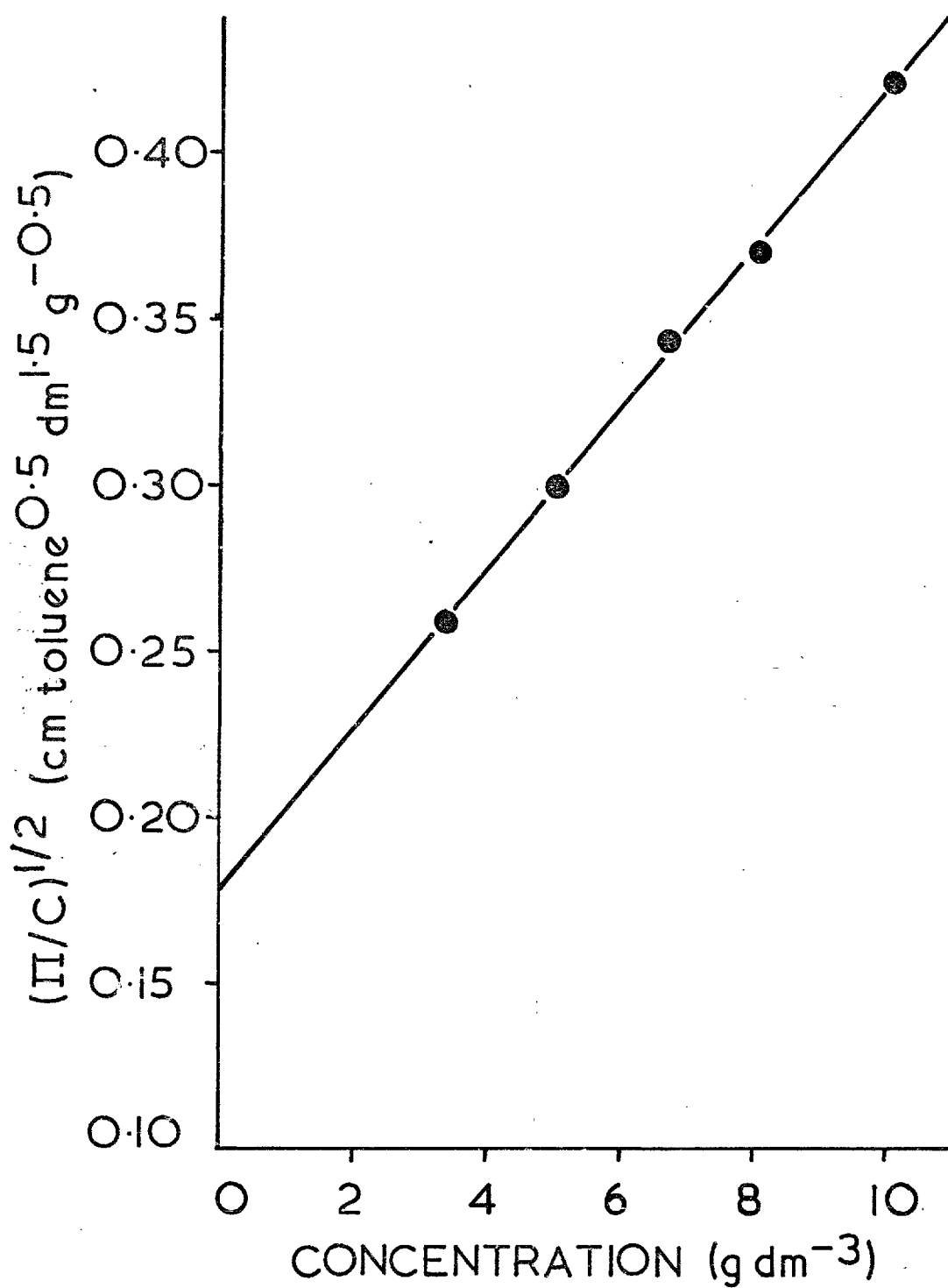


Fig. III.7

$(\Pi/C)^{1/2}$ as a function of concentration for toluene solutions of polystyrene, $\bar{M}_n = 947,000$ (c.f. fig. III.6)..

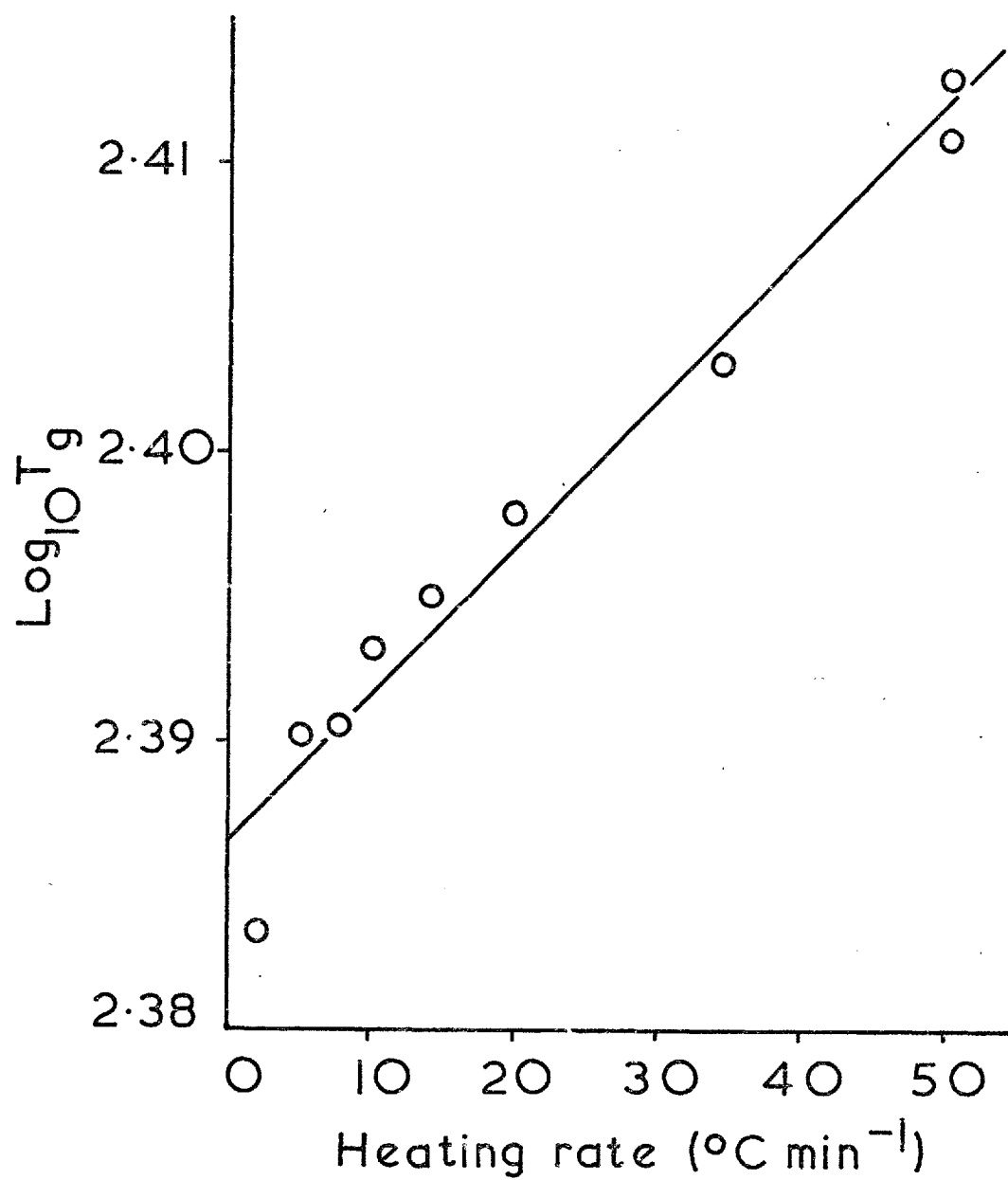


Fig. III.8

$\text{Log}_{10} T_g$ as a function of heating rate for polyvinylferrocene,
 $\bar{M}_n = 10,800$.

IV Ferrocene-olefin and ferrocene-aromatic interactions

A kinetic analysis of the polymerization of styrene in the presence of ferrocene derivatives (Section V) revealed that the behaviour of these systems could not be explained in terms of the accepted simple kinetic scheme for free-radical polymerization (Section II.A). The possibility of ferrocene-olefin or ferrocene-aromatic interactions therefore arose, and consequently a search was made, both of the literature and experimentally, for evidence of such interactions.

IV.A Spectrophotometric studies

The existence of charge-transfer complexes between ferrocene and halogenated organic solvents has been suggested⁷⁵⁻⁸², primarily on the basis of differences between the ultraviolet spectrum of ferrocene in these solvents and in hydrocarbon solvents or ethanol. The visible and ultraviolet (above 295 nm) spectra of ferrocene, n-butylferrocene and vinylferrocene were examined, therefore, in styrene, benzene, n-heptane and ethanol solution, these last two solvents being assumed to be inert (Figs. III.1, III.2 and III.3). Molar extinction coefficients were determined for the two maxima observed (in the case of vinylferrocene a shoulder, rather than a maximum, was observed in the ultraviolet spectrum) by obtaining spectra for five of six solutions in appropriate concentration ranges, and applying the Lambert-Beer law,

$$A = \epsilon CL \quad (1)$$

where A is the absorbance of a solution of concentration C, ϵ is the extinction coefficient (molar extinction coefficient if C is given in mol dm⁻³), and L is the path length of the cell

used (1 cm in this case). Plots of absorbance against concentration were constructed (for example, fig. IV.4) and the gradients of these were calculated by least mean squares analyses of the data. In order to allow for any cell mismatch, the origin was not taken as a point in these analyses. The results are summarized in table IV.1, and a selection of relevant literature values are given in table IV.2.

Also, the ultraviolet and visible spectra of polyvinylferrocene, vinylferrocene-styrene copolymers (Section VIII), and a polyvinylferrocene/polystyrene mixture were studied (Fig. IV.5). Molar extinction coefficients, based on vinylferrocene repeat unit concentration, were determined for the maxima, as before. The results for the homopolymer and homopolymer mixture are listed in table IV.3. The molar extinction coefficients for the copolymers are given in table IV.4, but these are susceptible to any error in the value of the vinylferrocene content of the polymer. This may be eliminated by considering the ratios of the two molar extinction coefficients. These values are also listed in table IV.4 and are depicted graphically, as a function of the mole-percentage of vinylferrocene repeat units (m_1) in the polymer, in fig IV.6.

The results for the simple ferrocene derivatives indicate that a small, but reproducible, overall increase in molar extinction coefficient occurs on changing from an inert solvent to benzene or styrene, the largest increase observed being ca. 15% for vinylferrocene in benzene at 340 nm. Styrene appeared to exert a slightly greater effect than benzene, but the difference between the two was marginal and probably within experimental error. It is therefore unfortunate that the high ultraviolet absorbance of styrene prevented a comparison of the effect of these two solvents on the more sensitive ultraviolet

peak.

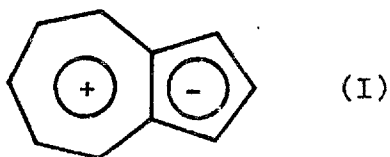
The absence of a shift in either peak and the small changes in extinction coefficients suggest a similarity with the ferrocene-piperylene system⁸⁵⁻⁸⁷, in which ferrocene was found to catalyse the photoisomerization of piperylene. However, in this case, the spectrum of ferrocene was found to be affected only below 320-310 nm. Additionally, it was reported^{85,86} that examination of the nmr spectrum of trans-piperylene revealed the presence of a new methyl doublet in the presence of ferrocene, although a similar study⁸⁷ failed to detect these absorptions. However, on the basis of the spectral evidence a ferrocene-olefin complex was proposed^{85,86} and the value of the equilibrium constant was estimated⁸⁶ to lie between 10 and 300. This estimate was based on a study of the difference between the absorbance of ferrocene/piperylene solutions in cyclohexane at 301 nm, a minimum, and 324 nm, a maximum, as a function of piperylene concentration; and on a study of the change in the chemical shifts between the higher field peaks in the methyl doublets of piperylene and tetramethylsilane, as standard, as a function of ferrocene concentration.

It should be noted that the ferrocene-olefin complex was proposed not only for the specific case of ferrocene and piperylene, but also in a wider sense in order to account for the ferrocene catalysis of the photodimerization of isoprene in benzene solution. It is noteworthy that ferrocene has been found to catalyse the thermal dimerization of butadiene to 1-vinylcyclohexane⁸⁸ in benzene solution.

A further feature of the ferrocene-piperylene system was that a marked solvent effect was observed⁸⁷. In trans-1,2-dimethylcyclohexane, it was proposed that ferrocene acted as a low-energy sensitizer⁸⁷, whilst it was suggested

that ferrocene acted as a high-energy sensitizer⁸⁵⁻⁸⁷ when in benzene solution. Also, the rate of isomerization was higher in benzene than in trans-1,2-dimethylcyclohexane. This markedly different behaviour in benzene has led to the suggestion⁷⁶ that a benzene-ferrocene complex was a possibility.

Ferrocene also has been reported⁸⁹ as catalysing the photo-induced alkoxy carbonylation of azulene (I) in carbon tetrachloride-alcohol solution. This reaction did not take place in the



absence of ferrocene, and no product of the photoinduced reaction of ferrocene with carbon tetrachloride and alcohol was found when azulene was present. Ultraviolet and nmr spectra were reported as suggesting the formation of a complex between azulene, ferrocene and carbon tetrachloride, but no details were given.

In comparison with the small changes observed in the spectra of the simple ferrocene derivatives in various solvents, a marked difference was apparent between the spectra of the vinylferrocene repeat unit in polyvinylferrocene and in vinylferrocene-styrene copolymers. The styrene repeat unit in the latter polymers had an insignificant absorption in this region at the concentrations employed. The greater effect might be explained by the enforced close proximity of the ferrocene and benzene nuclei in the copolymer. Such an explanation might also be invoked to account, in part, for the presence of this effect in spite of the apparent non-interaction of the repeat unit with toluene and benzene. A more important factor here

might be the exclusion of the solvent from the repeat unit. A study of polystyrene in toluene⁹⁰ indicated that more than three out of four neighbouring sites of a polystyrene segment are, on average, occupied by other segments of its own molecule, or that the fraction of the surface area of a polymer segment exposed to the solvent is less than one fourth. Further, it was suggested that there was no space for any solvent molecules between the benzene nuclei. Thus, it is also probable in the case of polyvinylferrocene that only a fraction of the total repeat units are exposed to the solvent. Furthermore, the configurations available for the solvent-repeat unit contact may not include those favouring or permitting any possible specific interaction between the ferrocene and benzene nuclei.

As with the simple ferrocene derivatives, the maximum in the ultraviolet spectrum of the polymers was affected more than the maximum in the visible region. This effect was used, when considering the extent of the possible interaction as a function of copolymer composition, to remove any inaccuracies arising from concentration errors, which were primarily due to errors in the values for copolymer composition. The ratio of the two molar extinction coefficients for these maxima (ϵ_1 for the visible, ϵ_2 for the ultraviolet) was taken to be an indicator of any change in the fraction of vinylferrocene repeat units involved in the proposed interactions, since this ratio should be constant unless there is such a change. As can be seen from fig. IV.6, the value of ϵ_1/ϵ_2 increased smoothly with increasing vinylferrocene content in the copolymer. The value for an anionically prepared copolymer (Section XI) also fitted the curve well. This curve suggests that there is some interaction between a fraction of the vinylferrocene and styrene repeat

units in the copolymer, and, since the value of ϵ_1/ϵ_2 for polyvinylferrocene is 1.37, that this fraction decreases as the vinylferrocene content of the copolymer increases, that is as the styrene content of the copolymer decreases. If the former proposition is accepted, the latter effect would follow, since for every vinylferrocene unit in the copolymer of lowest vinylferrocene content (3.92 mole-percent) there are ca. 24 styrene units, whereas the corresponding number in the copolymer of highest vinylferrocene content (20.8 mole-percent) is ca. 4.

IV.B Nmr studies

Specific interactions between two species in the ground state have been extensively studied by ^1H nmr. The reports of nmr evidence for specific interaction between ferrocene and an olefin^{85,86} were based on observations of the olefin absorptions. However, some of the systems studied here involved overlap of some absorptions from the two species present. The absorptions arising from the protons on the ferrocene nucleus were free from this effect, and, therefore, were selected for study. The ^1H nmr spectra of ferrocene and vinylferrocene were obtained in a variety of solvents, the chemical shifts of the protons on the ferrocene nucleus being recorded, together with relevant literature values, in table IV.5 and table IV.6 respectively. The small variations in these chemical shifts with solvent changes may be attributed to solvation effects. However, the absence of large shifts in the position of an absorption of a solute with changing solvent does not necessarily preclude the the presence of specific interaction between the solute and one or more of the solvents, since the effect of any such interaction may be somewhat negated by the solvation effect acting in opposition.

The ^1H nmr spectra of polyvinylferrocene, polystyrene, and a vinylferrocene-styrene copolymer (12.2 mole-percent vinylferrocene) were obtained in carbon disulphide solution (Figs. IV.7, IV.8 and IV.9 respectively). The chemical shifts observed are summarized in table IV.7. The spectrum of polyvinylferrocene resembles that of an alkylferrocene, and may be compared with spectra of such compounds available in the literature (Table IV.8), although the absorptions are much broader, as would be expected for a polymer (cf. polystyrene,

fig. IV.8). The absorptions arising from protons on the polymer backbone are not differentiated into two peaks, as they are in the polystyrene spectrum. This may be due to the greater peak width in the polyvinylferrocene spectrum. The low field absorption may be assigned to the protons on the unsubstituted cyclopentadiene ring and the slightly higher field shoulder to the protons on the substituted cyclopentadiene ring. The presence of only one absorption due to the latter protons may be caused by the broad nature of the peaks, but this is often the case for alkylferrocenes (Table IV.8).

It is apparent that the absorptions arising from the styrene repeat unit were unaffected by the incorporation of vinylferrocene repeat units. However, the absorptions due to the protons on the ferrocene nuclei exhibited considerable shifts on incorporation into polystyrene. Additionally, the form of these absorptions was altered, there being three peaks rather than two, although the width of the total absorption was reduced. A comparison of the total area of these three absorptions, obtained by integration, with the total area of the absorptions arising from the protons on the benzene nucleus was in good agreement (within 10%) with that calculated from the composition of the copolymer. This substantiates the interpretation of these three absorptions as being attributable solely to the protons on the ferrocene nuclei. A spectrum taken of an anionically prepared copolymer (7.86 mole-percent vinylferrocene) under similar conditions had substantially the same form as the spectrum of the free-radically prepared copolymer. However, the low vinylferrocene content of the copolymer resulted in a weak spectrum, which did not warrant a full analysis.

The peak height of the low field absorption of the three

attributable to the ferrocene protons in the copolymer was lower than those of the two higher field absorptions, this peak was broader than the other two. This would tend to suggest that it had a greater area than the combined area of the other two, and that it may be assigned to the protons on the unsubstituted cyclopentadiene ring. The two sharper peaks may be assigned, then, to the protons on the substituted cyclopentadiene ring, the higher field peak most probably being due to the protons α to the substituted carbon atom.

The change in the ^1H nmr spectrum of the vinylferrocene repeat unit, as a result of incorporating styrene units, may be summarized as a shift of ca. 0.25 ppm to high field in the absorptions due to the ferrocene protons, those in the substituted cyclopentadiene ring being affected to slightly different extents, thereby giving rise to two peaks for these protons. It is possible that such a shift might arise from a through space effect, if a benzene nucleus were to lie face on above a cyclopentadiene ring.

The ^{13}C nmr spectra of polyvinylferrocene, polystyrene, a vinylferrocene-styrene copolymer (12.2 mole-percent vinylferrocene), and some simple ferrocene derivatives were recorded in carbon disulphide solution. The chemical shifts are listed in table IV.9 and may be compared with literature values for chemical shifts in the ^{13}C nmr spectra of various other alkylferrocenes (Table IV.10). Again, the spectrum for polyvinylferrocene had a pattern similar to that of the alkylferrocenes, although the α and β carbon atoms of the substituted cyclopentadiene ring apparently gave only one absorption. This latter observation is probably due to the broad nature of the polymer peaks masking the presence of two closely

situated absorptions.

On incorporating styrene units into the polymer, the absorptions due to the α and β carbon atoms of the substituted cyclopentadiene ring and to the carbon atoms of the unsubstituted cyclopentadiene ring shifted to high field, 0.3 ppm and 0.4 ppm respectively. The magnitude of these shifts is of the order of those experienced in the ^1H nmr spectra of the vinylferrocene repeat unit and, therefore, might tend to substantiate the explanation offered for the latter shifts.

IV.C Physical measurements

The physical properties of ferrocene solutions have not been greatly studied. However, a study of intermolecular interactions in ferrocene solutions, by following the difference between experimental and additive dielectric constant values, has been reported⁹⁶. The solvents studied included benzene, cyclohexane and hexane and the most effective intermolecular interactions were observed in the benzene solutions of ferrocene.

As a part of the dilatometric study of the polymerization of styrene in the presence of vinylferrocene, the apparent density of the latter compound was determined in the presence of the former at 60°C. The density of pure vinylferrocene⁹⁷ at 60°C is 1.259 g cm⁻³, and that this value is maintained in benzene solution⁹⁷ was confirmed, dilatometrically, in this study. However, data from the dilatometric studies of styrene polymerization in the presence of vinylferrocene repeatedly suggested a higher value for the apparent density of the latter in the former. A dilatometric study of an inhibited (DPPH) solution of vinylferrocene in styrene at 60°C gave a value for this apparent density of 1.302 g cm⁻³. A similar measurement on pure styrene gave a value for the density of this compound of 0.8711 g cm⁻³, coinciding well with the literature value⁶⁶ of 0.8712 g cm⁻³. Thus, the 4% difference between the density of vinylferrocene at 60°C and the apparent density of vinylferrocene in styrene at 60°C would seem to be significant. This difference results from a decrease in overall volume on dissolving vinylferrocene in styrene, that is the principle of volume additivity is not obeyed by this system. This finding suggests the presence of some specific interaction between vinylferrocene and styrene.

IV.D Summary

The need to account for anomalies in the kinetics of the bulk polymerization of styrene in the presence of ferrocene derivatives prompted a search for evidence of ferrocene-aromatic and ferrocene-olefin interactions. The presence of the former interaction could cast light also on the anomalous nature of the kinetics of the free-radical homopolymerization of vinylferrocene in benzene solution¹⁴.

Reports in the literature suggest that specific interactions do occur between ferrocene and some olefins, an equilibrium constant having been estimated for the ferrocene-piperylene system⁸⁶, and the possibility of ferrocene-benzene interaction has been suggested⁷⁶. Also, complex formation between ferrocene, azulene and carbon tetrachloride, has been suggested⁸⁹.

Spectrophotometric studies of ferrocene derivatives in various aromatic and non-aromatic solvents and of the vinylferrocene repeat unit in the homopolymer and copolymer with styrene suggest the presence of an interaction between ferrocene and aromatic nuclei. However, the interpretation of ^1H and ^{13}C nmr spectra of similar systems does not require such an interaction. Nevertheless, the inapplicability of the principle of volume additivity to the vinylferrocene-styrene system suggests that specific interactions do take place in this case.

Table IV.1

Molar extinction coefficients^a of ferrocene derivatives as a function of solvent.

Ferrocene, maxima at 327 nm (2) and 445 nm (1)

Solvent	ϵ_2	ϵ_1
n-Heptane (puriss)	51	91
A.R. ethanol	51	91
A.R. benzene	56	96
Styrene (purified)	-	98

n-Butylferrocene, maxima at 327 nm (2) and 442 nm (1)

n-Heptane (puriss)	59	99
A.R. ethanol	56	96
A.R. benzene	65	105

Vinylferrocene, shoulder at ca. 340 nm (2) and maximum at 449 nm (1)

n-Heptane (puriss)	439	242
A.R. ethanol	448	241
A.R. benzene	510	253
Styrene (purified)	-	258

^a In $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$

Table IV.2

Literature values of molar extinction coefficients^a of ferrocene derivatives in different solvents

Ferrocene

Solvent	Max. (nm), ϵ	Max. (nm), ϵ	Ref.
n-Hexane	325, 48	-	80
Isooctane	325, 51	440, 87	83
	326, 55	440, 95	6
	326, 56	440, 96	76
95% ethanol	325, 50	440, 90	76
Carbon tetrachloride	311, 648	-	80
	307, 785	450, 105	84

Ethylferrocene

Isooctane	325, 57	438, 95	83
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n-Propylferrocene

Isooctane	325, 58	438, 97	83
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^a In $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

Table IV.3

Molar extinction coefficients^a for polyvinylferrocene, based on repeat unit concentration, as a function of solvent

Solvent	ϵ_{327}	ϵ_{445}
Tetrahydrofuran (puriss)	66	92
A.R. benzene	59	92
A.R. toluene	68	94, 92
^b Polystyrene/A.R. toluene	67	90

a In $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$.

b Concentration of mixed polymer solutions with respect to polystyrene was 8.4 g dm^{-3} .

Table IV.4

Molar extinction coefficients^a of vinylferrocene repeat units in vinylferrocene-styrene copolymers as a function of copolymer composition

Mole % vinylferrocene	Max. (nm), ϵ_2	Max. (nm), ϵ_1	^b ϵ_1/ϵ_2
3.92	325, 141	443, 114	0.809
5.54	326, 163	444, 138	0.847
8.65	326, 126	445, 120	0.952
12.2	325, 110	444, 106	0.964
15.6	328, 94	447, 103	1.09
20.8	328, 87	447, 103	1.19
7.86 ^c	324, 110	444, 101	0.918

^a In $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$, based on repeat unit concentration.

^b 1.37 for polyvinylferrocene.

^c Anionically prepared random copolymer (Section XI).

Table IV.5

Chemical shift, δ , of ferrocene in the ^1H nmr spectrum as a function of solvent

Solvent	δ^a ppm	Ref.
n-Hexane	4.05	This work ^b
Cyclohexane	4.05	" ^b
	4.04	91
CD_3OD	4.14	This work ^c
Styrene	4.00	" ^b
C_6D_6	4.01	" ^c
Carbon tetrachloride	4.05	92
CDCl_3	4.14	93
Carbon disulphide	4.01	95
Tetrahydrofuran	4.04	91

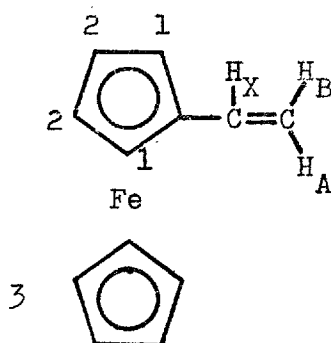
^a Tetramethylsilane as reference.

^b From 60 MHz spectrum.

^c From 100 MHz spectrum.

Table IV.6

Chemical shifts, δ^a , of vinylferrocene in the ^1H nmr spectrum as a function of solvent



Solvent	δ_3	δ_2^b	δ_1^b	δ_B	δ_A	δ_X	Ref.
Styrene ^c	3.95	4.02	4.20				This work
Benzene ^c	3.97	4.03	4.22				"
Cyclohexane ^d	4.00	4.09	4.25	4.94	5.27	6.37	"
CDCl_3	4.08	4.18	4.34	5.01	5.31	6.49	60
CCl_4	3.97	4.22	5.06	4.90	5.19	6.60	61
CS_2	3.95	4.05	4.19				94

a Tetramethylsilane as reference.

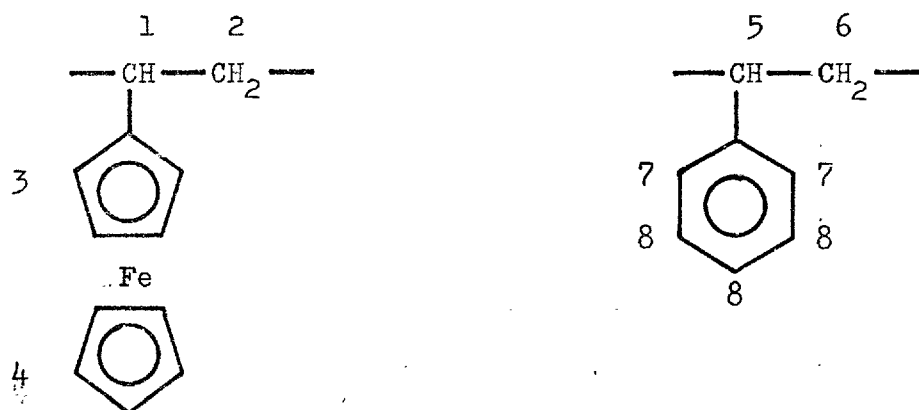
b Centre of multiplet, which had the form of a triplet.

c From a 60 MHz spectrum.

d From a 100 MHz spectrum.

Table IV.7

^1H nmr spectra^a of polyvinylferrocene, polystyrene and a vinylferrocene-styrene copolymer

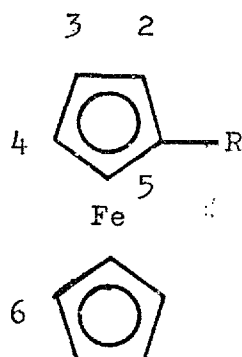


Shift	Polyvinylferrocene	Polystyrene	Copolymer
$\delta_{1,2}$	1.84	-	-
δ_3	3.81	-	3.52
		-	3.59
δ_4	3.98	-	3.74
δ_5	-	1.68	1.67
δ_6	-	1.36	1.36
δ_7	-	6.41	6.40
δ_8	-	6.87	6.88

^a 100 MHz spectra in carbon disulphide with tetramethylsilane as reference.

Table IV.8

Literature values for the ^1H nmr spectra^a of some ferrocene derivatives⁹¹

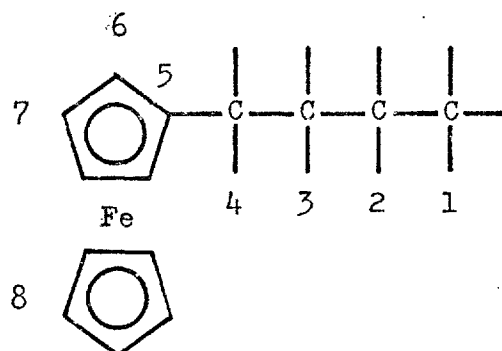


R	H	Me	Et	i-Pr	t-Bu
δ_6	4.04	3.97	4.00	3.99	4.04
$\delta_{2,5}$	-	} 3.94	3.92	} 3.94	3.92
$\delta_{3,4}$	-		3.95		3.98

^a Cyclohexane as solvent, chemical shifts given with tetramethylsilane as reference.

Table IV.9

^{13}C nmr spectra of polyvinylferrocene, a vinylferrocene-styrene copolymer and some ferrocene derivatives in carbon disulphide



Ferrocene

^a δ_8	δ_7 and δ_6	δ_5	δ_4	δ_3	δ_2	δ_1
68.1	-	-	-	-	-	-

Vinylferrocene

69.3	68.8, 66.7	88.7	134.3	110.8	-	-
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n-Butylferrocene

68.4	68.0, 67.1	88.7	33.4	29.4	22.9	14.2
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Polyvinylferrocene

68.5	67.0	95.4	43.6	31.6	-	-
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^b Vinylferrocene-styrene copolymer

68.1	66.7	94.7	^c	32.2	-	-
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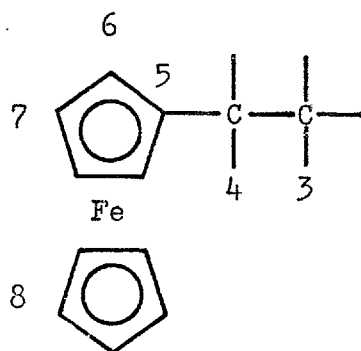
^a Chemical shifts from tetramethylsilane.

^b Peaks due to the styrene repeat unit omitted; these coincide with those for polystyrene.

^c Obscured by styrene repeat unit absorption.

Table IV.10

Literature values⁹⁵ for the ^{13}C nmr spectra of some ferrocene derivatives



Ferrocene

Solvent	^a δ_8	δ_7 and δ_6	δ_5	δ_4	δ_3
CHCl_3	67.9	-	-	-	-
C_6D_6	67.8	-	-	-	-

Methylferrocene

CHCl_3	68.7	69.2, 67.2	84.0	14.8	-
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Ethylferrocene

CHCl_3	68.2	67.3, 66.9	90.8	22.2	14.6
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i-Propylferrocene

C_6D_6	67.7	66.6, 65.8	96.5	27.6	23.6
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t-Butylferrocene

CHCl_3	68.0	66.7, 64.8	101.8	30.1	31.5
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^a Chemical shifts from tetramethylsilane.

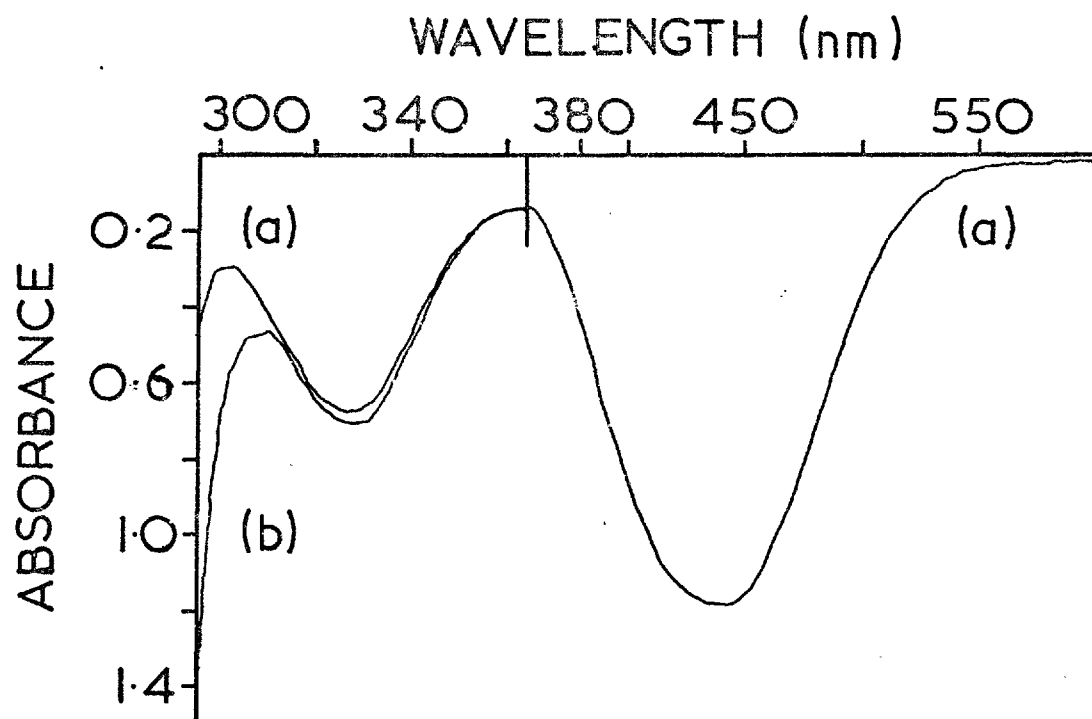


Fig. IV.1

Visible and ultraviolet spectrum of ferrocene; (a) A.R. ethanol solution, $[\text{HFcH}] = 1.32 \times 10^{-2} \text{ mol dm}^{-3}$, (b) A.R. benzene solution, $[\text{HFcH}] = 1.28 \times 10^{-2} \text{ mol dm}^{-3}$.

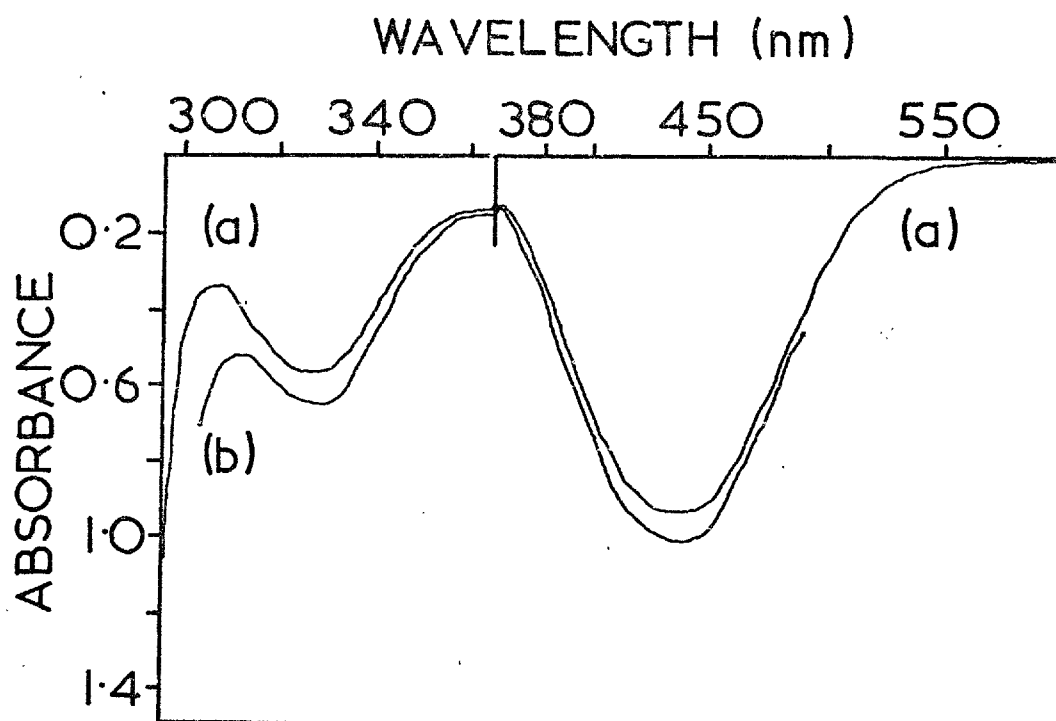


Fig. IV.2

Visible and ultraviolet spectrum of n-butylferrocene;

(a) n-heptane (puriss) solution, $[n\text{-BuFcH}] = 9.47 \times 10^{-3} \text{ mol dm}^{-3}$,

(b) A.R. benzene solution, $[n\text{-BuFcH}] = 9.71 \times 10^{-3} \text{ mol dm}^{-3}$.

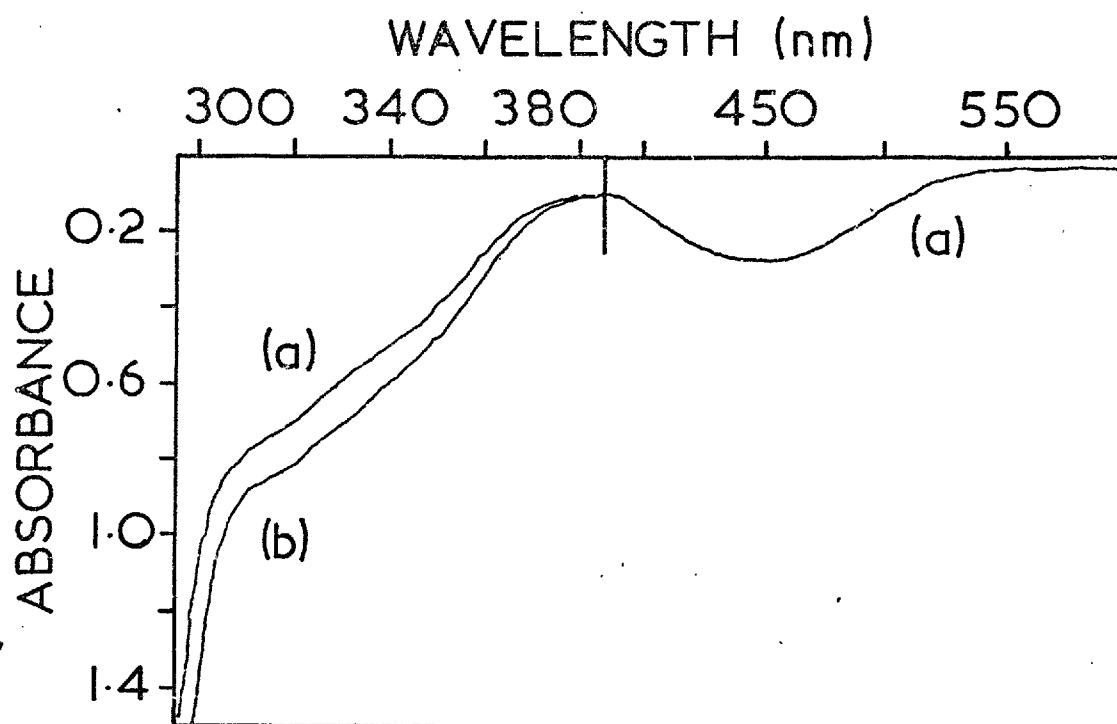


Fig. IV.3

Visible and ultraviolet spectrum of vinylferrocene;

(a) n-heptane (puriss) solution, $[\text{VFcH}] = 1.03 \times 10^{-3} \text{ mol dm}^{-3}$,

(b) A.R. benzene solution, $[\text{VFcH}] = 1.06 \times 10^{-3} \text{ mol dm}^{-3}$.

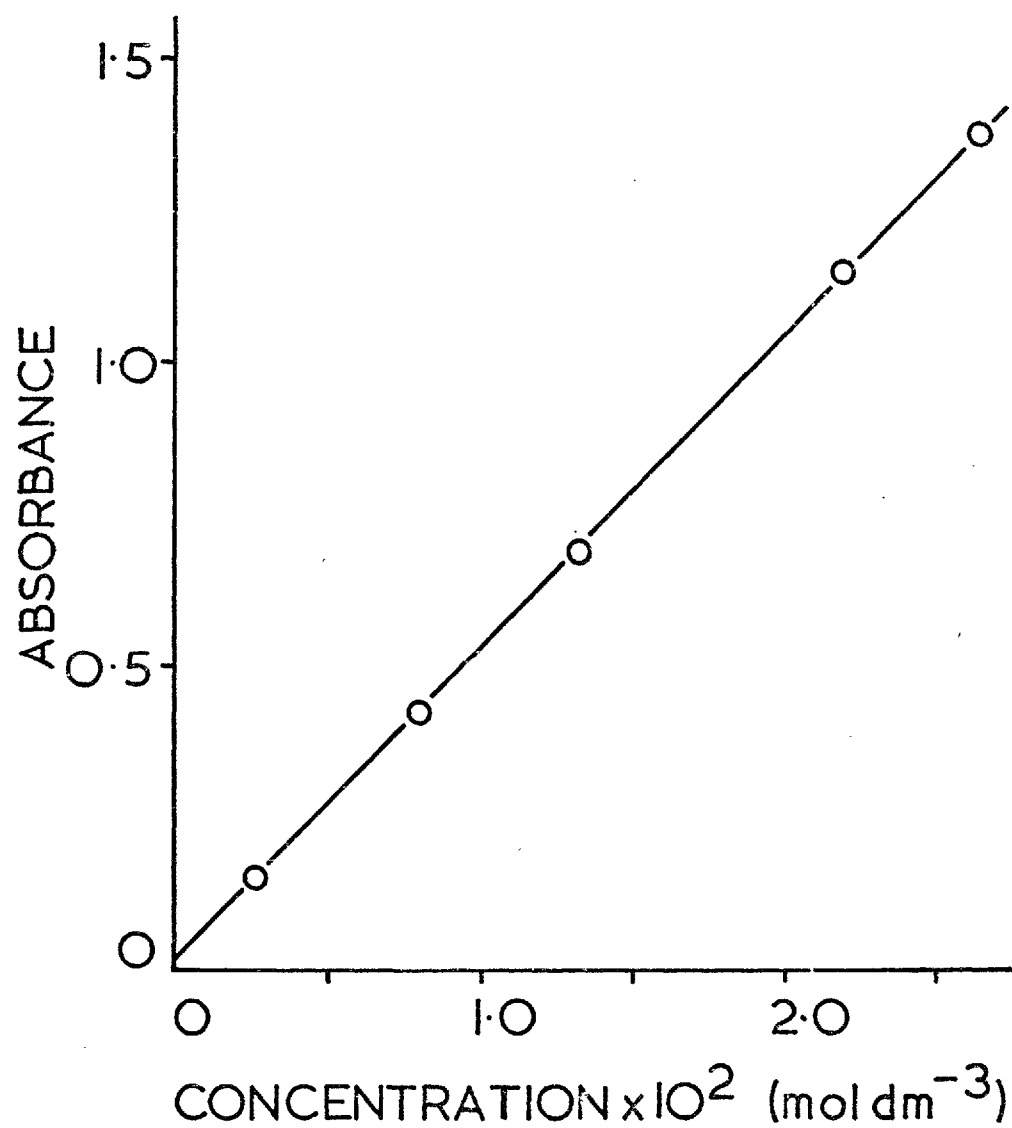


Fig. IV.4

Absorbance of A.R. ethanol solutions of ferrocene at 327 nm as a function of ferrocene concentration.

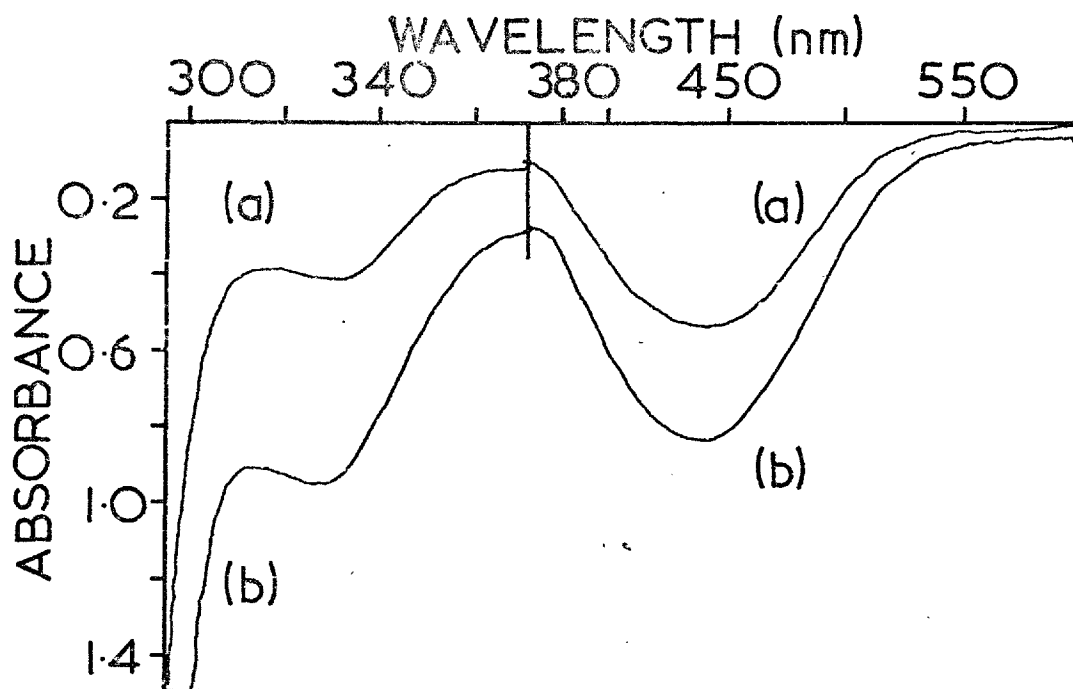


Fig. IV.5.

Visible and ultraviolet spectrum of polyvinylferrocene (a) and of a vinylferrocene-styrene copolymer (b).

- (a) A.R. toluene solution of polyvinylferrocene, concentration with respect to vinylferrocene repeat unit = $5.77 \times 10^{-3} \text{ mol dm}^{-3}$.
- (b) A.R. toluene solution of a vinylferrocene-styrene copolymer, vinylferrocene content 5.54-mole percent, concentration with respect to vinylferrocene repeat unit = $5.80 \times 10^{-3} \text{ mol dm}^{-3}$.

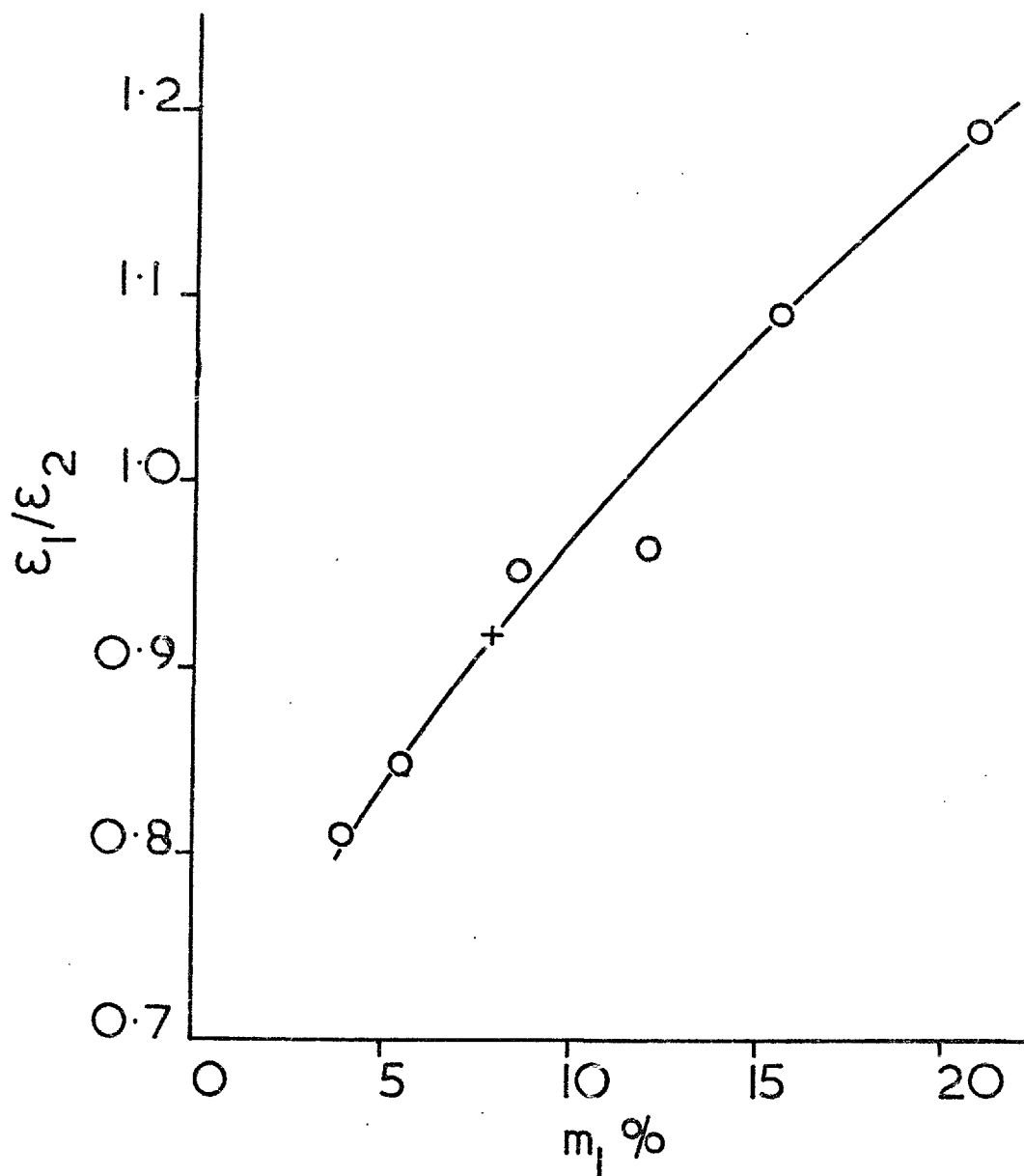


Fig. IV.6

The ratio of the molar extinction coefficients of the maxima in the visible and ultraviolet spectra of the vinylferrocene repeat unit in vinylferrocene-styrene copolymers as a function of vinylferrocene content of the copolymer, m_1 , in mole-percent.

O Free-radically prepared polymer (Section VIII).

+ Anionically prepared polymer (Section XI).

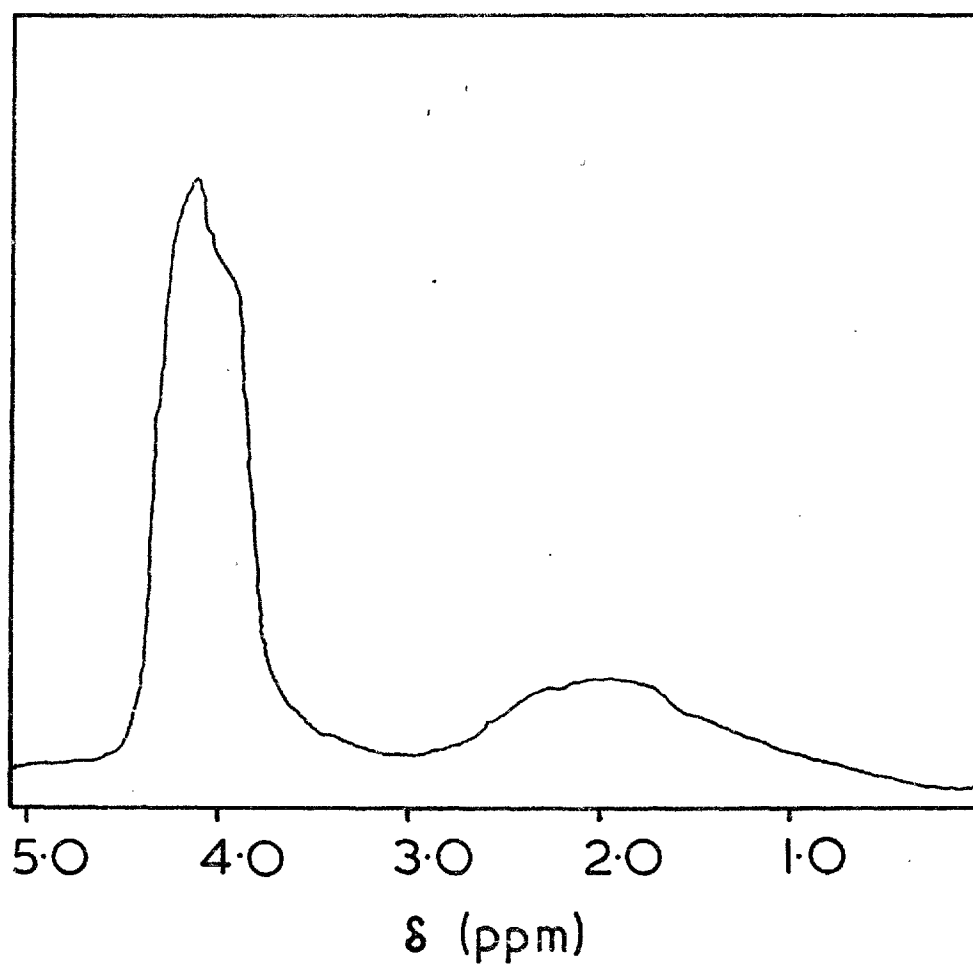


Fig. IV.7

^1H nmr spectrum of polyvinylferrocene in carbon disulphide, the chemical shift, δ , being expressed in ppm from tetramethylsilane.

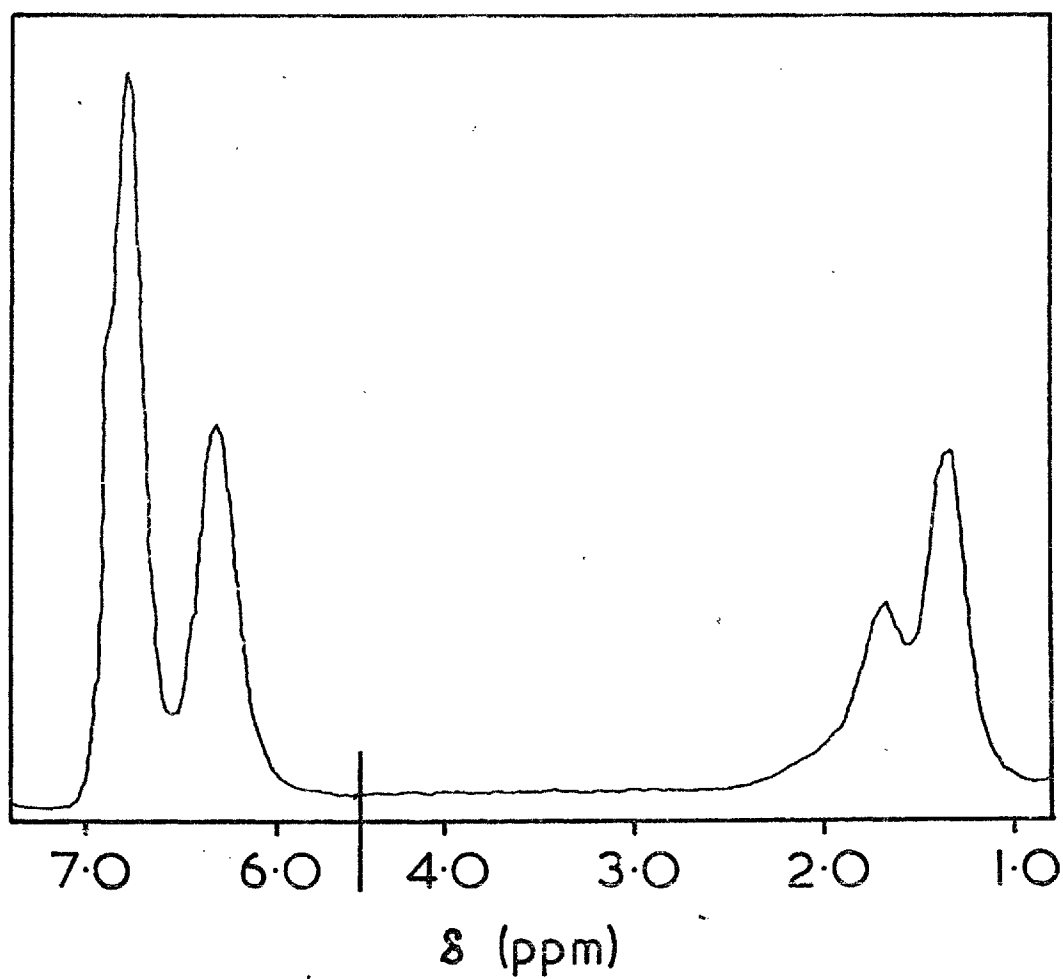


Fig. IV.8

^1H nmr spectrum of polystyrene in carbon disulphide, the chemical shift, δ , being expressed in ppm from tetramethylsilane.

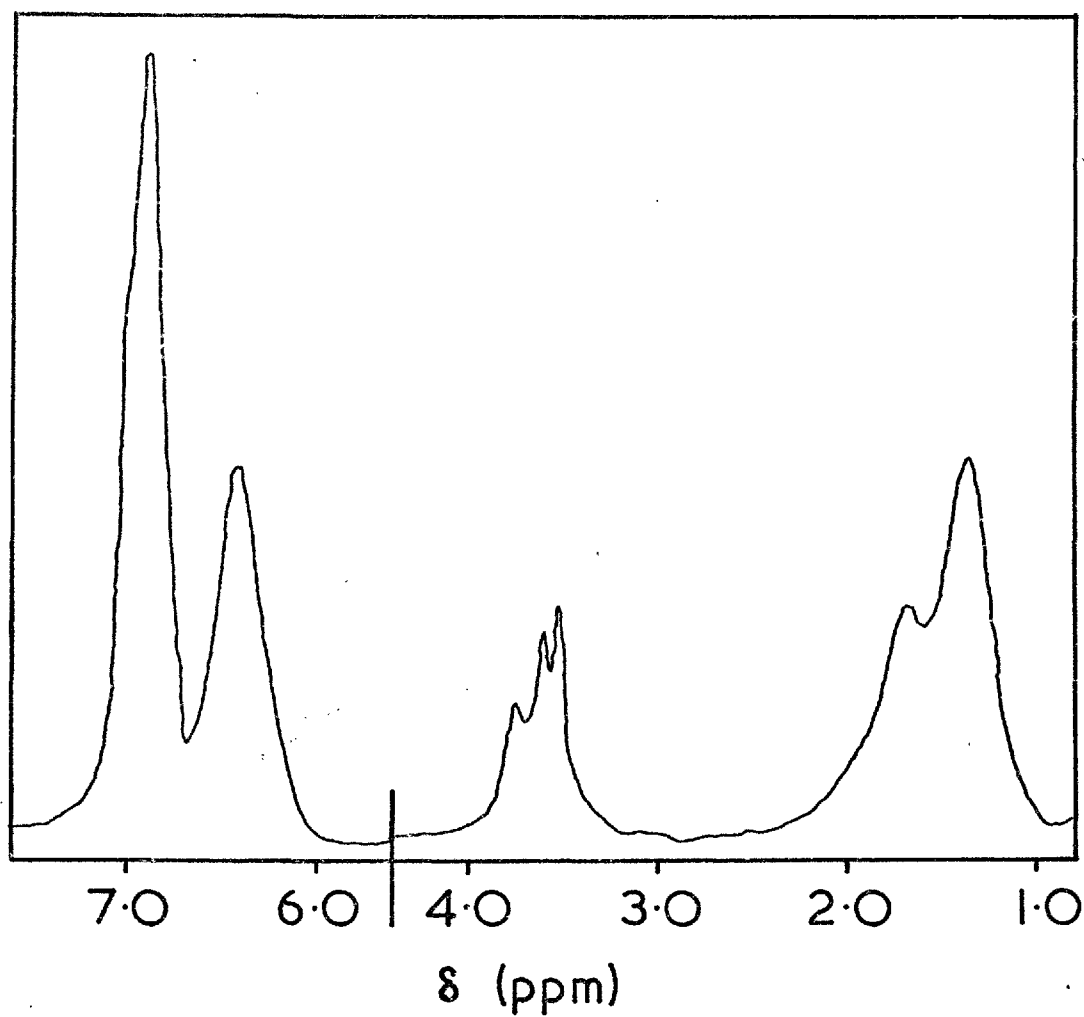


Fig. IV.9

^1H nmr spectrum of a vinylferrocene-styrene copolymer, vinylferrocene content 12.2 mole-percent, in carbon disulphide, the chemical shift, δ , being expressed in ppm from tetramethylsilane.

V The free-radical polymerization of styrene in the presence
 of some ferrocene derivatives

Although the free-radical homopolymerization and copolymerization of ferrocene-containing monomers have been studied quite extensively, there have been few investigations into the behaviour of the ferrocene nucleus in such polymerizations⁹⁸⁻¹⁰². Furthermore, because these studies have been concerned primarily with evaluating the ability of ferrocene to act as an initiator, the ferrocene concentrations employed have been low, typically 1 mole-percent and less. Such concentrations are not representative of the concentration of ferrocene nuclei present in a polymerization involving a ferrocene substituted monomer. Also, although vinylferrocene is the most studied ferrocene-containing monomer, there is no data available concerning the ability of this monomer, and the polymer formed from it, to act as a chain transfer agent in free-radical polymerizations.

A series of studies were undertaken, therefore, to investigate the effect of relatively substantial concentrations of ferrocene, vinylferrocene and ethylferrocene on the free-radical polymerization of styrene. Ethylferrocene was selected for study as a model compound for the vinylferrocene repeat unit in polymers. The concentrations of vinylferrocene used in these studies led to a vinylferrocene content in the polymer formed of less than 3.5 mole-percent, and, therefore, the polymerizations were treated as being solely homopolymerizations of styrene.

V.A The polymerization of styrene in the presence of
ferrocene without added initiator or solvent

The thermal, bulk polymerization of styrene at 60.5°C was carried out in the presence of varying concentrations of ferrocene. Dilatometric measurements indicated that the polymerizations were linear with respect to time, up to the low conversions used (Fig. V.1). However, the low rates of polymerization observed in this system rendered accurate rate determination by dilatometry difficult, and for this reason the gravimetrically determined mean rates of polymerization were preferred for use in the kinetic analysis. Both methods revealed a trend of increasing rate of polymerization with increasing ferrocene concentration (Table V.1), which is contrary to the normal diluent effect of decreasing rate of polymerization with decreasing monomer concentration (Equation II.6). In fact, theoretically, an approximately 25% drop in the rate of polymerization would be expected between the pure styrene and the most concentrated ferrocene solution. This finding does not necessarily conflict with previous reports^{100,101} that ferrocene did not affect the thermal polymerization of styrene in bulk, since the lowest concentration of ferrocene used in this study is greater than any previously reported, and the difference between the rate of polymerization for this solution and for pure styrene is very small.

The number average molecular weights of the polymers formed were determined by GPC analysis and were found to be virtually constant (Table V.1). A consideration of the simple kinetic scheme (Section II.A) reveals that this finding is contrary to such a scheme. It is well established that termination by reaction of two polystyryl radicals is almost exclusively by combination,

and thus equation II.12 becomes

$$\frac{1}{\overline{DP}} = \frac{k_{tc} R_p}{k_p^2 [M]^2} + C_m + C_s \frac{[S]}{[M]} \quad (1)$$

where k_{tc} is the velocity constant for termination by combination of polystyryl radicals. This equation predicts that as monomer concentration decreases or rate of polymerization increases, even if chain transfer to the diluent is negligible, the number average molecular weight of the polymer formed should decrease. Also, a plot of $\{(1/\overline{DP}) - (k_{tc} R_p / k_p^2 [M]^2)\}$ against $[S]/[M]$ should be a straight line with a positive gradient, the value of which is C_s the transfer to solvent constant. When such a plot was constructed, using mean values for styrene concentration, ferrocene concentration and rate of polymerization and literature values⁶⁷ for k_p and k_{tc} , of $176 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and $3.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively, the result was a curve (Fig. V.2) with a negative gradient at all points.

If the ferrocene were acting as an additional source of free-radicals, the rates of polymerization would tend to exhibit the observed trend with ferrocene concentration. However, it is clear from equation V.1 that such an effect could not account for the observed behaviour of polymer molecular weight with ferrocene concentration. Indeed, this inability is further illustrated by the anomalous form of fig. V.2. Two alternative explanations of the observed behaviour are apparent if any simple kinetic scheme, and hence some form of equation V.1, is applicable. Either an increase in the 'apparent' value of k_p or a decrease in the 'apparent' value of k_{tc} with ferrocene concentration would lead to the observed increase in the rate of polymerization, and also could give nearly constant polymer molecular weights. If the presence of specific interaction

between styrene and ferrocene is accepted (Section IV), the former alternative seems reasonable, since styrene molecules involved in such an interaction could well be activated toward free-radical attack. Not only is there the possibility of ground state activation, but, given the presence of such an interaction, there is also the probability of the transition state of the propagation step being favoured by the electron-rich ferrocene molecule.

The general simple kinetic scheme presented in section II.A may be adapted for the particular case of the thermal polymerization of styrene in the presence of ferrocene by replacing M by St, representing styrene, S by HFcH, representing ferrocene, and k_t by k_{tc} , the velocity constant for termination by combination of polystyryl radicals. It is also necessary to define the initiation step in the polymerization. The mode of initiation in the self-initiated thermal polymerization of styrene has been the point of much study and debate. However, a recent study¹⁰³ has demonstrated that initiating radicals are formed by a mechanism involving a Diels-Alder compound, which results in the overall initiating process having an apparently termolecular nature. Thus, the rate of initiation, I, is given by

$$I = k_i [\text{St}]^3 \quad (2)$$

This simple scheme may be amended further, to allow for the proposed behaviour between ferrocene and styrene, by the inclusion of:



Step V.(ii) suggests that ferrocene is rapidly regenerated after propagation via C and, thus, that the equilibrium V.(i) is quickly attained. Following the arguments in section II.A, the rate of polymerization, R_p , is given now by

$$R_p = k_p [R\cdot] [St] + k_5 [R\cdot] [C] \quad (3)$$

The equilibrium constant, K , may be expressed as

$$K = \frac{[C]}{[HFcH]_F [St]_F} \quad (4)$$

where $[HFcH]_F$ and $[St]_F$ are the concentrations of free ferrocene and free styrene respectively. Since the total concentration of styrene is much greater than the total concentration of ferrocene, the concentration of free styrene may be taken as the total styrene concentration, whilst the concentration of free ferrocene is given by

$$[HFcH]_F = [HFcH] - [C] \quad (5)$$

where $[HFcH]$ represents the total concentration of ferrocene.

Thus,

$$K = \frac{[C]}{[St]([HFcH] - [C])} \quad (6)$$

from which

$$[C] = \frac{K[St][HFcH]}{(1 + K[St])} \quad (7)$$

Introducing this equation into equation V.3 gives

$$R_p = k_p [R\cdot] [St] + \frac{k_5 K [R\cdot] [St] [HFcH]}{1 + K[St]} \quad (8)$$

Using the relationship $[R\cdot]$ is equal to $(I/2k_{tc})^{0.5}$ as in equation II.5, this becomes

$$R_p = k_p \left(\frac{I}{2k_{tc}} \right)^{0.5} [St] + \frac{k_5 K}{(1 + K[St])} \left(\frac{I}{2k_{tc}} \right)^{0.5} [St] [HFcH] \quad (9)$$

Combining with equation V.2

$$R_p = k_p \left(\frac{k_i}{2k_{tc}} \right)^{0.5} [St]^{2.5} + k_5 K \left(\frac{k_i}{2k_{tc}} \right)^{0.5} \frac{[St]^{2.5} [HFcH]}{(1 + K[St])} \quad (10)$$

Rearranging gives

$$\frac{R_p}{[St]^{2.5}} - k_p \left(\frac{k_i}{2k_{tc}} \right)^{0.5} = \frac{k_5 K}{(1 + K[St])} \left(\frac{k_i}{2k_{tc}} \right)^{0.5} [HFcH] \quad (11)$$

in which the term $k_p (k_i/2k_{tc})^{0.5}$ is given by $k_p/[St]^{2.5}$ for pure styrene. Since the styrene concentration employed here varied by less than $\pm 5\%$, for the purposes of this study, the term $K/(1 + K[St])$ may be approximated to be a constant. Thus, defining b as

$$b = \frac{K}{1 + K[St]} \quad (12)$$

equation V.11 becomes

$$\frac{R_p}{[St]^{2.5}} - k_p \left(\frac{k_i}{2k_{tc}} \right)^{0.5} = \left(\frac{k_i}{2k_{tc}} \right)^{0.5} b k_5 [HFcH] \quad (13)$$

Using the gravimetrically determined mean rates of polymerization and mean styrene concentrations, a plot of the left-hand side of equation V.13 against mean ferrocene concentration yields a straight line passing through the origin (Fig. V.3). The gradient of the plot gives a value of $1.18 \times 10^{-8} \text{ dm}^{7.5} \text{ mol}^{-2.5} \text{ s}^{-1}$ for $b k_5 (k_i/2k_{tc})^{0.5}$. When the value of $k_p (k_i/2k_{tc})^{0.5}$, obtained as above, and a literature value⁶⁷ of k_p are substituted, the value of $b k_5$ is calculated to be $174 \pm 20 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. From equation V.12, when K is much less than unity, b becomes approximately equal to K , but when K is greater than unity, b becomes approximately equal to $1/[St]$. Thus, although it is not possible to assign a lower limit for b , the upper limit may be given as $1/[St]$, or, in this case, as ca. $1/8$. This value may be used to set the lower limit of k_5 , using the value determined for $b k_5$. Thus, k_5 , the velocity constant for propagation via styrene interacting with ferrocene, may be assigned a lower limit of $1390 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which may be compared with a literature value⁶⁷ for k_p , the velocity

constant for propagation via styrene alone, of $176 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Under the proposed scheme, the degree of polymerization, $\overline{DP}$, of the polymer formed in the polymerization may be redefined as

$$\overline{DP} = \frac{k_p[R\cdot][St] + k_5[R\cdot][C]}{k_{tc}[R\cdot]^2 + k_{fm}[R\cdot][St] + k_{fs}[R\cdot][HFcH]} \quad (14)$$

Combining equations V.7 and V.12 gives

$$[C] = b[St][HFcH] \quad (15)$$

Hence,

$$\overline{DP} = \frac{k_p[R\cdot][St] + bk_5[R\cdot][St][HFcH]}{k_{tc}[R\cdot]^2 + k_{fm}[R\cdot][St] + k_{fs}[R\cdot][HFcH]} \quad (16)$$

and

$$\frac{k_p + bk_5[HFcH]}{\overline{DP}} = k_{tc} \frac{[R\cdot]}{[St]} + k_{fm} + k_{fs} \frac{[HFcH]}{[St]} \quad (17)$$

but from equation V.3

$$[R\cdot] = \frac{R_p}{k_p[St] + k_5[C]} \quad (18)$$

Combining equations V.15, V.17 and V.18, and rearranging gives

$$\left\{ \frac{k_p + bk_5[HFcH]}{\overline{DP}} \right\} - \left\{ \frac{k_{tc} R_p}{[St]^2 (k_p + bk_5[HFcH])} \right\} = k_{fm} + k_{fs} \frac{[HFcH]}{[St]} \quad (19)$$

When a plot of the left-hand side of equation V.19 against $[HFcH]/[St]$ is constructed, using mean values of the experimental parameters, the value for $b k_5$ obtained above, and literature values⁶⁷ of k_p and k_{tc} , the points, with one exception, fall on a straight line (Fig. V.4). A least mean squares analysis yields values for k_{fs} of $0.125 \pm 0.026 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and for k_{fm} of $(1.00 \pm 0.12) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the slope and intercept respectively. When the anomalous result ($[HFcH]/[St] = 2.61 \times 10^{-2}$) is omitted from the least mean squares analysis, the values obtained are $k_{fs} = 0.119 \pm 0.008 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ and

$k_{fm} = (1.06 \pm 0.04) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, which is identical to a previously determined⁶⁷ value of k_{fm} .

This value for k_{fs} infers a greater reactivity of ferrocene toward polystyryl radicals than would be expected from previous discussions²³ of the reactivity of ferrocene toward free-radicals. However, the value probably reflects chain transfer to styrene involved in an interaction with ferrocene, rather than to free ferrocene or ferrocene involved in such an interaction. Indeed, the styrene involved in this interaction would be activated toward chain transfer, which may be viewed as hydrogen atom (radical) transfer from polystyryl radicals, as well as toward propagation, that is polystyryl radical attack. It is of interest to note that a C_m term can be evaluated for styrene involved in the proposed interaction with ferrocene. This C_m term, C_{mc} , is given, by definition, by the velocity constant for chain transfer to styrene involved in the interaction, k_{fc} , divided by the velocity constant for propagation via this styrene, k_5 . Although the value of neither of these terms is known individually, the value of C_{mc} can be calculated, since from equation V.15

$$\frac{[C]}{[St]} = b[St] \frac{[HFcH]}{[St]} \quad (20)$$

and thus

$$k_{fc} = \frac{k_{fs}}{b[St]} \quad (21)$$

from which

$$C_{mc} = \frac{k_{fs}}{bk_5[St]} \quad (22)$$

Using the average mean styrene concentration and the values for k_{fs} and bk_5 obtained here, the value of C_{mc} is 8.87×10^{-5} . It is, perhaps, not insignificant that this value is close to that

of 6.02×10^{-5} for C_m , which may be calculated from literature values⁶⁷ of k_{fm} and k_p . Although possibly fortuitous, this similarity in the values of C_m and C_{mc} , suggesting that styrene involved in the proposed interaction with ferrocene is almost equally activated toward propagation and chain transfer, might be expected, if the model is correct, in view of the basic similarity between the mode of attack involved in the two processes.

V.B The polymerization of styrene in the presence of low concentrations of vinylferrocene without added initiator or solvent

The bulk thermal polymerization of styrene at 60°C was studied in the presence of vinylferrocene, the initial concentration of the latter varying from 0 to 0.679 mol dm⁻³. Dilatometric measurements revealed that the polymerizations in the presence of vinylferrocene were markedly non-linear with respect to time (Fig. V.5) and possessed large initial rates of polymerization, which increased with increasing vinylferrocene concentration. The initial rates of polymerization were obtained from the gradients of the tangents at zero time of plots of the type depicted in fig. V.5, and are listed in table V.2. In calculating these values, polymerization was taken to have occurred only via styrene, which seems to be a reasonable approximation in view of the fact that no more than 3.5 mole-percent vinylferrocene was incorporated into the polymer.

Since repeated attempts to homopolymerize vinylferrocene thermally, without added initiator, in benzene solution at both 60°C and 80°C failed, it is apparent that vinylferrocene does not produce free-radicals that attack vinylferrocene under these conditions. Furthermore, when the polymerization of pure styrene ([St] = 8.37 mol dm⁻³) and of a solution of vinylferrocene in styrene ([VFcH] = 0.402 mol dm⁻³ and [St] = 7.82 mol dm⁻³) were carried out at 60°C in the presence of equal amounts of diphenylpicrylhydrazyl (DPPH), the induction periods observed were 43 min. and 55 min. respectively. The induction period for the styrene solution of vinylferrocene would be expected to be greater than that for pure styrene, since the styrene concentration, and hence the rate of

initiation, is lower. This concentration effect may be eliminated by considering the ratio of the two induction periods, since, for styrene, the induction period, t , for a given amount of inhibitor is given by

$$t = \frac{\text{constant}}{[\text{St}]^3} \quad (23)$$

and thus for two different styrene concentrations

$$\left(\frac{t_1}{t_2}\right) = \left(\frac{[\text{St}]_2}{[\text{St}]_1}\right)^3 \quad (24)$$

In this case, the ratio of the two induction periods is 0.782 and the value of the corresponding concentration term is 0.816. This agreement between these two terms (4%) demonstrates not only the failure of vinylferrocene to produce free-radicals under these conditions, but also that the rate of initiation is not increased by any participation of vinylferrocene in the initiating mechanism.

A scheme similar to that proposed in the previous section (V.A), that is one involving a propagation step through styrene which is interacting with vinylferrocene, may be applied to the initial rates of polymerization observed in the presence of vinylferrocene. Omitting the anomalous result for $[\text{VFcH}] = 0.6 \text{ mol dm}^{-3}$, a plot of $\{(R_p/[\text{St}]^{2.5}) - k_p(k_i/2k_{tc})^{0.5}\}$ against $[\text{VFcH}]$, based on equation V.13, reproduced below in a suitably amended form, is a straight line through the origin (Fig. V.6).

$$\frac{R_p}{[\text{St}]^{2.5}} - k_p\left(\frac{k_i}{2k_{tc}}\right)^{0.5} = \left(\frac{k_i}{2k_{tc}}\right)^{0.5} b k_5 [\text{VFcH}] \quad (25)$$

The gradient of this plot is $(7.4 \pm 1.3) \times 10^{-7} \text{ dm}^{7.5} \text{ mol}^{-2.5} \text{ s}^{-1}$, from which a value for $b k_5$ of $14,000 \pm 2,500 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ may be calculated, by using a literature value⁶⁷ of k_p and the value of $k_p(k_i/2k_{tc})^{0.5}$ obtained from $R_p/[\text{St}]^{2.5}$ for pure styrene.

The difference between this value of k_5 and that obtained for ferrocene in section V.A ($174 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) may possibly reflect a greater degree of interaction between styrene and the larger delocalized system of vinylferrocene, and also a consequently greater activation of the styrene involved in this interaction.

The precise reason for the marked decline in the rate of polymerization of styrene in the presence of vinylferrocene cannot be ascertained from the available data. However, a possible explanation is the formation of a retarder, a species which reacts with polymer radicals to give polymer without regenerating an active free-radical. Further, it would be necessary for the concentration of this retarder to increase over a period of several hours. The effect of such a process would be two-fold. Step (vii) in the simple kinetic scheme (Section II.A), previously taken to be negligible, would become of importance, thus lowering the molecular weight of the polymer formed and the concentration of polymer radicals, and hence the rate of polymerization. Additionally, the failure to achieve a steady concentration of retarder over a period of several hours would invalidate equation II.3 and lead to a decrease in the rate of polymerization with time during this period. Possibly such a retarder could derive from chain transfer to vinylferrocene, particularly that involved in an interaction with styrene, since vinylferrocene has been found to be a relatively active chain transfer agent in its homopolymerization ($C_m = 1.17 \times 10^{-2}$, section VII). Alternatively, the retarder might derive from the vinylferrocenyl radical formed in such a transfer reaction, since Fe(III)-containing endgroups have been observed for polyvinylferrocene formed by the monomolecular termination of polyvinylferrocenyl radicals in benzene solution¹⁴, and it is

well known that Fe(III) compounds can act as retarders or inhibitors.

An observation supporting the suggestion that retardation is due, in some way, to vinylferrocene is that the gravimetrically determined mean rates of polymerization, although greater in the presence of vinylferrocene than for pure styrene, are not directly related to vinylferrocene concentration, rather they are randomly distributed in a band of ca. $\pm 20\%$ (Table V.2). This would suggest that the decline in the rate of polymerization, and hence the degree of retardation, was greatest for those polymerizations with the highest initial rates of polymerization, that is with the highest vinylferrocene concentration.

The possibility of retardation, whatever the source, renders a detailed analysis of the molecular weights of the polymers too difficult, since the overriding effect would be that of the retardation.

V.C The polymerization of styrene in the presence of low concentrations of vinylferrocene and azobisisobutyronitrile (AIBN), but without added solvent

The AIBN-initiated thermal bulk polymerization of styrene was studied in the presence of low concentrations of vinylferrocene at 60°C. As in the case of the self-initiated thermal polymerizations (Section V.B), dilatometric measurements revealed that the rates of polymerization in the presence of vinylferrocene exhibited a decline with time from a relatively high initial rate (Fig. V.7). As can be seen from the values given in table V.3, however, neither the relative increase in initial rate of polymerization with respect to pure styrene, nor the subsequent decline in rate were as pronounced as in the self-initiated thermal polymerizations, under similar conditions.

Clearly, since the initial rates of polymerization in the presence of vinylferrocene were much lower than would be expected by comparison with the values obtained in the absence of AIBN (Section V.B), the behaviour in the presence of the initiator cannot be fitted directly into the proposed scheme. However, the difference in conditions, namely the much higher radical concentration in the presence of AIBN, suggests a possible explanation for the apparent deviation from the expected behaviour. If a retarder is formed, the higher radical concentration could increase the rate of formation of retarder and decrease the time taken to acquire a steady retarder concentration. Certainly, a linear rate of polymerization is achieved more rapidly in the presence of AIBN than in its absence (c.f. fig. V.5 and fig. V.7), and an increase in the rate of formation of a retarder, causing a more rapid decline in the rate of polymerization, could lead to the observed initial rate of

polymerization being lower than the real value, because of the limitations of the mode of observation.

The relative effect of retardation on polymer molecular weight is diminished at high radical concentration, because of the increased importance of termination by the reaction of two polymer radicals. A limited discussion of the molecular weight data (Table V.3) is, therefore, feasible, and in spite of the possible retardation these molecular weights are somewhat analogous to those obtained for the ferrocene/styrene system (Section V.A), in that the molecular weights of the polymers vary little with vinylferrocene concentration. The increasing mean rates of polymerization and decreasing styrene concentrations would require, under a normal kinetic scheme, a pronounced decrease in polymer molecular weight. As before, the results suggest an increase in the 'apparent' value of the velocity constant for propagation, k_p , with increasing vinylferrocene concentration, possibly arising from propagation via styrene involved in a specific interaction with vinylferrocene.

V.D The benzene solution thermal polymerization of styrene
in the presence of low concentrations of vinylferrocene,
without added initiator

Styrene was thermally polymerized in benzene solution, at constant styrene concentration (4 mol dm^{-3}), in the presence of varying concentrations of vinylferrocene. Dilatometric studies indicated that the polymerizations were linear with respect to time, up to the low conversions employed, and that the initial rates of polymerization were independent of vinylferrocene concentration. However, the more accurate gravimetrically determined mean rates of polymerization suggest a slight fall in mean rate with increasing vinylferrocene concentration (Table V.4), but even these values must be treated with caution in view of the difficulties associated with the determination of such low rates of polymerization.

If the vinylferrocene is assumed to have little effect on the rate of polymerization of the styrene, this system appears to follow a normal kinetic scheme for free-radical polymerization (Section II.A) and thus equation V.1 may be applied to this system. A suitable form of this equation is

$$\frac{1}{\overline{DP}} - \frac{k_{tc}R_p}{k_p^2[St]^2} = C_m + C_s \frac{[VFCH]}{[St]} \quad (26)$$

A plot of $\left\{ (1/\overline{DP}) - (k_{tc}R_p/k_p^2[St]^2) \right\}$ against $[VFCH]/[St]$, using mean values of the experimental parameters and literature values⁶⁷ of k_{tc} and k_p , is a reasonable straight line (Fig. V.8). A least mean squares analysis of the data gives a value of $(1.98 \pm 0.36) \times 10^{-3}$ for C_s and of $(3.21 \pm 2.23) \times 10^{-5}$ for C_m , which may be compared with a literature value⁶⁷ for C_m of 6.02×10^{-5} . There must be uncertainty with regard to the precise nature of the species responsible for the value of C_s ,

since it may well be that vinylferrocene is involved in some interaction with benzene. Also, the slight decline in mean rate of polymerization and the suggestion of curvature in fig. V.8 with increasing vinylferrocene concentration might indicate slight retardation linked to the presence of vinylferrocene. However, a comparison of the values of C_s and C_m obtained here suggests that, under these conditions, vinylferrocene, in some form, is a more effective chain transfer agent than styrene.

The markedly different behaviour of the solution polymerization of this system compared with that of bulk polymerization may be explained if aromatic-vinylferrocene interactions are present. The benzene would exert a greater influence than an inert diluent, since it would compete with the styrene for the vinylferrocene, thus greatly reducing the amount of styrene-vinylferrocene interaction. Not only would this result in near normal rates of polymerization, but it could also alter chain transfer reactions and thereby largely prevent the formation of a retarder.

V.E The benzene solution polymerization of styrene in the presence of low concentrations of vinylferrocene and azobisisobutyronitrile (AIBN)

The AIBN-initiated polymerization of styrene in the presence of varying concentrations of vinylferrocene was studied in benzene solution at 60°C, with the styrene concentration held constant at 4 mol dm⁻³. Dilatometric measurements revealed that the polymerizations were linear with respect to time, up to the low conversions used, and that the initial rates of polymerization were, within the experimental limits, independent of vinylferrocene concentration (Table V.5). The gravimetrically determined mean rates of polymerization (Table V.5) exhibited a slight increase with increasing vinylferrocene concentration, but this was perhaps within the experimental limits.

The molecular weights of the polymers also exhibit a slight increase with increasing vinylferrocene concentration (Table V.5). However, this increase is very small for the majority of the polymers and even the largest increase is only 10%. This must be regarded as being within experimental limits when it is considered that these molecular weights were derived from viscometric measurements and, in the treatment of the results, the polymer was approximated to be pure polystyrene. This approximation would become less valid for polymers prepared in the presence of the higher vinylferrocene concentrations. Also, the limiting viscosity numbers, on which the calculations were based, varied by only 3% (Table V.5).

In view of the ability of vinylferrocene to act as a transfer agent, as demonstrated in the previous section (V.D), the molecular weights of the polymers would be expected to fall as vinylferrocene is introduced into the polymerization system.

However, the magnitude of this drop would be small under the conditions employed, as may be seen by considering equation V.26, given below in a suitably rearranged form. Since the styrene

$$\frac{1}{\overline{DP}} = \left(\frac{k_{tc} R_p}{k_p^2 [St]^2} + C_m \right) + C_s \frac{[VFcH]}{[St]} \quad (27)$$

concentration was constant and the mean rates of polymerization were very nearly so, the term $\left\{ (k_{tc} R_p / k_p^2 [St]^2) + C_m \right\}$ may be approximated to be constant, and is therefore given by $1/\overline{DP}$ for the polymer formed in the polymerization of the pure styrene solution, that is 2.21×10^{-3} . In this study, the maximum value of $C_s [VFcH]/[St]$ was 0.142×10^{-3} , if the value of C_s obtained in section V.D is used. Thus, assuming this value of C_s to be correct and that a normal kinetic scheme is applicable, the maximum decrease expected in $\overline{DP}$ in this study would be 6%, which would be within experimental error.

The results obtained in this study are, therefore, somewhat inconclusive with respect to the applicability of a normal kinetic scheme to this system. However, in the absence of any clear, positive evidence to the contrary, such a scheme may be taken to apply to this system. This is in agreement with the observations of this system in the absence of AIBN, given in the previous section (V.D), and the arguments presented there, when comparing it to the bulk systems, may be applied here.

V.F The thermal polymerization of styrene in the presence of ethylferrocene, without added initiator or solvent

The bulk thermal polymerization of styrene at 60°C was studied in the presence of varying concentrations of ethylferrocene. Dilatometric measurements were made on the pure styrene and on the two ethylferrocene solutions of highest concentration. These revealed that, whereas the polymerization of pure styrene was linear with respect to time, the polymerization in the presence of ethylferrocene exhibited relatively higher initial rates of polymerization followed by a slow decline in rate (Fig. V.9). The initial rate of polymerization was higher for the more concentrated ethylferrocene solution studied (Table V.6). The gravimetrically determined mean rates of polymerization also exhibited a general trend of increase with increasing ethylferrocene concentration (Table V.6), but these overall rates were much lower than the initial rates observed dilatometrically.

These findings bear a close resemblance to the behaviour of the styrene/vinylferrocene system (Section V.B), and this suggests that a scheme involving propagation via styrene participating in an interaction with ethylferrocene is applicable here. Although initial rates of polymerization are available for only two ethylferrocene solutions and the pure styrene, a value for bk_5 (Section V.A) can be estimated from a plot of $\{(R_p/[St]^{2.5}) - k_p(k_i/2k_{tc})^{0.5}\}$ against $[EtFch]$ for these solutions. The gradient of this plot (Fig. V.10), which is based on the appropriate form of equation V.13, given below, is

$$\frac{R_p}{[St]^{2.5}} - k_p \left(\frac{k_i}{2k_{tc}} \right)^{0.5} = \left(\frac{k_i}{2k_{tc}} \right)^{0.5} bk_5 [EtFch] \quad (28)$$

$(1.52 \pm 0.08) \times 10^{-7} \text{ dm}^{7.5} \text{ mol}^{-2.5} \text{ s}^{-1}$, giving a value of $2,200 \pm 120 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$ for bk_5 , when a literature value⁶⁷ of

k_p and the value of $k_p(k_i/2k_{tc})^{0.5}$, obtained from $R_p/[St]^{2.5}$ for pure styrene, are used. The difference between this value and that obtained for ferrocene in section V.A ($174 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$) possibly arises from an increase in the degree of interaction between the ferrocene nuclei and the styrene, and a consequent increase in the activation of this styrene, due to the favourable inductive effect of the ethyl group.

As with the bulk styrene/vinylferrocene system, the decline in the rate of polymerization with time observed for this system may be explained by the formation of a retarder, which only reaches a steady concentration after a period of several hours. It is interesting to note that chain transfer to ethylferrocene could result in the formation of a radical identical to that formed in chain transfer to vinylferrocene, although in this case the mechanism would be hydrogen radical abstraction by the polymer radical. This link between two different systems exhibiting similar behaviour tends to support the possible explanation offered in section V.B, that is that the retarder may be derived from the vinylferrocenyl radical formed in a chain transfer step. Certainly, there is a link between the decline in rate and the concentration of ethylferrocene, since the mean rates of polymerization vary relatively little with ethylferrocene concentration compared with the initial rates. This requires that the solutions with the highest ethylferrocene concentration, and thus the highest initial rates of polymerization, experienced the greatest decline in rate.

In view of the above complications, detailed analysis of the molecular weight data was not attempted. (Table V.6). However, it is interesting to note that the decrease in molecular weight with increasing ethylferrocene concentration is insufficient, if

a normal kinetic scheme were to apply, even in the absence of retardation.

If the explanation offered to account for the increase in the initial rates of polymerization is correct, ethylferrocene cannot be taken as a model compound for polyvinylferrocene, since the latter does not seem to undergo specific interaction with aromatic solvents (Section IV.A).

V.G Summary

Observations of the bulk thermal polymerization of styrene in the presence of ferrocene cannot be explained by a normal kinetic scheme (Section II.A). A scheme has been proposed here, including propagation via styrene involved in an interaction with ferrocene, and this can fully account for the behaviour of this system.

The polymerization of styrene in the presence of vinylferrocene is strongly dependent on the precise conditions under which it takes place. Both the bulk thermal and the AIBN-initiated bulk thermal polymerizations exhibit high initial rates of polymerization followed by a marked decline in rate, and in the former case the initial rates of polymerization can be accommodated by the scheme proposed for the styrene/ferrocene system. However, the initial rates of polymerization in the AIBN-initiated polymerizations are not as high as would be predicted using data obtained for the purely thermal polymerization. Since a possible explanation for the decline in rate is the formation of a retarder, this difference in the behaviour of the two systems might be attributed to a higher rate of formation of the retarder due to the higher radical concentration. The polymerization behaviour of benzene solutions of styrene and vinylferrocene is markedly different from that of the bulk systems and seems to be accounted for by a normal kinetic scheme. This difference between the bulk and benzene solution systems may be due to the benzene interacting with the vinylferrocene, that is competing with the styrene, and thus exerting a greater influence on the polymerization than that of an inert diluent.

The bulk thermal polymerization of styrene in the presence

of ethylferrocene is similar to that of the bulk styrene/vinylferrocene system.

It should be noted that these polymerizations are not charge-transfer polymerizations, which proceed via polar intermediates, since the observation of an induction period in the polymerization of a styrene/vinylferrocene mixture in the presence of DPPH indicates that free-radical intermediates are involved.

Little of a general nature can be drawn from these studies, although it might be inferred, from results for the benzene solution thermal polymerization of styrene in the presence of vinylferrocene, that vinylferrocene is a more active chain transfer agent than styrene. This is in agreement with a very brief report¹⁰⁴ of a chain transfer constant for methylferrocene in the self-initiated styrene polymerization of 0.7×10^{-4} , which may be compared with that for toluene, 0.12×10^{-4} . However, no details of the precise conditions employed, or of the results from which this value was derived, were given, other than 'by the usual techniques for measuring these quantities', and thus, in view of the dependence of the behaviour of these systems on the polymerization conditions, the applicability of this value to a discussion of this study is uncertain.

Table V.1

The bulk thermal polymerization of styrene in the presence of ferrocene at 60.5°C

Mean [HFcH] mol dm ⁻³	Mean [St] mol dm ⁻³	Mean R _p x 10 ⁶ mol dm ⁻³ s ⁻¹	^a $\overline{DP}$
0	8.05	2.20	9,970
0.104	7.91	2.38	10,100
0.204	7.80	2.40	11,600
0.297	7.68	2.57	10,500
0.396	7.54	2.78	10,200
0.488	7.47	2.57	10,500
0.583	7.36	2.64	10,500

^a Estimated by GPC analysis.

Table V.2

The bulk thermal polymerization of styrene in the presence of low concentrations of vinylferrocene at 60°C

Initial values			Mean values	
[VFcH] mol dm ⁻³	[St] mol dm ⁻³	^a R _p x 10 ⁵ mol dm ⁻³ s ⁻¹	^a R _p x 10 ⁶ mol dm ⁻³ s ⁻¹	^b $\overline{DP}$
0	8.37	0.188	2.32	10,300
0.186	8.12	3.81	4.18	5,960
0.270	8.02	3.25	3.42	5,010
0.360	7.88	4.78	3.47	5,220
0.445	7.77	4.76	4.40	3,340
0.522	7.66	6.41	3.09	2,780
0.600	7.53	11.1	4.37	3,580
0.679	7.44	7.79	3.44	2,950

^a Calculated assuming that only styrene polymerized.

^b Determined by membrane osmometry.

Table V.3

The AIBN-initiated bulk thermal polymerization of styrene in the presence of low concentrations of vinylferrocene at 60°C
 $[AIBN] = (2.2 \pm 0.2) \times 10^{-3} \text{ mol dm}^{-3}$

Initial values			Mean values	
$[VFcH]$ mol dm ⁻³	$[St]$ mol dm ⁻³	^a $R_p \times 10^5$ mol dm ⁻³ s ⁻¹	^{a,b} $R_p \times 10^5$ mol dm ⁻³ s ⁻¹	^c $\overline{DP}$
0	8.37	^d 3.78	3.78	2090
0.0543	8.29	4.20	3.59	2400
0.109	8.22	4.22	3.58	2430
0.213	8.07	6.13	3.92	2430
0.318	7.92	7.99	4.66	2010
0.416	7.78	10.1	4.60	1710
0.512	7.65	11.3	4.43	1790
0.609	7.51	17.9	4.40	1980

^a Calculated assuming that only styrene polymerized.

^b Gravimetrically determined.

^c Determined by membrane osmometry.

^d This value from a gravimetric measurement,

$$[AIBN] = 2.84 \times 10^{-3} \text{ mol dm}^{-3}.$$

Table V.4

The benzene solution thermal polymerization of styrene in the presence of low concentrations of vinylferrocene at 60°C

Mean [St] mol dm ⁻³	Mean [VFcH] mol dm ⁻³	^a Mean R _p x 10 ⁷ mol dm ⁻³ s ⁻¹	^b $\overline{DP}$
3.92	0	8.90	9,040
3.92	0.0184	8.94	9,090
3.93	0.0575	8.05	8,120
3.94	0.0942	7.75	7,630
3.91	0.151	9.15	6,110
3.91	0.208	7.90	5,260
3.93	0.283	6.11	4,240

^a Calculated assuming that only styrene polymerized.

^b Determined by membrane osmometry.

Table V.5

The AIBN-initiated benzene solution polymerization of styrene.
in the presence of vinylferrocene at 60°C

$$[\text{AIBN}] = (1 \pm 0.01) \times 10^{-2} \text{ mol dm}^{-3}$$

$$[\text{St}] = 4 \pm 0.02 \text{ mol dm}^{-3}$$

Initial values		Mean values			
$[\text{VFcH}]$ mol. dm ⁻³	^a $R_p \times 10^5$ mol dm ⁻³ s ⁻¹	^a $R_p \times 10^5$ mol dm ⁻³ s ⁻¹	^b $[\eta]$ 100cm ³ g ⁻¹	$\overline{DP}_n$	$\overline{DP}_c$
0	6.67	6.36	0.372	680	452
0.0187	6.64	6.41	0.379	697	469
0.0571	7.03	6.55	0.371	676	455
0.0948	6.93	6.56	0.373	684	461
0.154	6.82	6.61	0.372	682	462
0.208	6.80	6.68	0.381	703	484
0.287	6.84	6.87	0.384	710	497

^a Calculated assuming that only styrene polymerized.

^b In toluene at 30°C.

^c Calculated from $\overline{DP}_n$ (Section III.B.15).

Table V.6

The bulk thermal polymerization of styrene in the presence of ethylferrocene at 60°C

Initial values			Mean values	
$[\text{EtFcH}]$ mol dm ⁻³	$[\text{St}]$ mol dm ⁻³	$R_p \times 10^5$ mol dm ⁻³ s ⁻¹	$R_p \times 10^6$ mol dm ⁻³ s ⁻¹	^a $\overline{DP}$
0	8.37	0.246	2.23	11,800
0.103	8.21	-	2.84	12,100
0.182	8.08	-	3.13	10,200
0.272	7.94	-	3.18	10,500
0.354	7.81	-	3.12	9,360
0.429	7.74	1.24	3.59	9,420
0.751	7.11	1.73	2.71	7,740

^a Estimated by GPC analysis.

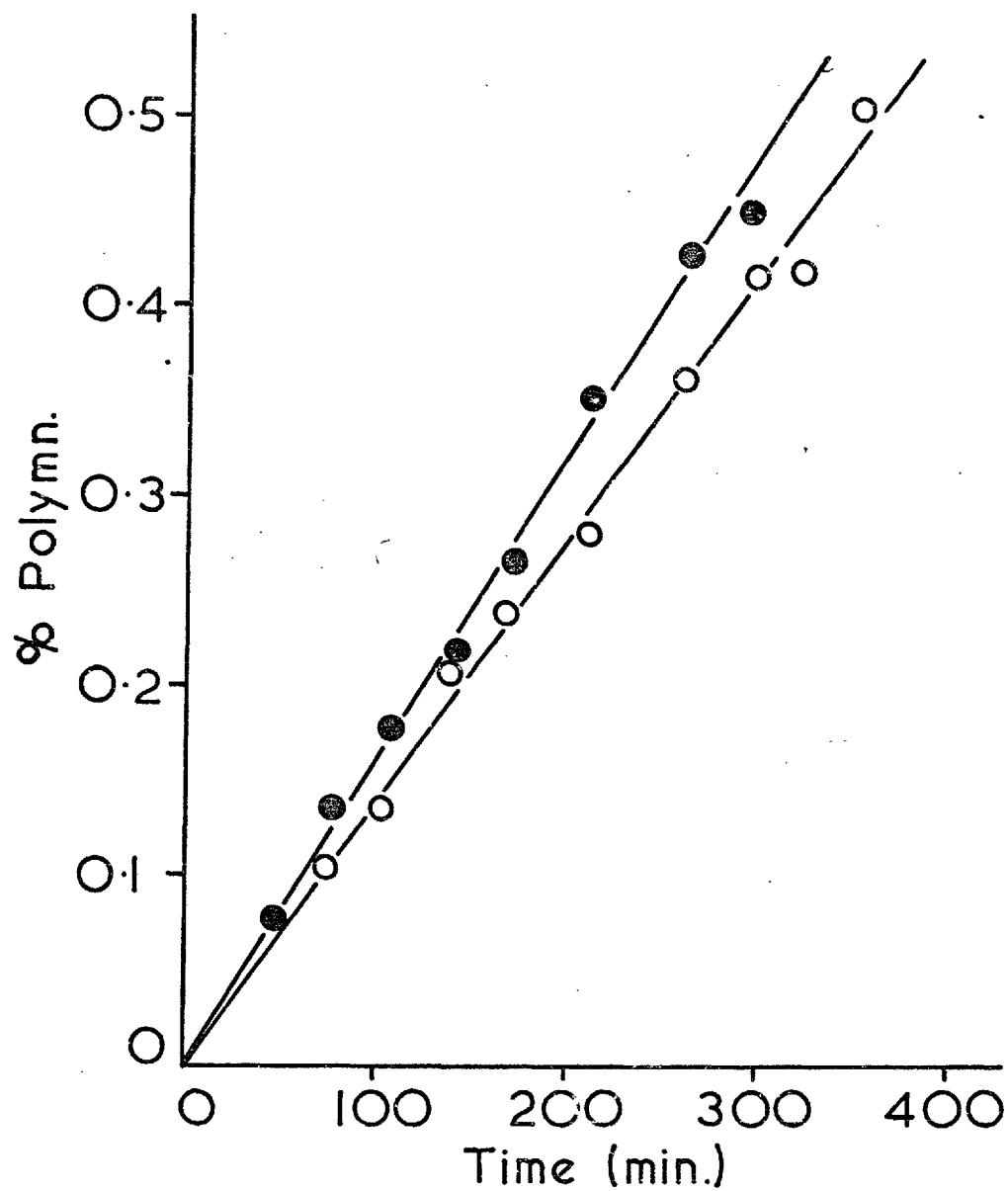


Fig. V.1

Percentage polymerization against time at 60.5°C,

○ pure styrene, ● initial concentration of ferrocene = 0.578 mol dm⁻³.

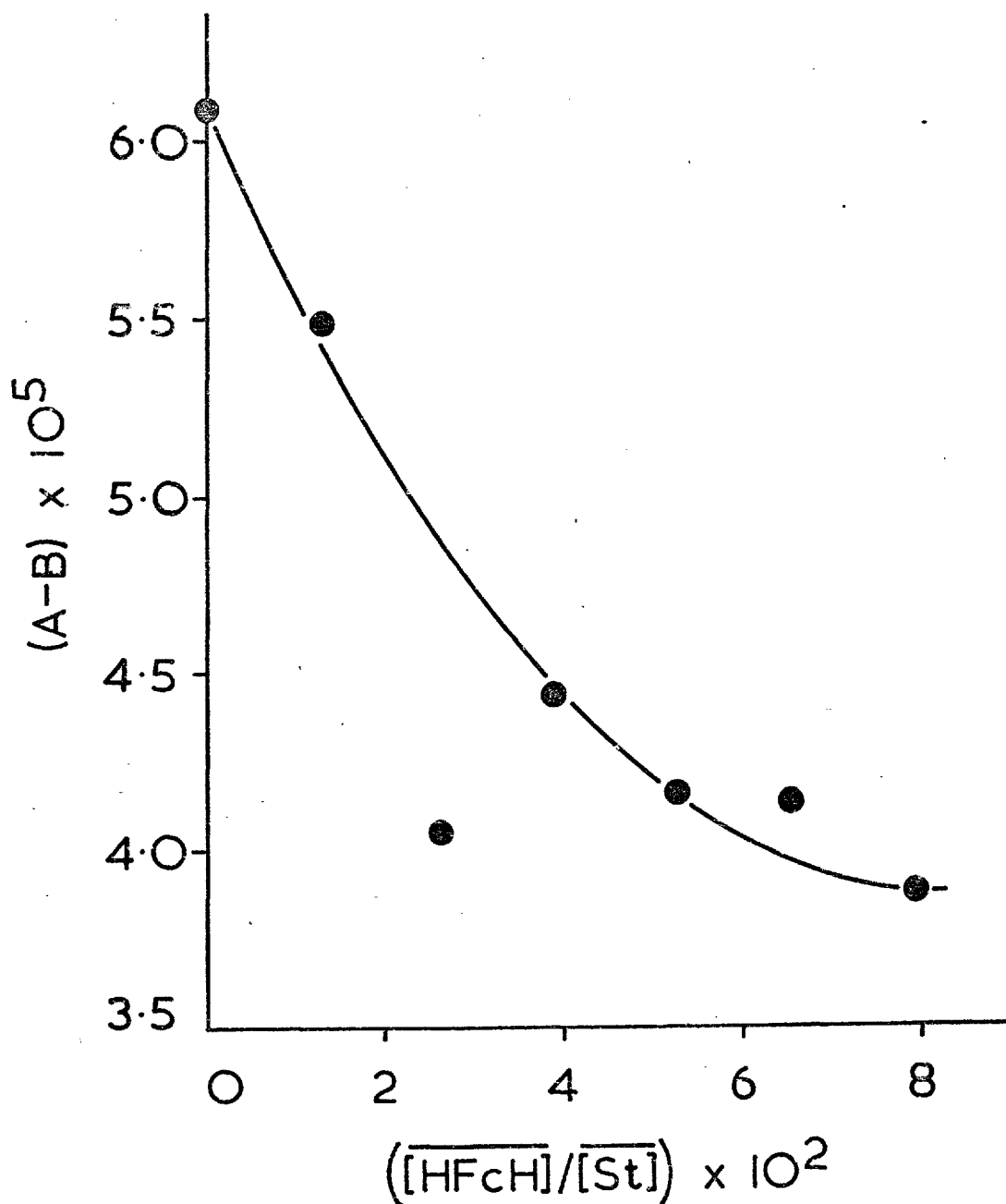


Fig. V.2

$(A - B)$ as a function of $[\text{HFcH}]/[\text{St}]$, where $A = 1/\overline{DP}$,
 $B = k_{tc}\overline{R}_p/k_p^2[\text{St}]^2$ and $[\text{St}]$ and $[\text{HFcH}]$ are the mean concentrations
of styrene and ferrocene respectively, for the bulk thermal
polymerization of styrene in the presence of ferrocene at 60.5°C .

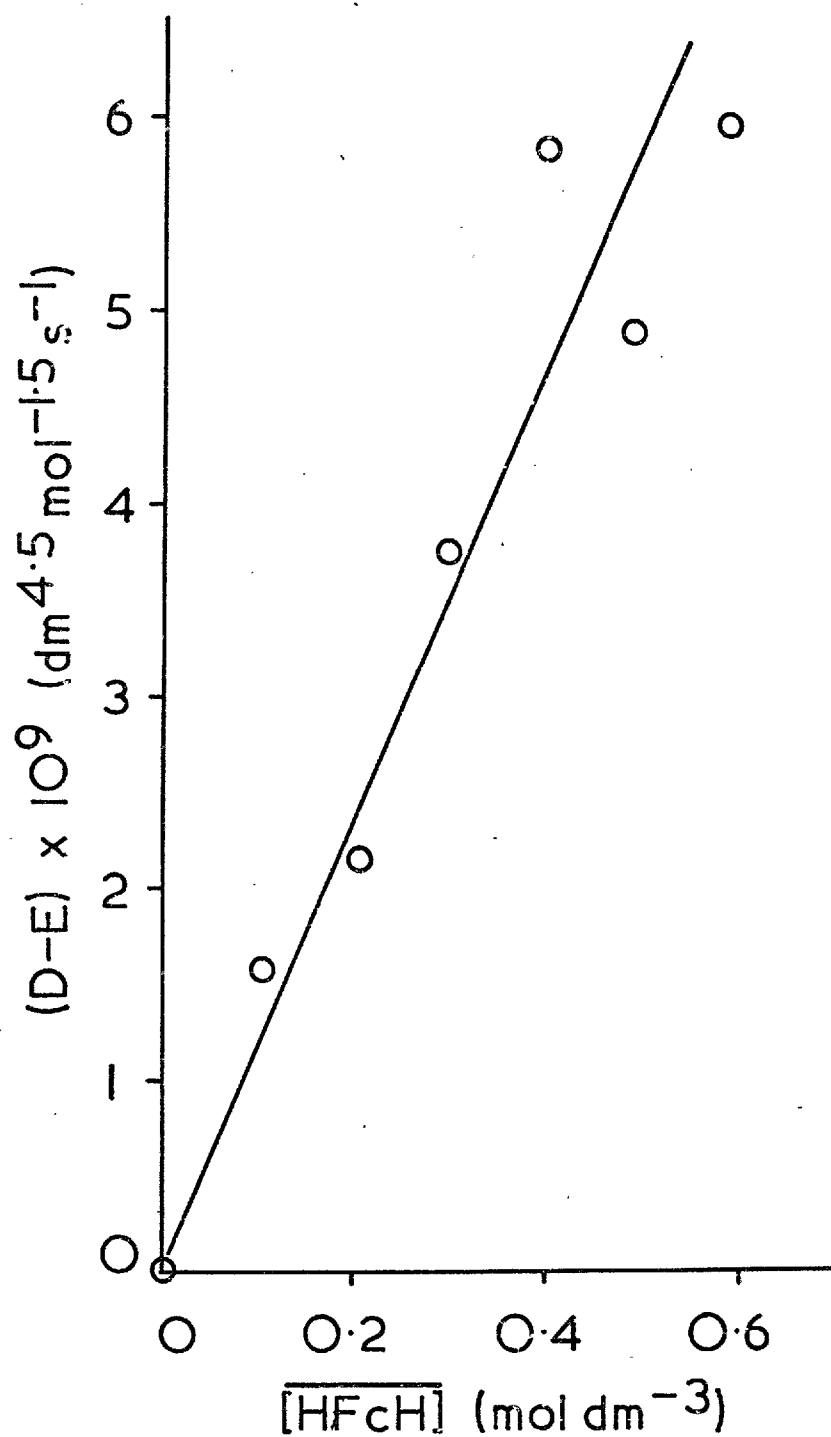


Fig. V.3

$(D - E)$ as a function of mean ferrocene concentration, where

$D = \bar{R}_p / [\text{St}]^{2.5}$ and $E = k_p (k_i / 2k_{tc})^{0.5}$, for the bulk thermal polymerization of styrene in the presence of ferrocene at 60.5°C .

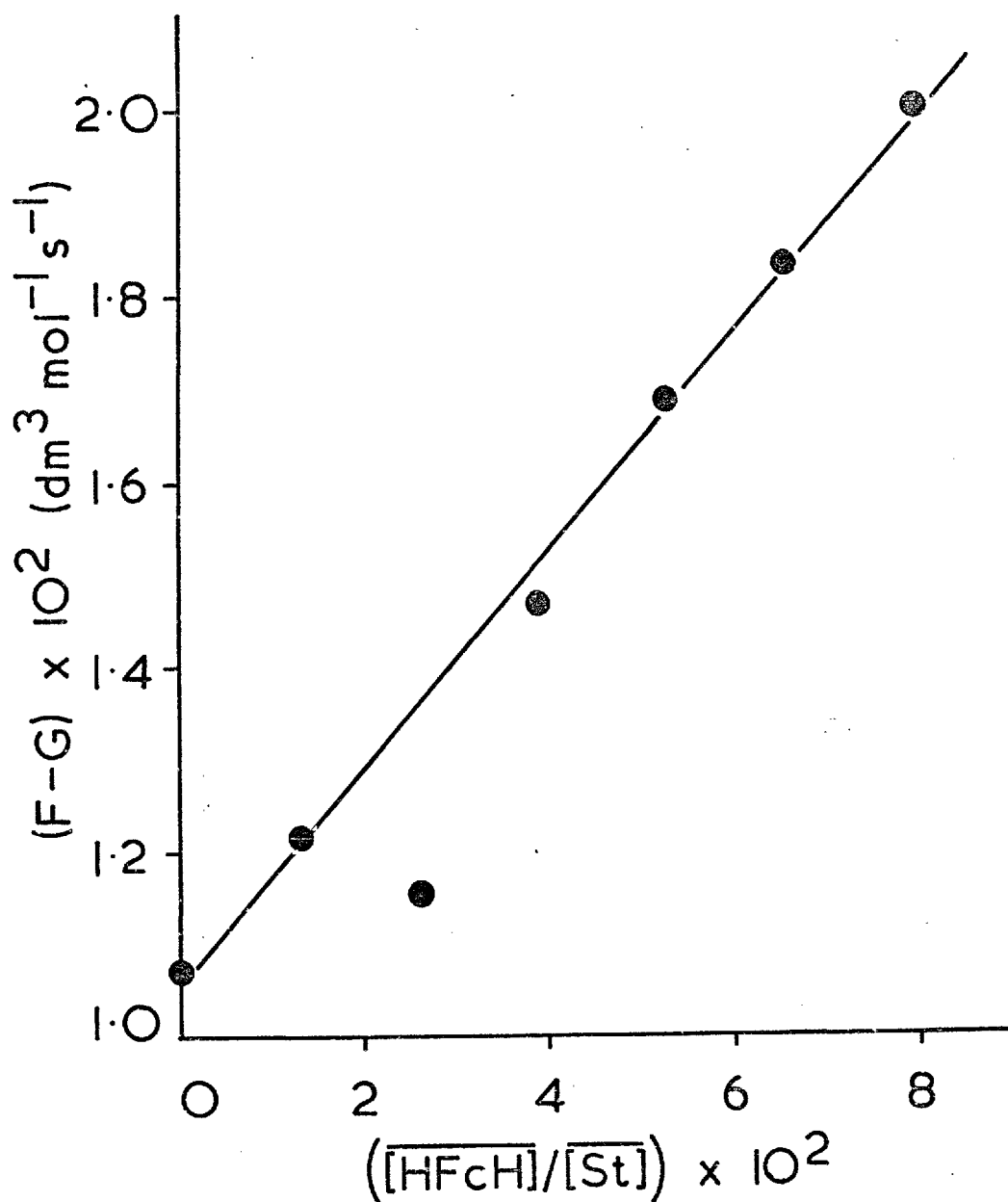


Fig. V.4

$(F - G)$ as a function of $[\text{HFcH}]/[\text{St}]$, where

$$F = (k_p + bk_5[\text{HFcH}])/\overline{DP} \text{ and } G = k_{tc}\overline{R}_p/[\text{St}]^2(k_p + bk_5[\text{HFcH}]),$$

for the bulk thermal polymerization of styrene in the presence of ferrocene at 60.5°C . The line drawn is obtained by omitting the point $[\text{HFcH}]/[\text{St}] = 2.61 \times 10^{-2}$ from the fitting.

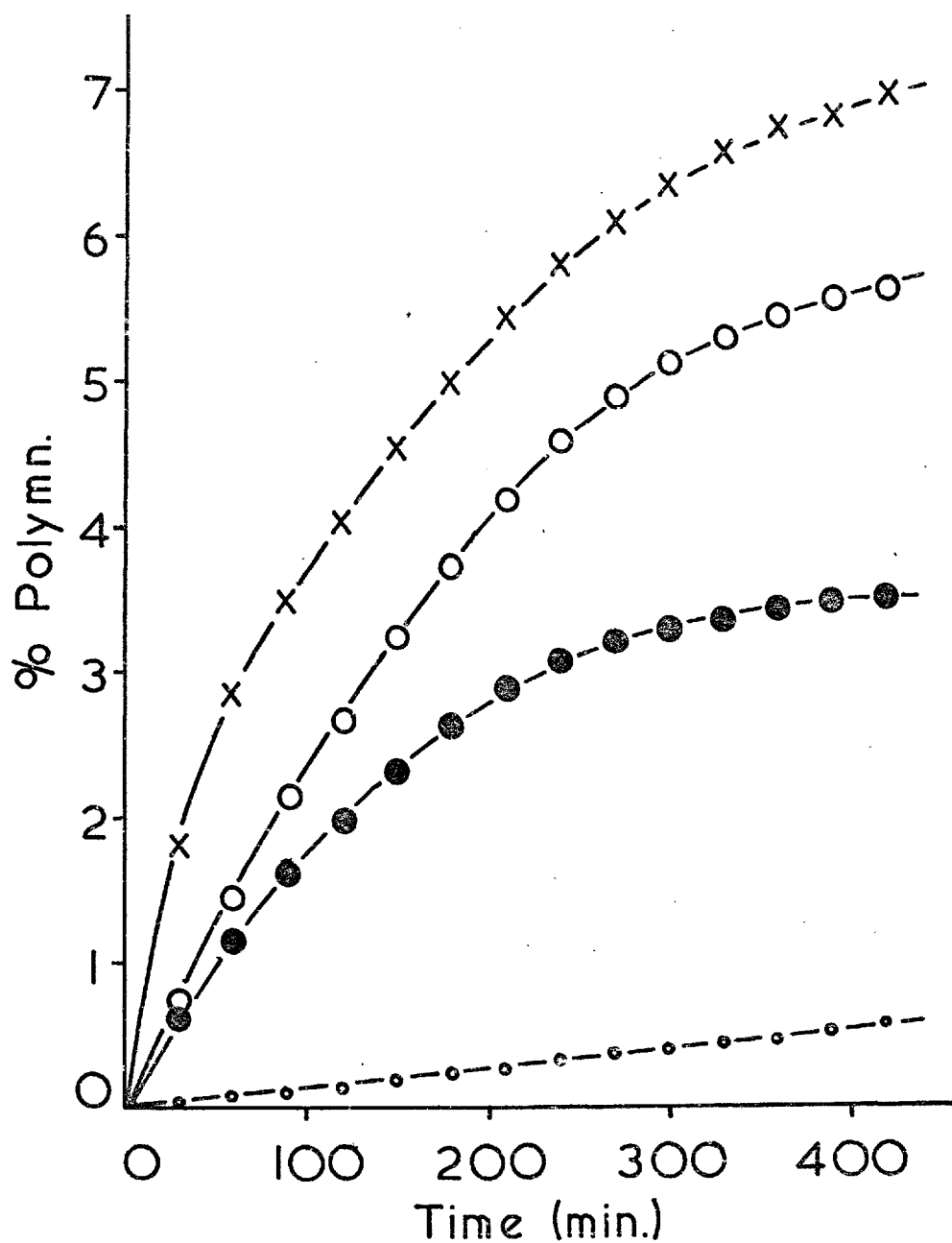


Fig. V.5

Percentage polymerization against time at 60°C, assuming that only styrene polymerized, ○ pure styrene, ●, ○ and × initial concentrations of vinylferrocene of 0.27 mol dm⁻³, 0.445 mol dm⁻³ and 0.6 mol dm⁻³ respectively.

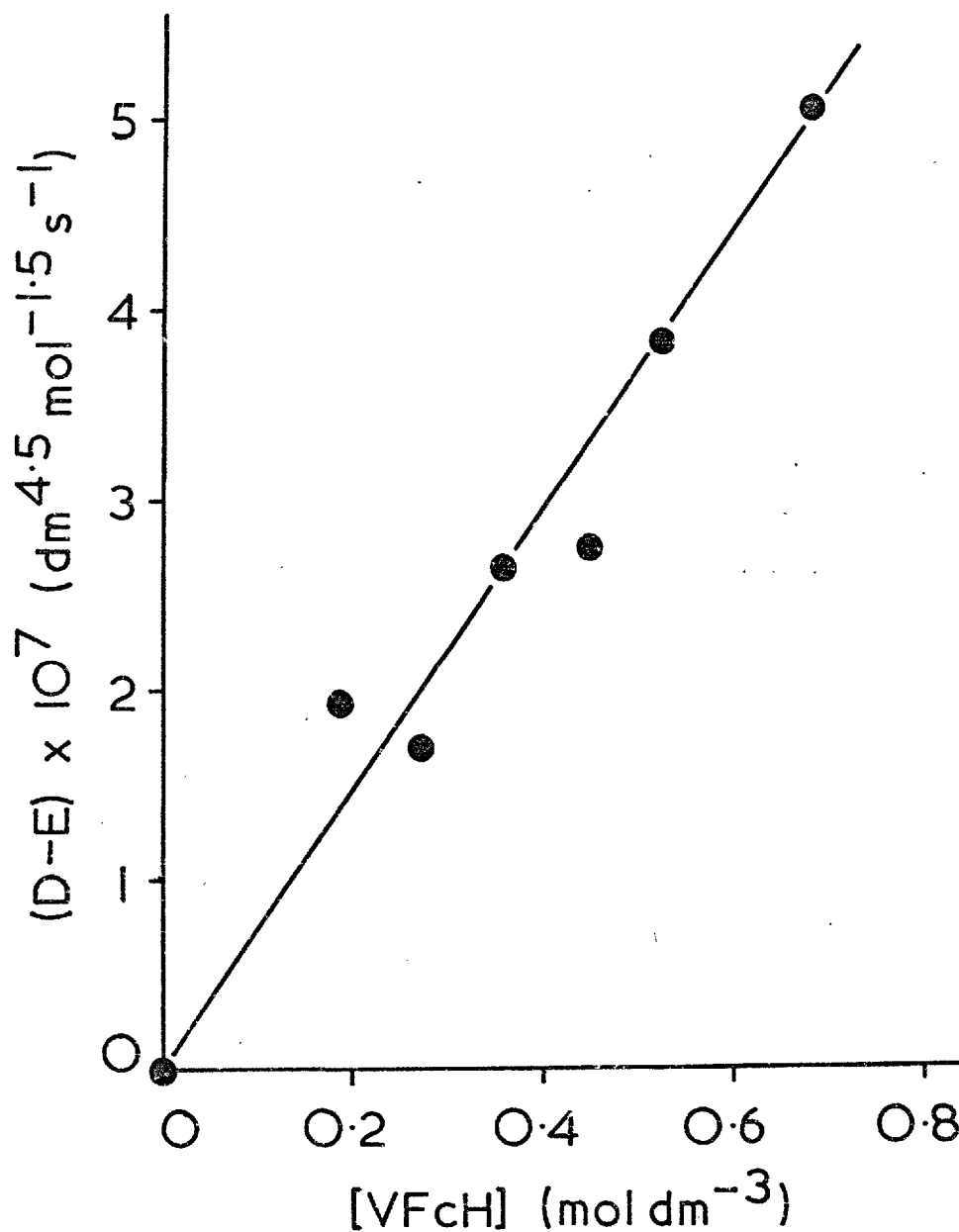


Fig. V.6

(D - E) as a function of initial vinylferrocene concentration, where $D = R_p/[St]^{2.5}$ and $E = k_p(k_i/2k_{tc})^{0.5}$, for the bulk thermal polymerization of styrene in the presence of low concentrations of vinylferrocene at 60°C.

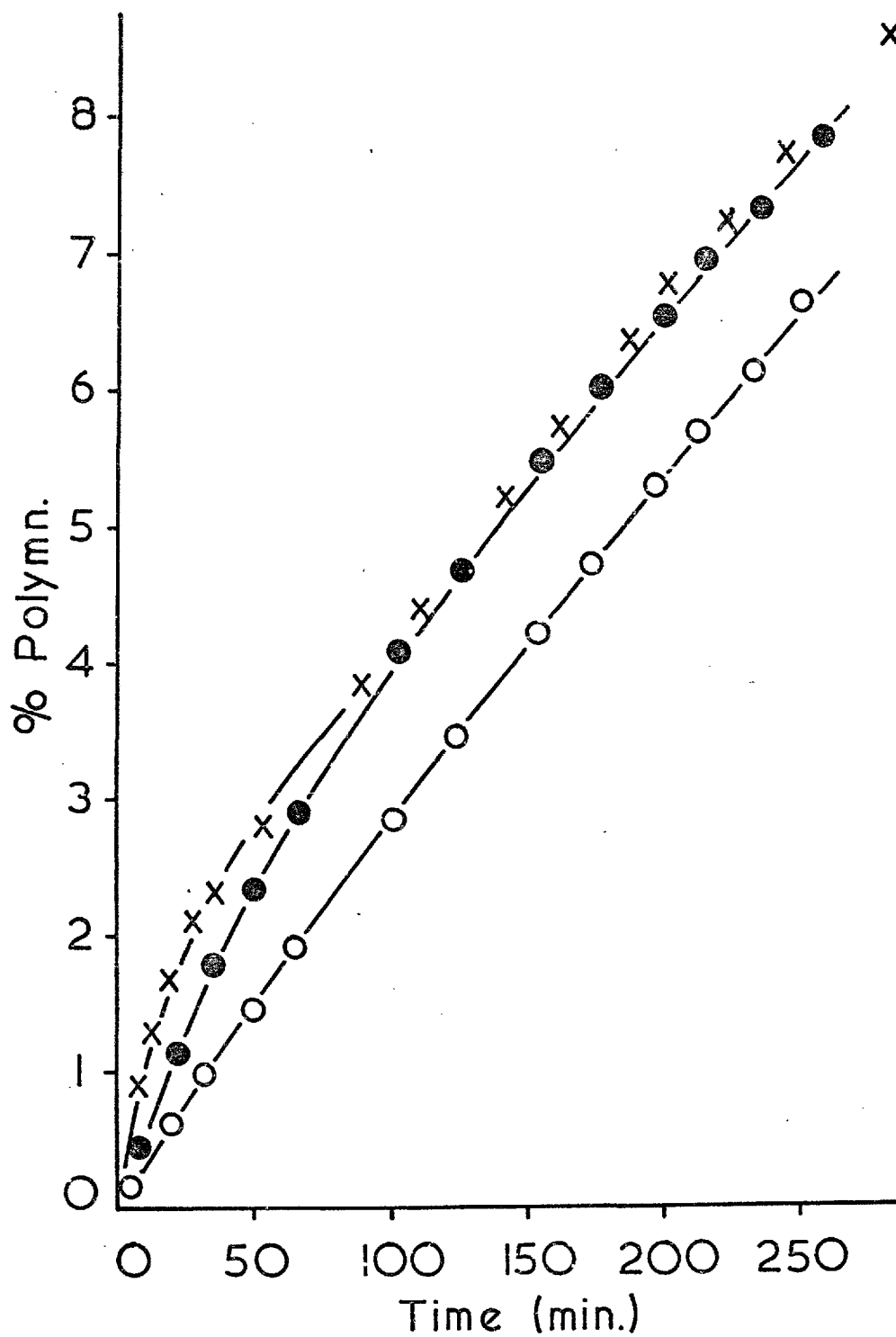


Fig. V.7

Percentage polymerization against time at 60°C, assuming that only styrene polymerized. Initial $[AIBN] = (2.2 \pm 0.2) \times 10^{-3} \text{ mol dm}^{-3}$ and initial $[VFcH]$ of $0.109 \text{ mol dm}^{-3}$ (O), $0.318 \text{ mol dm}^{-3}$ (●) and $0.609 \text{ mol dm}^{-3}$ (X).

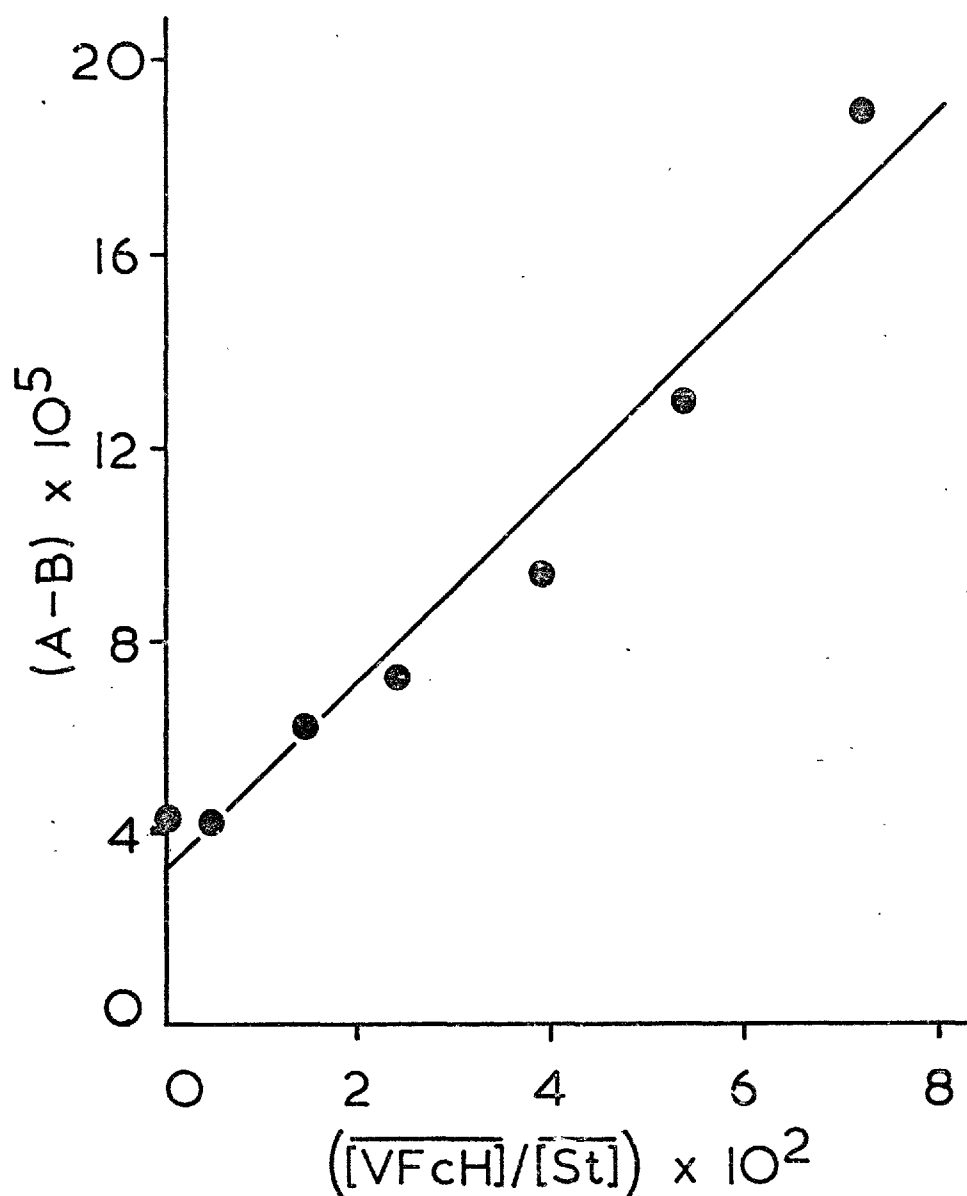


Fig. V.8

$(A - B)$ as a function of $[\overline{\text{VFcH}}]/[\overline{\text{St}}]$, where $A = 1/\overline{\text{DP}}$ and $B = k_{tc}\bar{R}_p/k_p^2[\overline{\text{St}}]^2$, for the benzene solution thermal polymerization of styrene in the presence of low concentrations of vinylferrocene at 60°C .

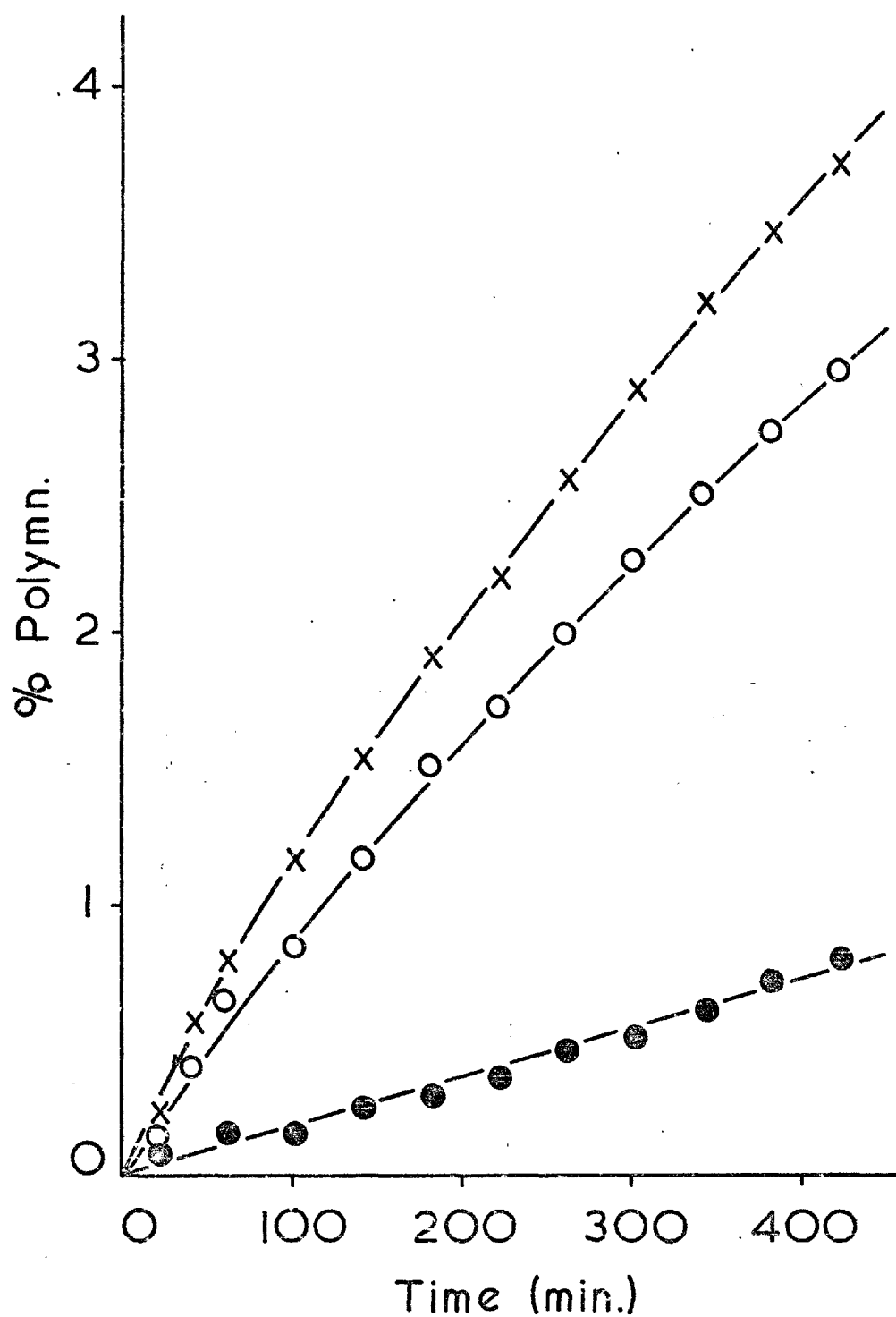


Fig. V.9

Percentage polymerization against time at 60°C, ● pure styrene, O and X initial concentrations of ethylferrocene of 0.429 mol dm⁻³ and 0.751 mol dm⁻³ respectively.

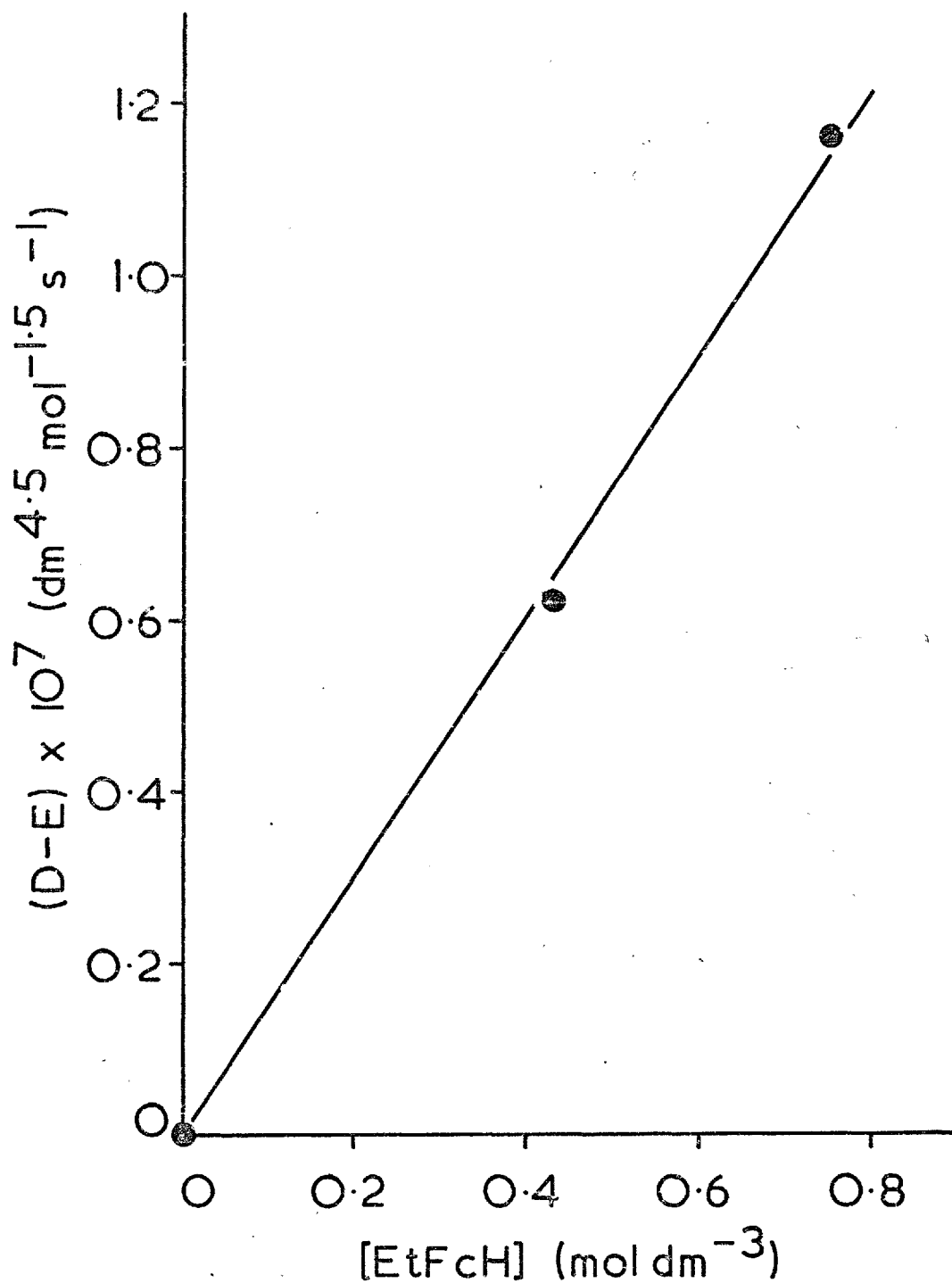


Fig. V.10

(D - E) as a function of initial ethylferrocene concentration, where $D = R_p/[St]^{2.5}$ and $E = k_p(k_i/2k_{tc})^{0.5}$, for the bulk thermal polymerization of styrene in the presence of ethylferrocene at 60°C.

VI The polymerization of styrene in the presence of
ferrocene and cyclohexanone

The presence of ferrocene and a ketone, particularly a cyclic ketone such as cyclohexanone, has been found¹⁰¹ to increase greatly the rate of polymerization of methyl methacrylate, whilst ferrocene alone had little effect. Ferrocene was shown to have no effect on the polymerization of styrene in benzene solution and, because the yields were lower than in the methyl methacrylate polymerizations, it was concluded also that ferrocene/cyclohexanone did not polymerize styrene¹⁰¹. However, in spite of the low ferrocene concentration used (ca. 2.5×10^{-2} mol dm⁻³), with cyclohexanone as solvent, there was a four-fold increase in conversion after 20 hr, with respect to the benzene solution polymerization of styrene.

In view of the small effects observed for the ferrocene/styrene system (Section V.A), a more complete kinetic study of the ferrocene/cyclohexanone/styrene system was undertaken. As a part of this study, a value was determined for the chain transfer constant for cyclohexanone in the self-initiated polymerization of styrene.

VI.A The determination of the chain transfer constant for
cyclohexanone in the self-initiated polymerization of
styrene

Styrene was polymerized thermally, at 60°C, in the presence of varying concentrations of cyclohexanone (CXON). Dilatometric measurements demonstrated that all of the polymerizations were linear with respect to time, up to the low conversions used. The gravimetrically determined mean rates of polymerization were

virtually independent of cyclohexanone concentration (Table VI.1). The diluent effect requires that the rate of polymerization decreases with decreasing monomer concentration, but since the total decrease in monomer concentration was only ca. 6%, the observed behaviour was, within experimental limits, normal.

The system may be taken, therefore, to follow a normal, simple kinetic scheme (Section II.A) and a suitably amended form of equation V.1, given below, may be applied to the molecular

$$\frac{1}{\overline{DP}} - \frac{k_{tc} R_p}{k_p^2 [St]^2} = C_m + C_s \frac{[CXON]}{[St]} \quad (1)$$

weights of the polymers formed (Table VI.1). A plot of the left-hand side of equation VI.1 against $[CXON]/[St]$, using mean values for the experimental parameters and literature values⁶⁷ for k_p ($176 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and k_{tc} ($3.6 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$), is a reasonable straight line (Fig. VI.1). A least mean squares analysis of the data gives a value of $(5.33 \pm 1.8) \times 10^{-4}$ for C_s and of $(7.43 \pm 0.75) \times 10^{-5}$ for C_m , which may be compared with a literature value⁶⁷ for C_m of 6.02×10^{-5} .

The value of C_s obtained here indicates that cyclohexanone is only a moderate chain transfer agent in the polymerization of styrene.

VI.B The bulk thermal polymerization of styrene in the presence of a constant concentration of ferrocene and varying concentrations of cyclohexanone

The bulk thermal polymerization of styrene solutions of ferrocene ($4.73 \times 10^{-2} \text{ mol dm}^{-3}$) were carried out at 60°C in the presence of varying concentrations of cyclohexanone. Dilatometric measurements demonstrated that the polymerizations were linear with respect to time, up to the low conversions employed, and the initial rates of polymerization obtained from these measurements exhibited a trend of increasing rate with increasing cyclohexanone concentration. This trend was also apparent in the gravimetrically determined mean rates of polymerization (Table VI.2). The general trend of decline in molecular weight of the polymers formed (Table VI.2) with increasing rate of polymerization suggests that this rate increase derives from an increase in the rate of initiation in the system. This is further substantiated by results obtained in a study of styrene polymerization at constant cyclohexanone concentration and varying ferrocene concentration (Section VI.C). At this very low ferrocene concentration, therefore, a normal kinetic scheme (Section II.A) may be applied to this system and then, from equation II.6,

$$\left(\frac{R_p}{[St]} \right)^2 = \frac{k_p^2 I}{2k_{tc}} \quad (2)$$

Since I , the rate of initiation, seems to be some function of cyclohexanone concentration, a plot of $(R_p/[St])^2$ against $[CXON]$ is an appropriate way of depicting the behaviour of the rate of polymerization with cyclohexanone concentration. Using mean values, this plot is a curve (Fig. VI.2). This demonstrates that the rate of initiation associated with ferrocene and

cyclohexanone is not first order in cyclohexanone concentration.

If a normal kinetic scheme is applicable to this system, the molecular weight data should fit equation VI.1. These results are given in a suitable form in table VI.3. When a correction is applied to the value for the polymer formed in the polymerization of pure styrene, to allow for the absence of ferrocene (Fig. V.2 indicates that a reduction of ca. 5% is necessary), the values obtained for $\left\{ (1/\overline{DP}) - (k_{tc}\overline{R}_p/k_p^2[\text{St}]^2) \right\}$ are constant to within ca. $\pm 6\%$. This is well within experimental limits. However, these values should increase as $[\text{CXON}]/[\text{St}]$ increases; a total change of ca. 23% would be expected if the value for C_s obtained in section VI.A is correct. Failure to exhibit this change may be due, in part, to experimental error in the values obtained here and also to an overestimation of the value of C_s for cyclohexanone. Furthermore, for all but the most concentrated cyclohexanone solution, the predicted change would be less than 9%, which is within experimental limits. If the contribution of the term involving C_s in equation VI.1 is taken to be small under these conditions, the values obtained for $\left\{ (1/\overline{DP}) - (k_{tc}\overline{R}_p/k_p^2[\text{St}]^2) \right\}$ may be compared with a literature value⁶⁷ for C_m for styrene of 6.02×10^{-5} .

Thus, the molecular weights of the polymers obtained in this system may be best considered as being not inconsistent with polymerization proceeding by the normal mechanisms, with an increased rate of initiation attributable to the presence of both ferrocene and cyclohexanone.

VI.C The bulk thermal polymerization of styrene in the presence of a constant concentration of cyclohexanone and varying concentrations of ferrocene

The thermal polymerization of styrene solutions of cyclohexanone ($0.489 \text{ mol dm}^{-3}$) were carried out at 60°C in the presence of varying concentrations of ferrocene. As with the styrene polymerizations at constant ferrocene concentration and varying cyclohexanone concentrations (Section VI.B), dilatometric measurements demonstrated that the polymerizations were linear with respect to time, up to the low conversions used, and initial rates of polymerization derived from these measurements exhibited a trend of increasing rate with increasing ferrocene concentration. The gravimetrically determined mean rates of polymerization confirmed this trend (Table VI.4).

The lower molecular weights of polymers formed in the presence of ferrocene, with respect to that formed in its absence (Table VI.4), is contrary to the behaviour of this system in the absence of cyclohexanone (Section V.A), and suggests that ferrocene and cyclohexanone together give rise to an increased rate of initiation. Thus, as with the results obtained at constant ferrocene concentration and varying cyclohexanone concentrations (Section VI.B), an appropriate means of representing the behaviour of the rate of polymerization with additive concentration, in this case ferrocene concentration, is a plot of $(R_p/[St])^2$ against $[HFcH]$. This plot, using mean values, is a curve (Fig. VI.3), similar to that obtained for $(R_p/[St])^2$ against $[CXON]$ (Fig. VI.2). It is noteworthy that the value of $(R_p/[St])^2$ obtained from fig. VI.3 for $[HFcH]$ of $4.73 \times 10^{-2} \text{ mol dm}^{-3}$ and $[CXON]$ of $0.489 \text{ mol dm}^{-3}$ ($12.1 \times 10^{-14} \text{ s}^{-2}$) would fit well into fig. VI.2, indicating

the compatibility of the two studies on which these plots are based. The curve obtained for the plot of $(R_p/[St])^2$ against $[HFcH]$ indicates that the rate of initiation associated with ferrocene and cyclohexanone is not first order in ferrocene concentration.

When equation VI.3, a suitably modified form of equation V.1, which derives from a normal kinetic scheme, is applied to the molecular weight data, it would seem that the ferrocene is

$$\frac{1}{\overline{DP}} - \frac{k_{tc} R_p}{k_p^2 [St]^2} = C_m + C_s \frac{[HFcH]}{[St]} \quad (3)$$

exerting also the anomalous effect observed in the absence of cyclohexanone (Section V.A), since there is, perhaps, a general decline in the value of the left-hand side of equation VI.3 as $[HFcH]/[St]$ increases (Table VI.5).

VI.D Summary

A value of $(5.33 \pm 1.8) \times 10^{-4}$ was determined for the chain transfer constant for cyclohexanone in styrene polymerization.

The results obtained here for the styrene/cyclohexanone/ferrocene system indicate that ferrocene and cyclohexanone together give rise to free-radical initiating species. However, at sufficiently high ferrocene concentrations, the anomalous behaviour previously observed in the presence of ferrocene alone (Section V.A) also may exert an effect.

This study does not provide any information on the precise mechanism of radical formation from ferrocene and cyclohexanone, although curves obtained for plots of $(R_p/[St])^2$, which is proportional to the rate of initiation, against ferrocene or cyclohexanone concentration suggest that this mechanism is complex, involving a series of steps.

It has been suggested¹⁰¹ that the carbonyl group of the cyclohexanone coordinates to the metal atom of ferrocene in an activated state, and leads to the generation of an initiating radical. The findings of this study are not consistent with such a simple mechanism. Furthermore, no significant difference was found between the visible spectrum of ferrocene in cyclohexanone and in ethanol or n-heptane solution, the latter solvents being assumed to be inert.

Table VI.1

The bulk thermal polymerization of styrene in the presence of cyclohexanone at 60°C

Mean [CXON] mol dm ⁻³	Mean [St] mol dm ⁻³	Mean R _p x 10 ⁶ mol dm ⁻³ s ⁻¹	^a $\overline{DP}$
0	8.15	1.93	8,840
0.0976	8.06	2.01	8,790
0.183	7.98	2.06	8,010
0.270	7.90	2.07	7,710
0.361	7.81	2.15	7,390
0.440	7.74	2.18	7,050
0.530	7.67	2.10	6,220

^a Determined by membrane osmometry.

Table VI.2

The bulk thermal polymerization of styrene at 60°C in the presence of ferrocene and varying concentrations of cyclohexanone

$$[\text{HFcH}] = (4.73 \pm 0.06) \times 10^{-2} \text{ mol dm}^{-3}$$

Mean [CXON] mol dm ⁻³	Mean [St] mol dm ⁻³	Mean R _p x 10 ⁶ mol dm ⁻³ s ⁻¹	^a $\overline{\text{DP}}$
^b 0	8.22	1.97	9,400
0.0113	8.18	2.15	9,430
0.0207	8.13	2.20	9,860
0.0289	8.12	2.26	9,300
0.0421	8.10	2.42	9,200
0.0476	8.09	2.50	8,770
0.1010	8.04	2.50	8,710
0.2540	7.90	2.61	9,040

^a Estimated by GPC analysis.

^b No ferrocene added.

Table VI.3

Treatment of the molecular weights of polymers formed in the polymerization of styrene at 60°C in the presence of a constant concentration of ferrocene and varying concentrations of cyclohexanone

$1/\overline{DP}$ A x 10 ⁵	$k_{tc}\overline{R}_p/k_p^2[\text{St}]^2$ a B x 10 ⁵	A - B x 10 ⁵	$[\text{CXON}]/[\text{St}]$ x 10 ²
10.6	3.39	b 7.21	0
10.6	3.74	6.86	0.138
10.2	3.87	6.33	0.254
10.8	3.97	6.83	0.356
10.9	4.28	6.62	0.520
11.4	4.44	6.96	0.588
11.5	4.50	7.00	1.25
11.1	4.86	6.24	3.21

a Literature values⁶⁷ of k_p (176 dm³ mol⁻¹ s⁻¹) and k_{tc} (3.6 x 10⁷ dm³ mol⁻¹ s⁻¹) used.

b No ferrocene added.

Table VI.4

The bulk thermal polymerization of styrene at 60°C in the presence of cyclohexanone and varying concentrations of ferrocene

$$[\text{CXON}] = 0.489 \pm 0.009 \text{ mol dm}^{-3}$$

Mean [HFch] mol dm ⁻³	Mean [St] mol dm ⁻³	Mean R _p x 10 ⁶ mol dm ⁻³ s ⁻¹	^a $\overline{\text{DP}}$
0	7.78	2.01	9,230
0.0204	7.73	2.31	8,260
0.0394	7.69	2.62	6,190
0.0610	7.66	2.77	7,310
0.0777	7.63	3.09	8,470
0.0983	7.61	2.85	8,370
0.147	7.56	2.90	8,330
0.239	7.47	2.87	8,410

^a Estimated by GPC analysis.

Table VI.5

Treatment of the molecular weights of polymers formed in the polymerization of styrene at 60°C in the presence of a constant concentration of cyclohexanone and varying concentrations of ferrocene

$1/\overline{DP}$ A x 10 ⁵	$k_{tc} \overline{R}_p / k_p^2 [St]^2$ a B x 10 ⁵	A - B x 10 ⁵	$[HFcH] / [St]$ x 10 ²
10.8	3.86	6.94	0
12.1	4.50	7.60	0.264
16.2	5.14	11.1	0.512
13.7	5.49	8.21	0.796
11.8	6.18	5.62	1.02
12.0	5.71	6.29	1.29
12.0	5.90	6.10	1.94
11.9	5.98	5.92	3.20

a Using literature values⁶⁷ of k_p (176 dm³ mol⁻¹ s⁻¹) and k_{tc} (3.6 x 10⁷ dm³ mol⁻¹ s⁻¹).

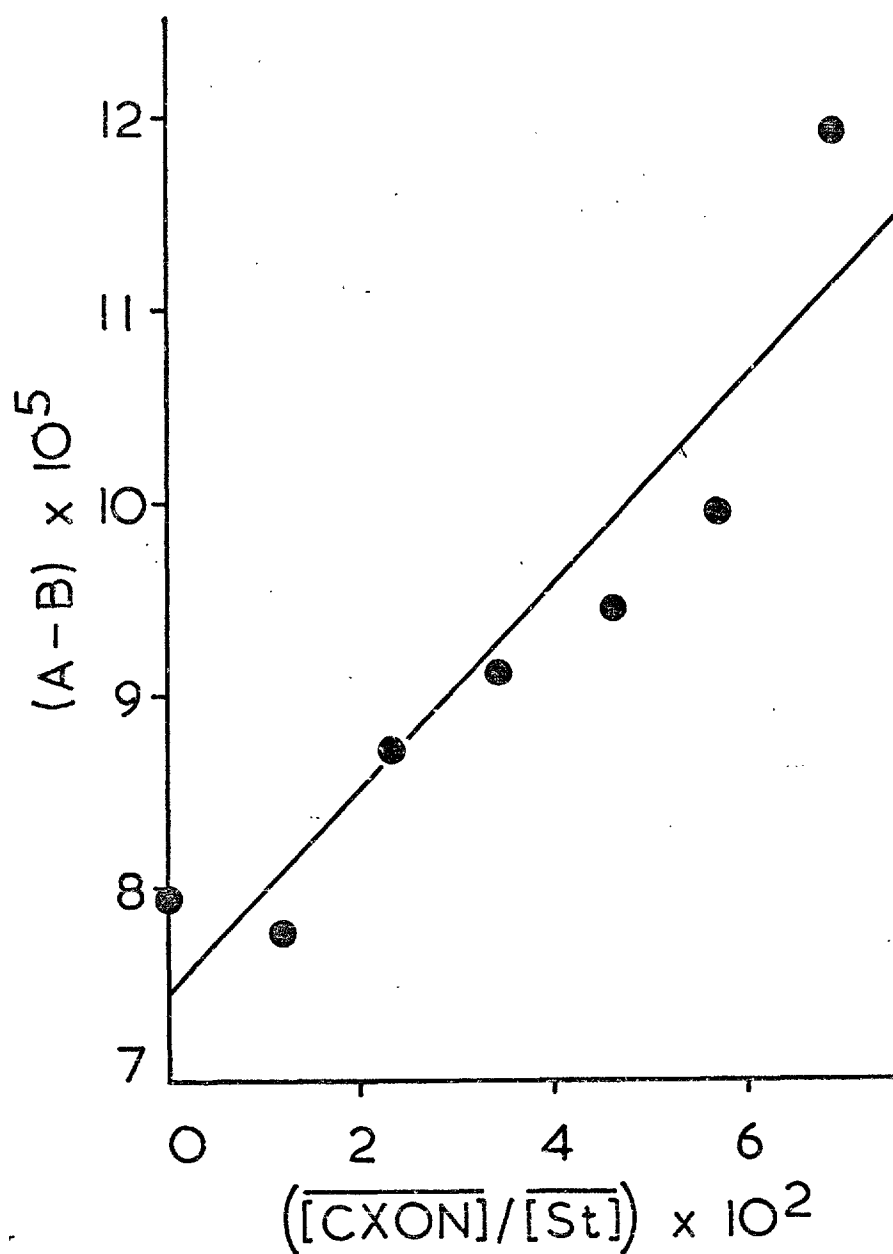


Fig. VI.1

$(A - B)$ as a function of $[CXON]/[St]$, where $A = 1/\overline{DP}$ and $B = k_{tc}\overline{R}_p/k_p^2[St]^2$, for the bulk thermal polymerization of styrene in the presence of cyclohexanone at $60^\circ C$.

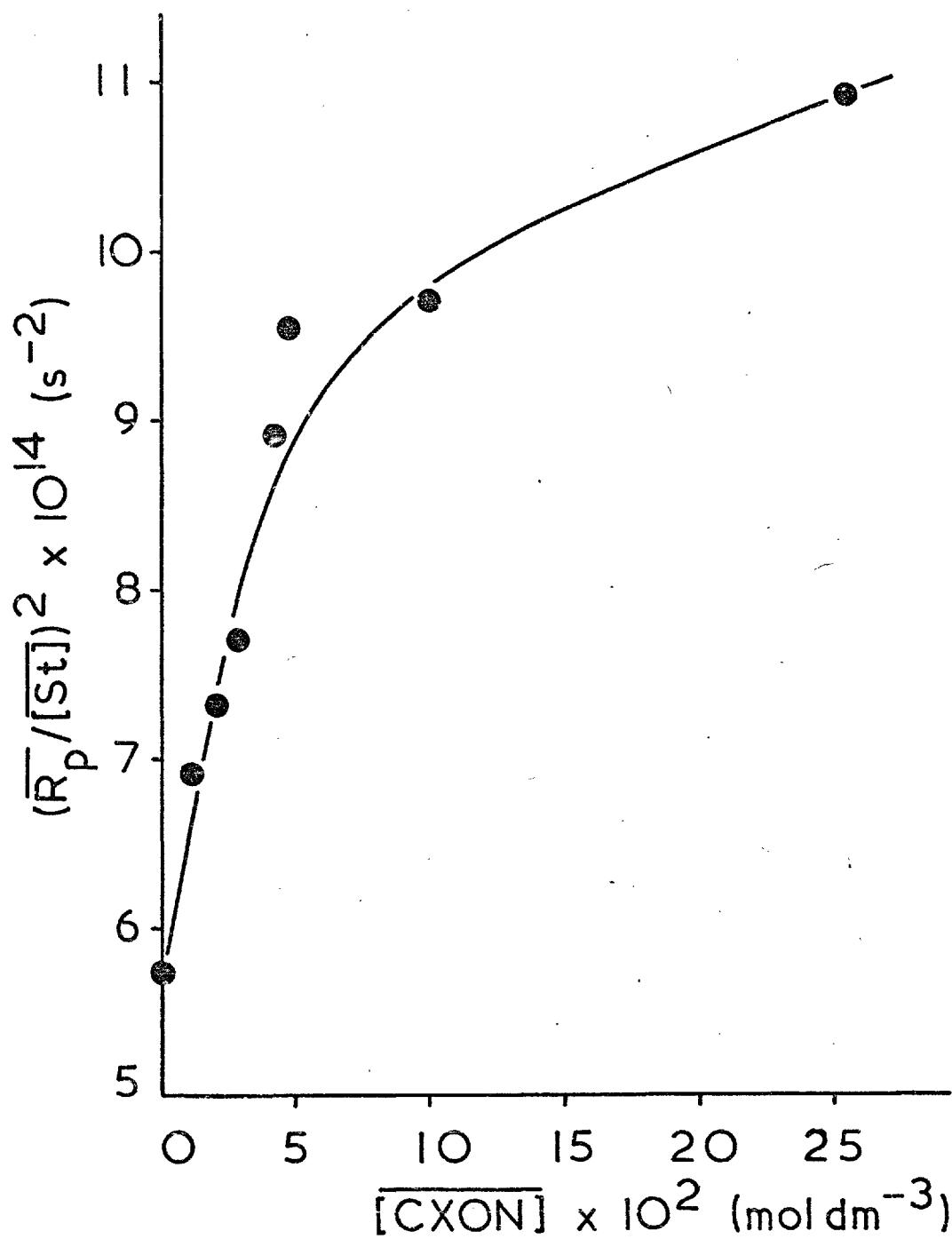


Fig. VI.2

$(\bar{R}_p/[St])^2$ as a function of mean cyclohexanone concentration, for the bulk thermal polymerization of styrene at 60°C in the presence of ferrocene and cyclohexanone.

$$[HFch] = (4.73 \pm 0.06) \times 10^{-2} \text{ mol dm}^{-3}.$$

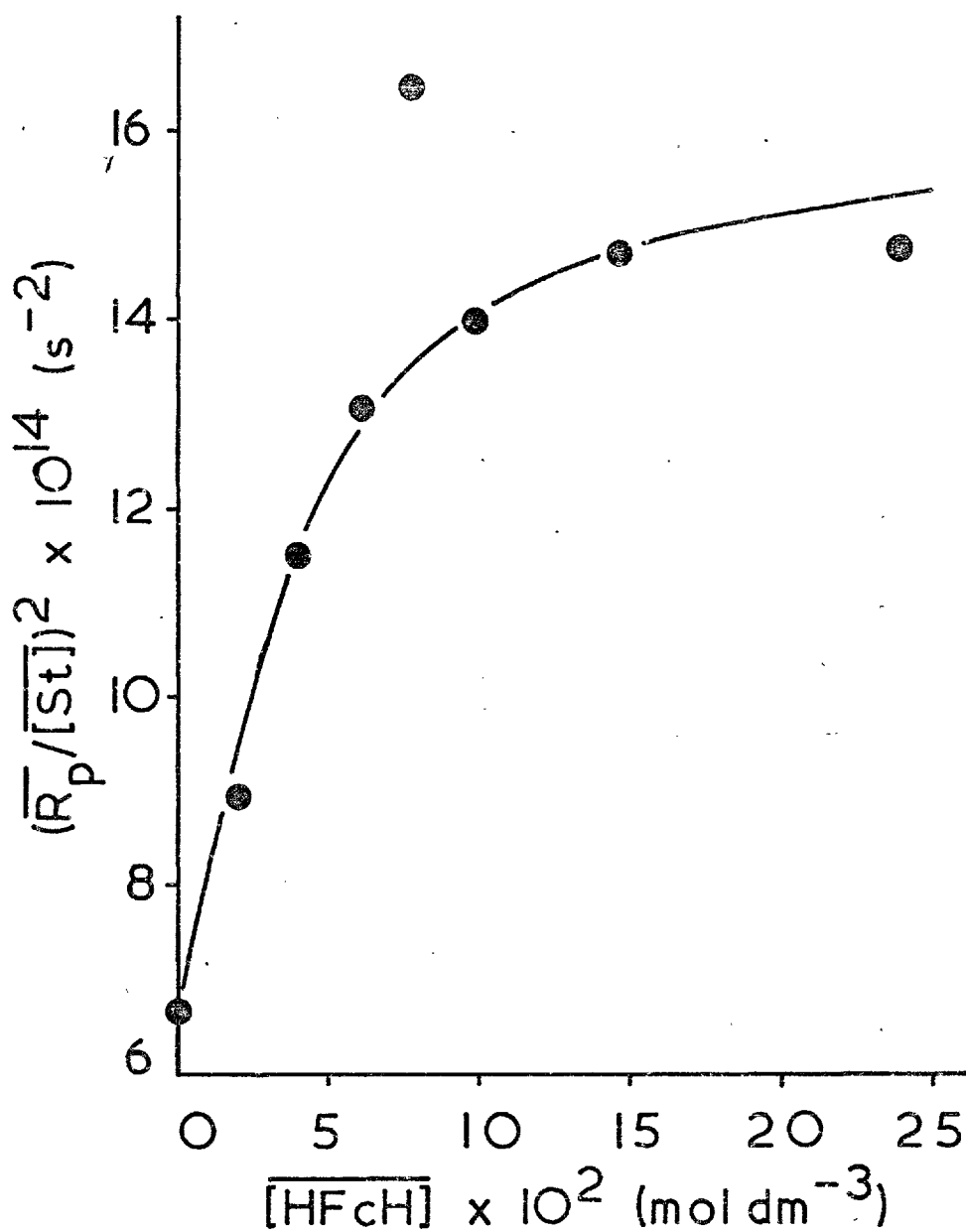


Fig. VI.3

$(\bar{R}_p/[\text{St}])^2$ as a function of mean ferrocene concentration, for the bulk thermal polymerization of styrene at 60°C in the presence of ferrocene and cyclohexanone.

$$[\text{CXON}] = 0.489 \pm 0.009 \text{ mol dm}^{-3}.$$

VII The AIBN-initiated homopolymerization of vinylferrocene
 in dioxane

The free-radical homopolymerization of vinylferrocene has been reported on a number of occasions^{1,2,7-12,14,15}, the majority of these studies being performed on benzene solutions, although the bulk polymerization has received some attention^{2,15}. One of the more detailed studies¹⁵ concerned the effect of temperature and the mode of initiator (AIBN) addition (single or sequential) on the polymer yield and molecular weight from solution and bulk polymerizations. As would be expected, higher yields were obtained by continuous or multiple AIBN addition and higher polymer molecular weights were observed at higher monomer concentrations and lower polymerization temperatures. Also, considerable branching was detected in the higher molecular weight polymers, indicative of the chain transfer activity of the homopolymer. However, even when solution polymerizations were taken to quite high conversion, polymer molecular weights were low (4,000-5,000) and independent of both the mode of addition of AIBN and of the overall concentration of AIBN. This is contrary to expected behaviour if a normal kinetic scheme (Section II.A) is to apply to this monomer, since higher initiator concentration leads to a higher rate of polymerization (Equation II.8) and, as can be seen from equation II.12, this should result in a lower polymer molecular weight.

Although a brief early study⁹ suggested that the benzene solution polymerization of vinylferrocene was accommodated by the normal kinetic scheme, a recent and more detailed kinetic study¹⁴ of the AIBN-initiated homopolymerization of vinylferrocene in benzene demonstrated that the kinetics were

not normal. The dependence of the rate of polymerization, R_p , on initiator concentration, $[In]$, was found to be to the power 1.11, rather than the normal dependence of R_p on $[In]^{0.5}$. This anomaly was explained in terms of monomolecular termination of the polymer radical, step (vi) in section II.A being replaced, therefore, by



As before, equation II.1 applies and

$$R_p = k_p [R\cdot] [M] \quad (1)$$

but now equation II.5 becomes

$$[R\cdot] = \frac{I}{k_t} \quad (2)$$

and thus,

$$R_p = \frac{k_p}{k_t} I [M] \quad (3)$$

Combining with equation II.7 gives

$$R_p = 2fk_d \frac{k_p}{k_t} [M] [In] \quad (4)$$

This scheme may be extended to redefine the degree of polymerization, $\overline{DP}$, of the polymer as

$$\overline{DP} = \frac{k_p [R\cdot] [M]}{k_t [R\cdot] + k_{fm} [R\cdot] [M] + k_{fs} [R\cdot] [S]} \quad (5)$$

and hence

$$\frac{1}{\overline{DP}} = \frac{k_t}{k_p [M]} + \frac{k_{fm}}{k_p} + \frac{k_{fs} [S]}{k_p [M]} \quad (6)$$

The observed lack of dependence of polymer molecular weight on initiator concentration^{14,15} in the benzene solution homopolymerization of vinylferrocene is accounted for, therefore, by this scheme.

Spectral evidence¹⁴ indicated that the monomolecular

termination step resulted in the formation of a paramagnetic high spin Fe(III) complex in the polymer.

Although values of K and a in the Mark-Houwink equation (III.16) have been evaluated¹⁵ for polyvinylferrocene in benzene and in tetrahydrofuran at 30°C ($K = 6.64 \times 10^{-4} \text{ 100cm}^3 \text{ g}^{-1}$, $a = 0.48$ and $K = 7.2 \times 10^{-5} \text{ 100cm}^3 \text{ g}^{-1}$, $a = 0.72$ respectively), there has been little study of homopolymer properties. This particularly applies to the glass transition temperature, T_g , of the polymer. Although a value of approximately 190°C has been estimated^{10,11} from broad DSC curves, this value is considerably lower than reported softening points (280-285°C¹ and 280-290°C²) would suggest it should be.

In view of the indications of ferrocene-aromatic interactions (Section IV) and the suggested¹⁴ possibility of solvent interaction in the monomolecular termination of the polyvinylferrocenyl radical in benzene solution, a study of the kinetics of the homopolymerization of vinylferrocene in dioxane was undertaken, prior to an investigation of the copolymerization of vinylferrocene and vinyl acetate in this solvent (Section IX). The study also provided polyvinylferrocene, of varying molecular weight, for an investigation of the variation of T_g with molecular weight for this polymer.

VII.A The kinetics of the AIBN-initiated homopolymerization of vinylferrocene in dioxane

The thermal homopolymerization of vinylferrocene in dioxane solution was studied dilatometrically at 60°C at constant initiator (AIBN) concentration with varying vinylferrocene concentrations, and at constant vinylferrocene concentration with varying AIBN concentrations. Gravimetric determinations were performed on the same polymerizations. The dilatometric studies demonstrated that the polymerizations were all linear with respect to time, for conversions less than about 10%, and gave a value for the apparent density of vinylferrocene in dioxane at 60°C of 1.262 g cm⁻³. This value is sufficiently close to that determined⁹⁷ for bulk vinylferrocene (1.259 g cm⁻³) to indicate that the principle of volume additivity applies to this system, and therefore the latter value was used in calculating the rates of polymerization from the dilatometric measurements.

In addition to providing the mean rates of polymerization (Table VII.1), the simultaneous gravimetric determinations permitted the calculation of the density of polyvinylferrocene in dioxane at 60°C, since the total volume change observed dilatometrically during the polymerization time, Δv , is given by

$$\Delta v = W_p \left(\frac{1}{D_m} - \frac{1}{D_p} \right) \quad (7)$$

where W_p is the weight of polymer formed in this time and D_m and D_p are the monomer and polymer densities respectively. The mean value for $1/D_p$ obtained over all of the polymerizations was 0.693 cm³ g⁻¹, giving a value of 1.44(4) g cm⁻³ for the density of polyvinylferrocene in dioxane at 60°C. This value was used to calculate the rates of polymerization from the

dilatometric measurements (Table VII.1).

A plot of $\log_{10} R_p$ against $\log_{10} [\text{VFcH}]$ (Fig. VII.1), using initial values of the rate of polymerization and vinylferrocene concentration, for the polymerizations at constant initiator concentration ($[\text{AIBN}] = (5 \pm 0.06) \times 10^{-2} \text{ mol dm}^{-3}$) has a gradient of 0.974 and an intercept of -4.727, as calculated by least mean squares analysis. Also, when initial values are used, a least mean squares analysis gives a gradient of 0.416 and an intercept of -3.969 for the plot of $\log_{10} R_p$ against $\log_{10} [\text{AIBN}]$ (Fig. VII.2) for the polymerizations at constant vinylferrocene concentration (2.01 mol dm^{-3}). Because of the magnitude of the values involved, no accurate estimate of the error limits could be made from either of the least mean squares analyses. The rate equation for the homopolymerization of vinylferrocene in dioxane may be given, therefore, as

$$R_p = k [\text{VFcH}]^{0.974} [\text{In}]^{0.416} \quad (8)$$

where k is an overall constant. The fit between this expression and the experimental data is illustrated in figs. VII.3 and VII.4.

This experimentally determined expression is sufficiently close to that expected (Equation II.8) for a system following normal vinyl free-radical polymerization mechanisms that the simple kinetic scheme given in section II.A may be taken to apply to this polymerization. Then, considering an appropriately amended form of equation II.8, given below, the overall constant,

$$R_p = k_p \left(\frac{fk_d}{k_t} \right)^{0.5} [\text{VFcH}] [\text{AIBN}]^{0.5} \quad (9)$$

k , in equation VII.8 may be given as

$$k = k_p \left(\frac{fk_d}{k_t} \right)^{0.5} \quad (10)$$

Values for k may be calculated from the intercepts of figs. VII.1

and VII.2, since

$$\log_{10}(k[\text{AIBN}]^{0.416}) = -4.727 \quad (11)$$

for $[\text{AIBN}]$ of $5 \times 10^{-2} \text{ mol dm}^{-3}$, and

$$\log_{10}(k[\text{VFCH}]^{0.974}) = -3.969 \quad (12)$$

for $[\text{VFCH}]$ of 2.01 mol dm^{-3} . These relationships give values for k of 6.51×10^{-5} and 5.47×10^{-5} respectively.

In the absence of any values for f , the initiator efficiency, in vinylferrocene polymerization, a reasonable approximation would seem to be to take a value determined for f in the AIBN-initiated polymerization of styrene. A number of studies have given values for f , under these conditions, which lie in the region¹⁰⁵ $0.48\text{--}0.80$, a convenient value being that¹⁰⁶ combined with a value of k_d :

$$fk_d = 0.94 \times 10^{15} \exp(-15,450/T) \text{ s}^{-1} \quad (13)$$

This expression gives a value of $6.97 \times 10^{-6} \text{ s}^{-1}$ for fk_d for the AIBN-initiated styrene polymerization at 60°C . Using this value for fk_d and a mean value of 6×10^{-5} for k in equation VII.10, a value of $2.27 \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ may be calculated for $k_p/(k_t)^{0.5}$ for vinylferrocene at 60°C .

A study of vinylferrocene polymerization in dioxane, at constant monomer ($[\text{VFCH}] = 2 \pm 0.09 \text{ mol dm}^{-3}$) and initiator ($[\text{AIBN}] = (5 \pm 0.25) \times 10^{-2} \text{ mol dm}^{-3}$) concentration, at ten degree intervals over the range $50^\circ\text{C}\text{--}80^\circ\text{C}$ allowed an estimation of the overall activation energy for the polymerization. The polymerizations were observed dilatometrically, and all were found to be linear with respect to time, for conversions of less than 10%. However, in the absence of polymer density values over this temperature range, the gravimetrically determined mean rates of polymerization (Table VII.1) were used in the construction of an Arrhenius plot (Fig. VII.5) of $\log_{10} R_p$ against $1/T$. The gradient of this plot was calculated, by least

mean squares analysis, to be $-(4.38 \pm 0.56) \times 10^3$ °K, and, similarly, the intercept was given as 8.54 ± 0.98 . The overall activation energy, E_A , for the polymerization under these conditions is, therefore:

$$E_A = 10,100R \quad (14)$$

where R is the gas constant. Thus, E_A is given as 84 kJ mol^{-1} .

In the presence of an initiator, for a normal kinetic scheme the overall activation energy is given by

$$E_A = \frac{E_D}{2} + \left(E_P - \frac{E_T}{2} \right) \quad (15)$$

where E_D , E_P and E_T are the activation energies for the initiating radical formation, propagation and termination steps respectively. Using the literature value¹⁰⁶ for E_D of 128 kJ mol^{-1} , which is contained in equation VII.13, a value may be calculated for $\{E_P - (E_T/2)\}$ for vinylferrocene in dioxane of 20 kJ mol^{-1} . This may be compared with a literature value⁶⁷ for $\{E_P - (E_T/2)\}$ for styrene of 27.5 kJ mol^{-1} .

Since this system seems to follow a normal kinetic scheme, the molecular weight data obtained in this study (Table VII.1) may be treated using equation II.12, which may be amended to

$$\frac{1}{\overline{DP}} = \frac{k_{\text{ter}} R_p}{k_p^2 [\text{VFcH}]^2} + C_m + \frac{C_s [DX]}{[\text{VFcH}]} \quad (16)$$

where $[DX]$ is the concentration of dioxane. However, it should be noted that these molecular weights were estimated by GPC analysis, and it has been suggested¹⁵ that the universal calibration method employed overestimates the polydispersity of polyvinylferrocene. This seems to result from an overestimation of $\overline{M}_w$, and it is also possible that the $\overline{M}_n$ values obtained here are somewhat overestimated. Combining equations VII.9 and VII.16 gives

$$\frac{1}{\overline{DP}} = \frac{k_{ter}}{k_p[VFCH]} \left(\frac{fk_d}{k_t} \right)^{0.5} [AIBN]^{0.5} + C_m + \frac{C_s[DX]}{[VFCH]} \quad (17)$$

Also, k_{ter} and k_t are related by

$$k_{ter} = Fk_t \quad (18)$$

where $1 \leq F \leq 2$, the limits being the values of F when termination by reaction of two polymer radicals is solely by combination or solely by disproportionation respectively. Then, equation VII.17 becomes

$$\frac{1}{\overline{DP}} = \frac{F(fk_d k_t)^{0.5} [AIBN]^{0.5}}{k_p[VFCH]} + C_m + \frac{C_s[DX]}{[VFCH]} \quad (19)$$

A plot of $1/\overline{DP}$ against $[AIBN]^{0.5}$, using initial AIBN concentrations, is a straight line (Fig. VII.6), which further demonstrates the applicability of a normal kinetic scheme to this system. Least mean square analysis of the data gives the gradient of the plot as $(5.23 \pm 1.2) \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5}$ and the intercept as $(1.20 \pm 0.28) \times 10^{-2}$. Thus, from these values,

$$\frac{F(fk_d k_t)^{0.5}}{k_p} = 0.1046 \quad (20)$$

and

$$C_m + 3.7C_s = 1.2 \times 10^{-2} \quad (21)$$

A plot of $\{(1/\overline{DP}) - F(fk_d k_t)^{0.5} [AIBN]^{0.5} / k_p [VFCH]\}$ against $[DX]/[VFCH]$, for the polymers prepared at varying monomer concentrations, should be a straight line, with C_s as gradient and C_m as intercept. However, the values of the former term merely exhibit scatter in the region of $(1.17 \pm 0.15) \times 10^{-2}$. This suggests a relatively low value for C_s , in which case the term $C_s[DX]/[VFCH]$ may be approximated to be negligible, and $1/\overline{DP}$ may be plotted against $1/[VFCH]$, for these polymers. Least mean squares analysis of the data gives the gradient of this plot (Fig. VII.7) as $(2.40 \pm 0.52) \times 10^{-2} \text{ dm}^3 \text{ mol}^{-1}$ and the

intercept, C_m , as $(1.17 \pm 0.32) \times 10^{-2}$. The agreement between this latter value and that obtained from equation VII.21 when C_s is taken to be very small, that is 1.2×10^{-2} , suggests that the approximation of the term C_s as being negligibly small is justified. From the value calculated for the gradient,

$$\frac{F(fk_d k_t)^{0.5}}{k_p} = 0.1076 \quad (22)$$

This in good agreement with the value obtained for this term from the plot of $1/\overline{DP}$ against $[AIBN]^{0.5}$ (Equation VII.20). Using a mean value for this term of $0.1061 \text{ mol}^{0.5} \text{ dm}^{-1.5}$ and the value of fk_d used in the discussion of the rate results ($6.97 \times 10^{-6} \text{ s}^{-1}$), a value of $2.45 \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ may be calculated for $k_p/F(k_t)^{0.5}$. Combining this result with the value of $2.27 \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ for $k_p/(k_t)^{0.5}$ calculated from the rate results gives F as 0.927. Since the value of F cannot be less than unity (Equation VII.18), this low value, although possibly fortuitous, may be taken to suggest that termination by reaction of two polymer radicals is primarily, if not wholly, by combination, that is that F is approximately unity. If this approximation is accepted, it becomes possible to calculate a potentially more accurate value for $k_p/(k_t)^{0.5}$, since the term fk_d , and hence any uncertainty associated with it, may be eliminated. This is accomplished by combining the result from the kinetics, that is

$$k_p \left(\frac{fk_d}{k_t} \right)^{0.5} = 6 \times 10^{-5} \quad (23)$$

with the result from the molecular weight data, that is

$$\frac{(fk_d k_t)^{0.5}}{k_p} = 0.1061 \quad (24)$$

to give a value of $2.38 \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ for $k_p/(k_t)^{0.5}$.

This may be compared with a literature value⁷¹ for this term for styrene, at this temperature, of $3.41 \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$.

The value obtained here for C_m (1.2×10^{-2}) clearly indicates a high degree of chain transfer to monomer. This value sets an upper limit of ca. 18,000 on the number average molecular weight of polyvinylferrocene formed under conditions similar to those employed here. However, number average molecular weights greater than this have been reported^{2,15} for polymers prepared in bulk polymerizations, the highest value² being 48,600. This suggests that the value for C_m obtained from this study might be too high, but these high molecular weights may, in part, arise from the high degree of branching, caused by chain transfer to polymer, observed¹⁵ in bulk polymerizations.

Clearly, the kinetics of the free-radical homopolymerization of vinylferrocene in dioxane solution differ markedly from those of this polymerization in benzene solution¹⁴. Both rate and molecular weight results demonstrate that a normal kinetic scheme is applicable to this system, as opposed to the first order dependence of the rate of polymerization on initiator concentration observed¹⁴ in the benzene solution polymerization. Furthermore, the overall activation energy observed for the dioxane solution polymerization (84 kJ mol^{-1}) is much less than that determined¹⁴ for the benzene solution polymerization over a similar temperature range ($139.7 \text{ kJ mol}^{-1}$). It is interesting to note that the difference between these two values (56 kJ mol^{-1}) is close to the literature value¹⁰⁶ for $E_D/2$ (64 kJ mol^{-1}). The overall activation energy for the benzene solution polymerization, from equation VII.4, may be given as

$$E_A = E_D + (E_P - E_T') \quad (25)$$

where E_T' is the activation energy for the monomolecular

termination step. Comparing this expression with that for the polymerization in dioxane (Equation VII.15), the difference between the two is $E_D/2$ and the difference between $E_T/2$ and E_T' . However, E_T values are generally small (10 kJ mol^{-1} for styrene⁶⁷) relative to $E_D/2$ (64 kJ mol^{-1}). Thus, the difference between the two polymerization systems is emphasised in the overall activation energies for the polymerizations.

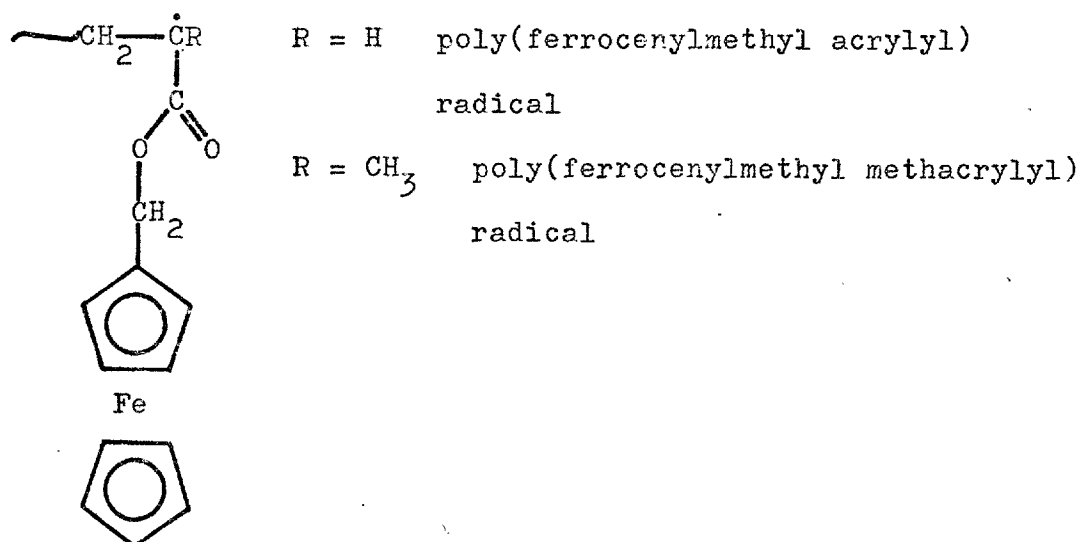
That the polymers prepared in dioxane solution are formed by normal termination mechanisms, rather than by monomolecular termination to give a paramagnetic Fe(III)-containing species, as is suggested¹⁴ for the polymers prepared in benzene solution, receives further support from the esr and Mössbauer spectra of polyvinylferrocene prepared here. Even at high gain settings, no absorption was detected in the esr spectrum of either the solid polymer or of a carbon disulphide solution of the polymer, at room temperature. This contrasts sharply with the reported¹⁴ esr spectrum of polyvinylferrocene prepared in benzene, which exhibited a broad absorption in both solid and solution state, at room temperature and at liquid nitrogen temperature. Also, a styrene-vinylferrocene copolymer (15.6 mole-percent vinylferrocene) prepared in benzene solution (Section VIII) exhibited an esr absorption, at lower gain settings than those employed for the homopolymer prepared in dioxane, in the solid state at room temperature and in both solid and solution states at -154.5°C . No attempt was made to obtain a solution spectrum at room temperature. The 'g' value for the centre of the absorption in the solid state spectrum at -154.5°C was 2.11 and that for the centre of the absorption in the solution spectrum at -154.5°C was 2.04. These values are close to that (2.06) reported¹⁴ for the esr spectrum of polyvinylferrocene prepared

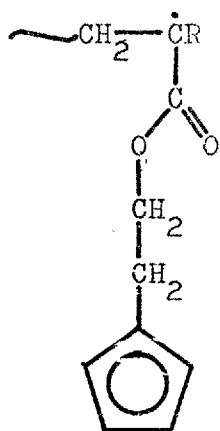
in benzene, and, therefore, the absorption possibly derives from a similar source. In view of the higher molecular weight and low vinylferrocene content of the copolymer, a larger absorption would have been expected for the homopolymer prepared in dioxane than for the copolymer. Since no absorption was detected, even at higher gain settings, it must be concluded that no paramagnetic species were present in the homopolymer prepared in dioxane.

The Mössbauer spectrum of polyvinylferrocene prepared in dioxane confirms the absence in this polymer of the Fe(III)-containing species reported¹⁴ to be present in polyvinylferrocene prepared in benzene solution. The spectrum comprised two peaks, there being no third peak attributable to the paramagnetic species. The precise position of this third peak is unclear, since the isomer shift was reported as 0.17 mm s^{-1} , but the standard on which this shift was based was not given. The spectrum of polyvinylferrocene obtained here was taken at room temperature (Fig. VII.8) and gave an isomer shift (δ) of 0.460 mm s^{-1} relative to natural iron and a quadrupole splitting (ΔE_Q) of 2.40 mm s^{-1} . These may be compared with values obtained for polyvinylferrocene relative to other standards by applying the appropriate correction factor. At 77°K , values for δ and ΔE_Q of 0.78 mm s^{-1} , relative to sodium nitroprusside, and 2.44 mm s^{-1} , respectively, were obtained for polyvinylferrocene prepared in benzene¹⁰. The corrected isomer shift relative to natural iron is 0.522 , taking the shift¹⁰⁷ of sodium nitroprusside relative to natural iron to be 0.258 mm s^{-1} . At 80°K , the Mössbauer spectrum of the soluble fraction of polyvinylferrocene prepared with zinc chloride as catalyst¹⁰⁸ gave δ as 0.55 mm s^{-1} , relative to stainless steel, and ΔE_Q as 2.25 mm s^{-1} . The isomer shift

relative to natural iron is 0.46 mm s^{-1} , if the shift of stainless steel relative to natural iron¹⁰⁹ is taken to be 0.09 mm s^{-1} . The absence of a third peak in the Mössbauer spectrum of the polymer prepared in benzene solution¹⁰ quoted above may be due to the high conversion to which the polymerizations were taken, since this is reported¹⁴ to affect the area of this third peak.

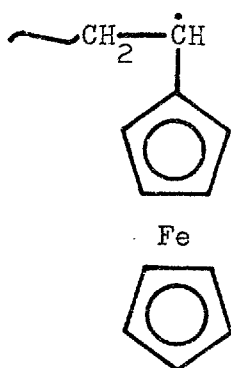
It may be concluded, then, that the monomolecular termination step, giving rise to a paramagnetic Fe(III)-containing species, does not take place when the polymerization is carried out in dioxane. This suggests that the monomolecular termination step involves, in some way, benzene. Furthermore, the free-radical homopolymerizations of ferrocenylmethyl acrylate²⁸ and methacrylate²⁸ and 2-ferrocenylethyl acrylate²⁹ and methacrylate²⁹ in benzene solution have been shown to follow a normal kinetic scheme, being first order in monomer concentration and half-order in initiator (AIBN) concentration. All of the polymer radicals generated from these monomers have the ferrocene nucleus of the end unit removed some distance from the site of the radical, as can be seen from the diagrams below. This would tend to indicate that the terminal ferrocene





$R = H$ poly(2-ferrocenylethyl acrylyl)
radical

$R = CH_3$ poly(2-ferrocenylethyl methacrylyl)
radical



polyvinylferrocenyl radical

nucleus is involved in the monomolecular termination step, as has been suggested¹⁴.

VII.B Polymer properties

The visible and ultraviolet spectra and the ^1H and ^{13}C nmr spectra of polyvinylferrocene are presented in sections IV.A and IV.B respectively. The differences between the visible and ultraviolet spectra recorded here and those given previously¹⁰ may be attributed to the different solvents employed. The higher extinction coefficients in the latter study¹⁰ probably arise from charge-transfer complexing between the ferrocene nuclei and the dichloromethane solvent, since this behaviour is well established for ferrocene and halogenated solvents⁷⁶. The ^1H nmr spectrum of polyvinylferrocene has not yet been reported, primarily because spectra for polymers prepared free-radically in benzene solution have exhibited pronounced paramagnetic broadening. The absence of paramagnetic broadening in the spectra obtained for polymers prepared in dioxane solution cannot be taken as further evidence against the presence of paramagnetic species in these polymers. The ^1H nmr spectra of a styrene-vinylferrocene copolymer (Section IV.B) prepared in benzene did not appear to exhibit paramagnetic broadening, although a similar copolymer with only a slightly higher vinylferrocene content (15.6 rather than 12.2 mole-percent) exhibited an absorption in its esr spectrum.

The esr and mössbauer spectra of polyvinylferrocene prepared in dioxane were discussed in the previous section (VII.A). The infrared spectrum of these polymers (Fig. VII.9) contains the absorptions previously reported¹⁰.

The thermal properties of polyvinylferrocene were studied, as a function of molecular weight, by differential scanning calorimetry (DSC). As has been reported previously^{10,11} the traces obtained for polyvinylferrocene by this method (Section

III.B.18) are broad curves. However, in this study two transitions were observed for all samples and at all heating rates employed. The first transition was broad, the second relatively sharp (Figs. VII.10.a, VII.10.b and VII.11.a), resembling, in form, the glass transition for polystyrene. The presence of two transitions was confirmed by differential thermal analysis (Fig. VII.10.c). Upon cooling a polymer sample to room temperature and recycling at the same heating rate, both of the transitions occurred at lower temperatures (Fig. VII.11). The second transition was more affected in this respect, and became more diffuse. This behaviour might suggest that some thermal degradation had occurred on the first run after the second transition.

Eight heating rates were employed for each different molecular weight sample, fresh polymer being used for every run. Both the transition temperatures and the magnitude of the dips in the trace increased with increasing heating rate. The first, broad transition became more distinct as the heating rate increased. The transition temperatures at zero heating rate were obtained from plots of $\log_{10}(\text{transition temperature})$ against heating rate (Section III.B.18, fig. III.8), and these are given in table VII.2.

Clearly, the first transition temperature is virtually independent of polymer molecular weight, the majority of the values being between 171°C and 178°C , whilst the second transition temperature increases markedly as molecular weight increases. This scatter of values is a feature of the first transition temperature, it being far less reproducible than the second transition temperature, though this may be due to the more diffuse nature of the former. The dependence of the second transition temperature on polymer molecular weight suggests

that this is the glass transition temperature, T_g , since a relationship between T_g and molecular weight has been derived from temperature-volume considerations¹¹⁰. This relationship has the form

$$T_g = T_g^{\infty} - \frac{k}{\bar{M}_n} \quad (26)$$

where T_g^{∞} is the glass transition temperature at infinite molecular weight and k is a constant. An observation which substantiates this assignment of the second transition temperature as T_g is that when polymer samples were heated to beyond the first transition and held at that temperature for several minutes prior to cooling, the form and appearance of the polymers were unchanged. However, polymer samples which were heated to beyond the second transition before being cooled to room temperature all exhibited marked changes in form, and appeared to have been softened at some point. This latter interpretation is based on the manner in which the original powdery samples became aggregated and took on the form of the sample pan. Indeed, the changes observed in samples of polyvinylferrocene, which had passed through the second transition, were very similar to those observed in samples of polystyrene which had been heated through the glass transition.

Thus, equation VII.26 may be applied to the second transition temperatures, which now will be referred to as the glass transition temperatures. A plot of T_g against $1/\bar{M}_n$ (Fig. VII.12) is a straight line and, when the anomalous point ($\bar{M}_n = 8,200$) is omitted, a least mean squares analysis of the data gives the gradient as $-(2.54 \pm 0.4) \times 10^5$ °C and the intercept as 268 ± 5 °C, which is somewhat greater than a value (1×10^5 °C) obtained for polystyrene¹¹¹. It is noteworthy, though perhaps

fortuitous, that the ratio of these two values is very similar to the ratio of the two repeat unit molecular weights. There would be, therefore, a close similarity between the values of k for these two polymers, if $\overline{DP}$ rather than $\overline{M}_n$ was used in equation VII.26. The value of 268°C for T_g^∞ and the values of T_g observed here are in better agreement with reported softening points of $280\text{--}285^\circ\text{C}^1$ and $280\text{--}290^\circ\text{C}^2$, the latter being for polymer with a $\overline{M}_n$ of 48,600, than previously reported^{10,11} estimates of T_g in the region of 190°C . The range of the latter values¹⁰ for T_g was $184\text{--}194^\circ\text{C}$, but the polymer molecular weights varied from 5,560–11,400. These observations correlate better with the first transition temperatures than with the T_g values observed here.

The nature of the change associated with the first transition temperature is unclear. However, the lack of dependence of this event on polymer molecular weight, suggests that it is also largely independent of free volume, since the molecular weight effect on T_g arises from the free volume associated with chain ends. This would tend to indicate that this transition involves the repeat unit rather than polymer segments. Clearly, this transition is associated also with the presence of the ferrocene nucleus and, therefore, a possible cause is rotation of the unsubstituted cyclopentadiene ring. The onset of ring rotation would result in an increase in heat capacity, just as occurs when segmental motion begins, and the transition would, therefore, give a similar DSC trace to that of a glass transition. The rotation could be somewhat dependent upon the local environment of the repeat unit and, if this was the case, in the polymer sample as a whole the transition would take place over a pronounced temperature range, giving rise to

a diffuse DSC curve.

Glass transition temperatures have been reported for poly(ferrocenylmethyl acrylate)¹⁰, 197-210°C, poly(ferrocenylmethyl methacrylate)¹⁰, 185-195°C, poly(2-ferrocenylethyl acrylate)^{10,29}, 157°C, and poly(2-ferrocenylethyl methacrylate)^{10,29}, 209°C. However, assignment of these transitions as glass transitions was not completely certain, since the DSC curves were not always sharp. In the cases of poly(2-ferrocenylethyl acrylate) and poly(2-ferrocenylethyl methacrylate), sharp breaks were reported²⁹ in the DSC traces at 157°C and 209°C, respectively, no such breaks being found before or after to above 240°C. However, since a second transition, thought to be the glass transition, in the region of 225-247°C was observed here for polyvinylferrocene, it is possible that a second transition, beyond 240°C, occurs for the ferrocene-containing polyacrylates and polymethacrylates.

VII.C Summary

The kinetics of the free-radical homopolymerization of vinylferrocene in dioxane at 60°C were found to follow a normal kinetic scheme, the polymerization being first order in monomer concentration and half-order in initiator (AIBN) concentration. A value for $k_p/(k_t)^{0.5}$ of $2.38 \times 10^{-2} \text{ dm}^{1.5} \text{ mol}^{-0.5} \text{ s}^{-0.5}$ was calculated from rate and molecular weight data. These data also form the basis of a tentative suggestion that, in dioxane solution, termination by reaction of two polyvinylferrocenyl radicals occurs predominantly by combination. The overall activation energy for the polymerization between 50°C and 80°C was determined to be 84 kJ mol^{-1} .

The esr spectrum of polymer prepared under these conditions indicated that the polymer did not contain any paramagnetic species, and the Mössbauer spectrum exhibited only absorptions due to iron in the ferrocene nucleus.

These findings are in contrast to those obtained for the benzene solution free-radical polymerization of vinylferrocene¹⁴. In that case, the polymerization was reported as being first order in both monomer and initiator (AIBN) concentration. The polymer formed was reported to contain a paramagnetic Fe(III)-containing species, which was thought to be formed in a monomolecular termination step.

Thermal analysis of the polymers by DSC indicated the presence of two transitions. The first, in the region of 175°C, was diffuse and independent of molecular weight. The second was sharper and the temperature at which it occurred increased with increasing polymer molecular weight, from 225°C for a $\bar{M}_n$ of 5,790 to 247°C for a $\bar{M}_n$ of 11,500. Because of this molecular weight dependence and changes observed in the form of the

polymer after it had passed through the second transition, this transition was assigned as the glass transition. A value of 268°C was calculated for T_g^{∞} , the glass transition temperature for polymer of infinite molecular weight. Rotation of the unsubstituted cyclopentadiene ring of the ferrocene nucleus was suggested as a possible cause of the first transition.

The infrared spectrum of polyvinylferrocene was given here, the visible and ultraviolet spectra and ^1H and ^{13}C nmr spectra having been presented and discussed in sections IV.A and IV.B respectively.

Table VII.1

The AIBN-initiated thermal homopolymerization of vinylferrocene
in dioxane at 60°C

Initial values			Mean values	
[VFcH] mol dm ⁻³	[AIBN] x 10 ² mol dm ⁻³	R _p x 10 ⁵ mol dm ⁻³ s ⁻¹	R _p x 10 ⁵ mol dm ⁻³ s ⁻¹	^a $\bar{M}_n$
0.999	4.99	1.98	1.98	5,790
1.49	4.77	2.78	3.13	8,200
2.01	5.01	3.14	3.20	8,900
2.51	4.95	4.64	4.49	9,520
3.01	5.06	6.00	5.32	10,800
2.01	3.75	2.72	2.75	10,100
2.01	7.54	3.62	3.54	7,760
2.01	10.0	4.15	3.89	7,480
2.00	1.04	-	-	11,500
2.00	2.50	-	-	11,100
^b 2.02	5.08	-	0.936	-
^c 1.91	4.75	-	5.91	-
^d 1.99	5.00	-	14.2	-

- ^a Estimated by GPC analysis using the values¹⁵ $K = 7.2 \times 10^{-5}$ 100cm³ g⁻¹ and $a = 0.72$ for calibration conversion.
- ^b Polymerization temperature 50°C.
- ^c Polymerization temperature 70°C.
- ^d Polymerization temperature 80°C.

Table VII.2

The thermal behaviour of polyvinylferrocene as a function of molecular weight

^a $\bar{M}_n$	^b First transition temperature, °C	^b Second transition temperature (T_g), °C
5,790	181	225
7,480	171	232
7,760	165	235
8,200	176	228
8,900	184	238
9,520	178	239
10,100	176	244
10,800	175	244
11,100	173	245
11,500	171	247

^a Estimated by GPC analysis, using the values¹⁵ $K = 7.2 \times 10^{-5}$ $100\text{cm}^3 \text{g}^{-1}$ and $a = 0.72$ for calibration conversion.

^b Determined by DSC, under nitrogen, and extrapolated to zero heating rate.

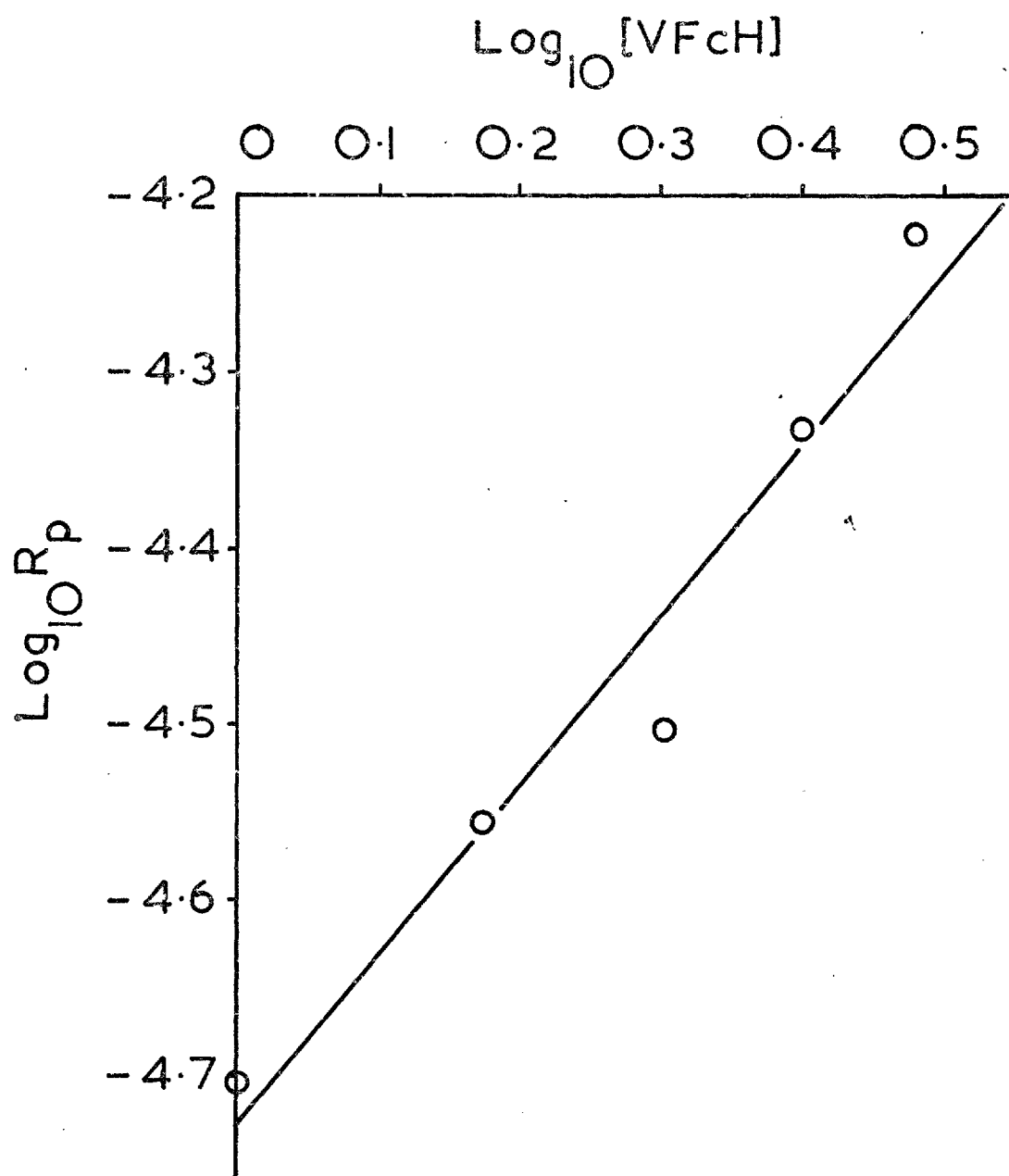


Fig. VII.1

$\text{Log}_{10} R_p$ as a function of $\text{log}_{10} [\text{VFcH}]$ for the homopolymerization of vinylferrocene in dioxane at 60°C , $[\text{AIBN}] = (5 \pm 0.06) \times 10^{-2} \text{ mol dm}^{-3}$.

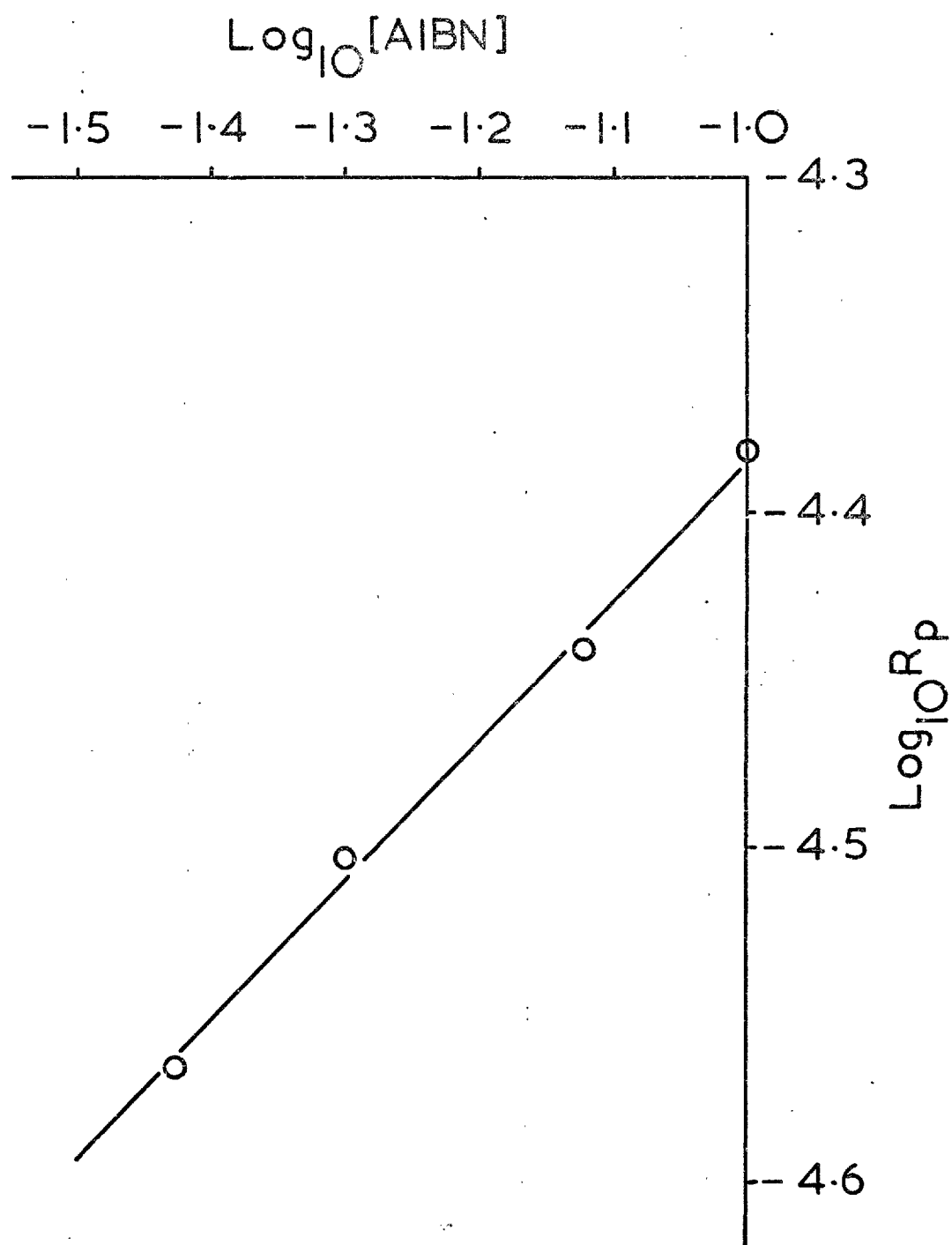


Fig. VII.2

$\text{Log}_{10} R_p$ as a function of $\text{log}_{10} [\text{AIBN}]$ for the homopolymerization of vinylferrocene in dioxane at 60°C , $[\text{VFch}] = 2.01 \text{ mol dm}^{-3}$.

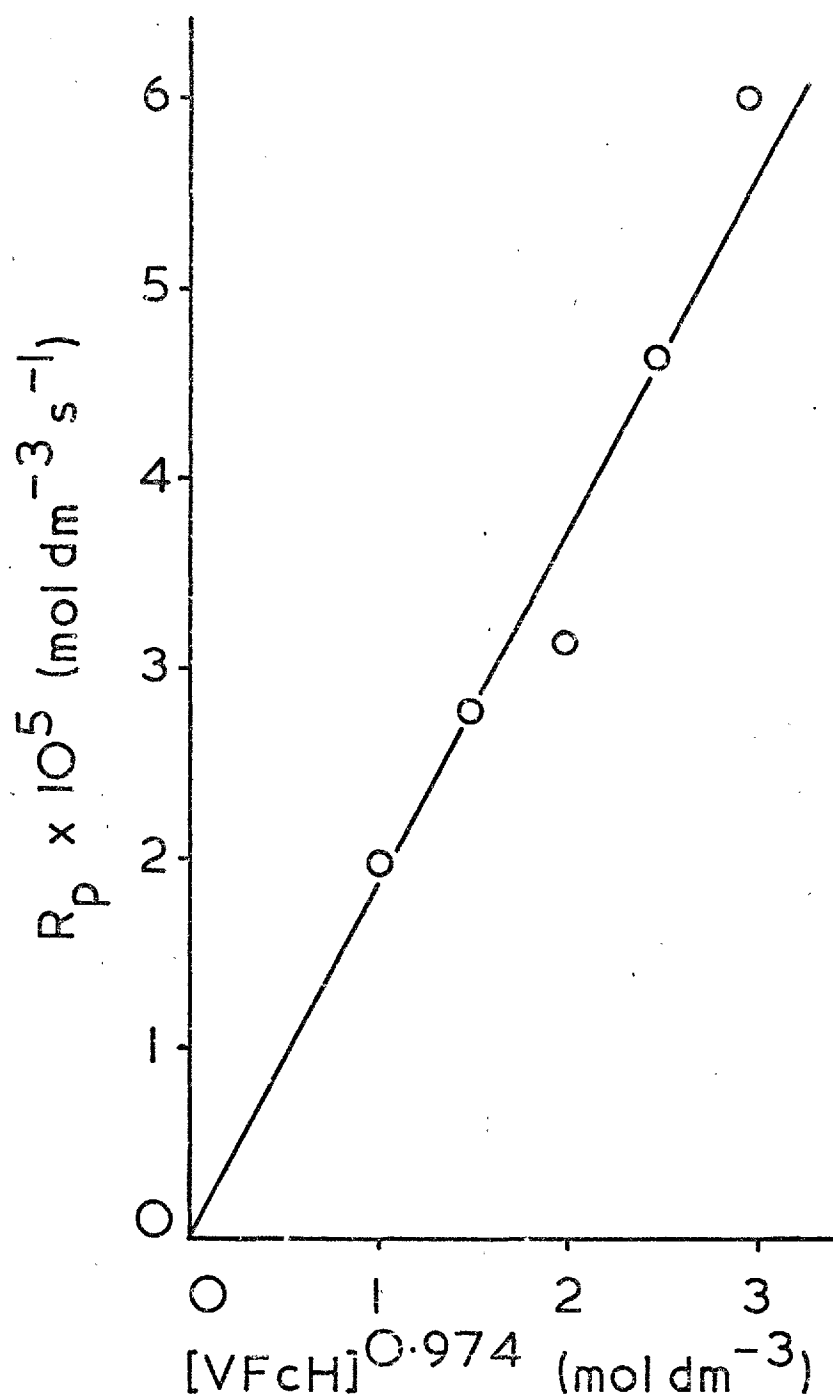


Fig. VII.3

Initial rate of polymerization, R_p , as a function of $[VFcH]^{0.974}$ for the homopolymerization of vinylferrocene in dioxane at 60°C , $[AIBN] = (5 \pm 0.06) \times 10^{-2} \text{ mol dm}^{-3}$.

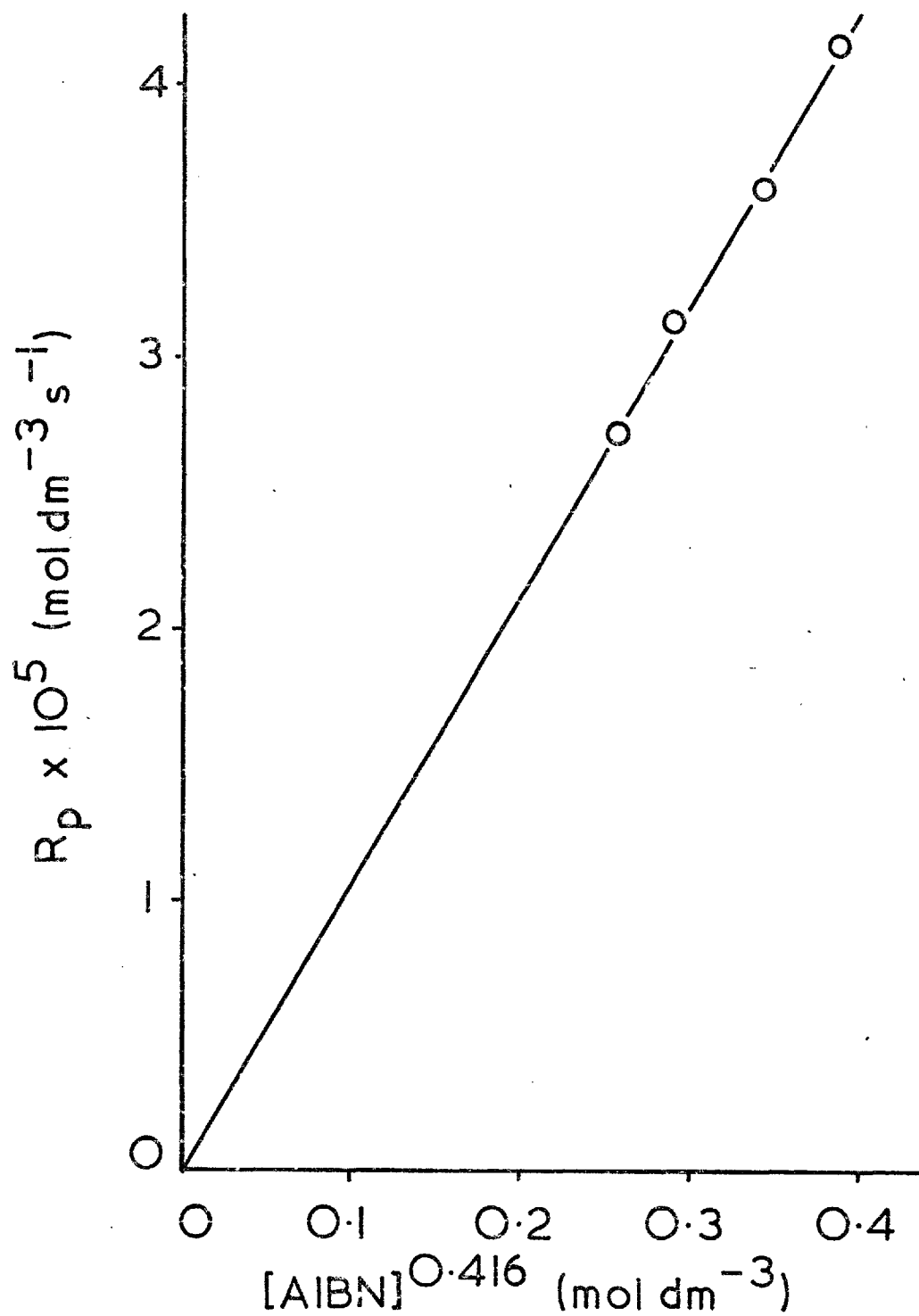


Fig. VII.4

Initial rate of polymerization, R_p , as a function of $[AIBN]^{0.416}$ for the homopolymerization of vinylferrocene in dioxane at 60°C, $[VFcH] = 2.01$ mol dm⁻³.

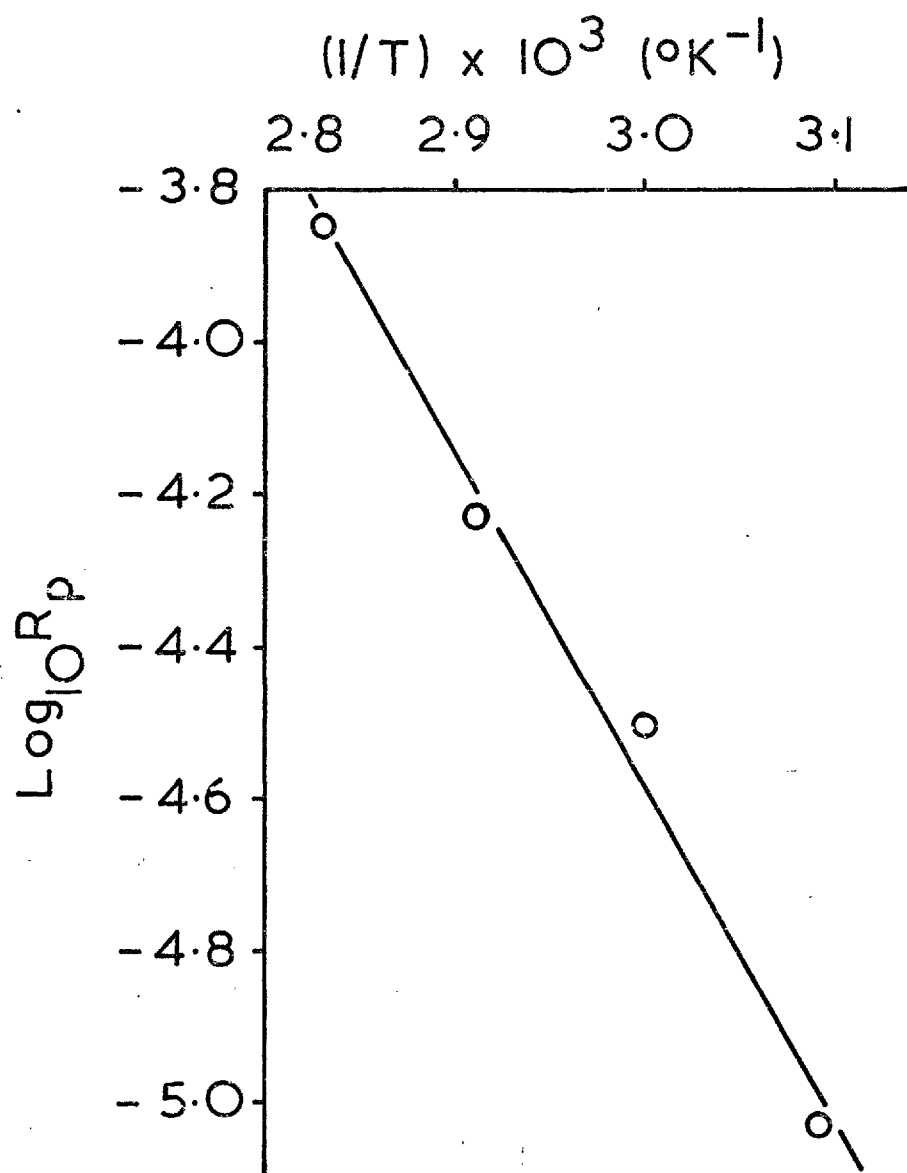


Fig. VII.5

$\text{Log}_{10} R_p$ as a function of $1/T$ for the homopolymerization of vinylferrocene in dioxane, $[\text{VFcH}] = 2 \text{ mol dm}^{-3}$ and $[\text{AIBN}] = 5 \times 10^{-2} \text{ mol dm}^{-3}$.

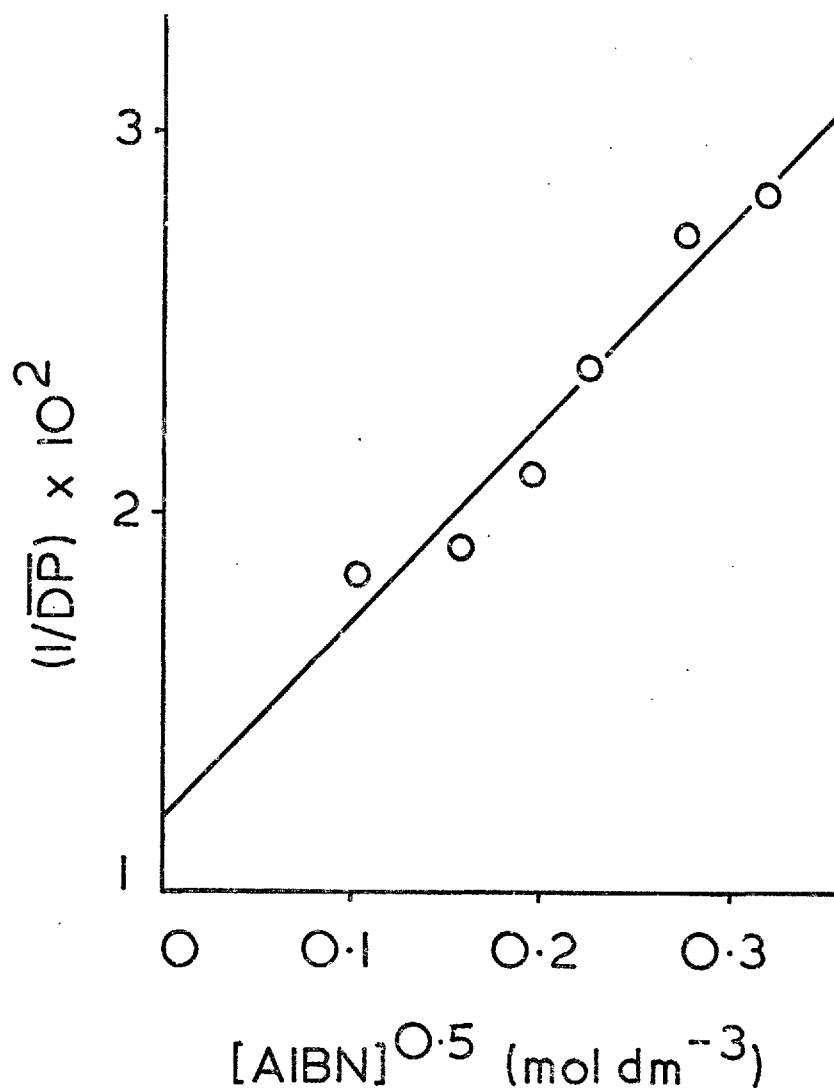


Fig. VII.6

$1/\overline{DP}$ as a function of $[AIBN]^{0.5}$, using initial values of the AIBN concentrations, for the homopolymerization of vinylferrocene in dioxane at 60°C , $[VFCH] = 2.0 \text{ mol dm}^{-3}$.

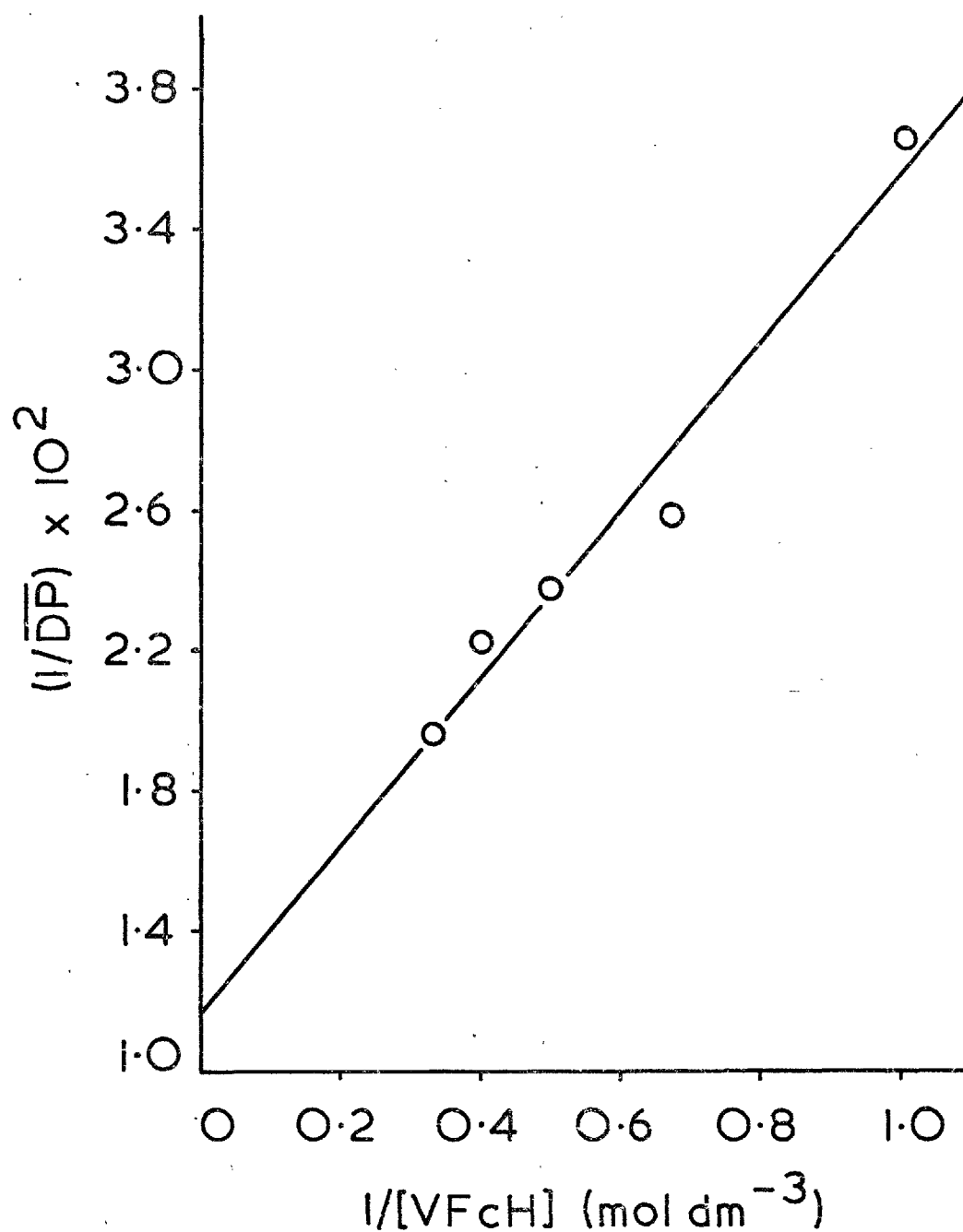


Fig. VII.7

$1/\overline{DP}$ as a function of $1/[VFcH]$, using initial values of the vinylferrocene concentration, for the homopolymerization of vinylferrocene in dioxane at 60°C , $[AIBN] = 5 \times 10^{-2} \text{ mol dm}^{-3}$.

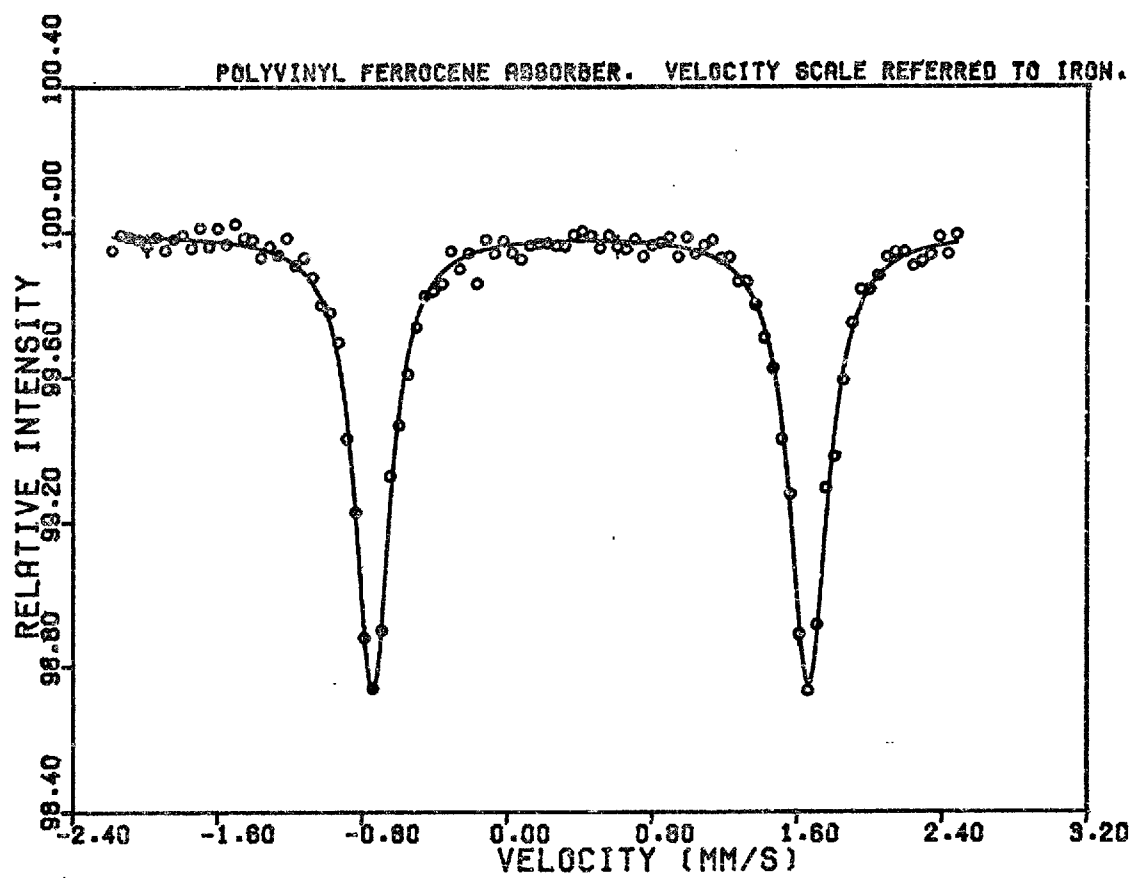


Fig. VII.8

Mössbauer spectrum of polyvinylferrocene.

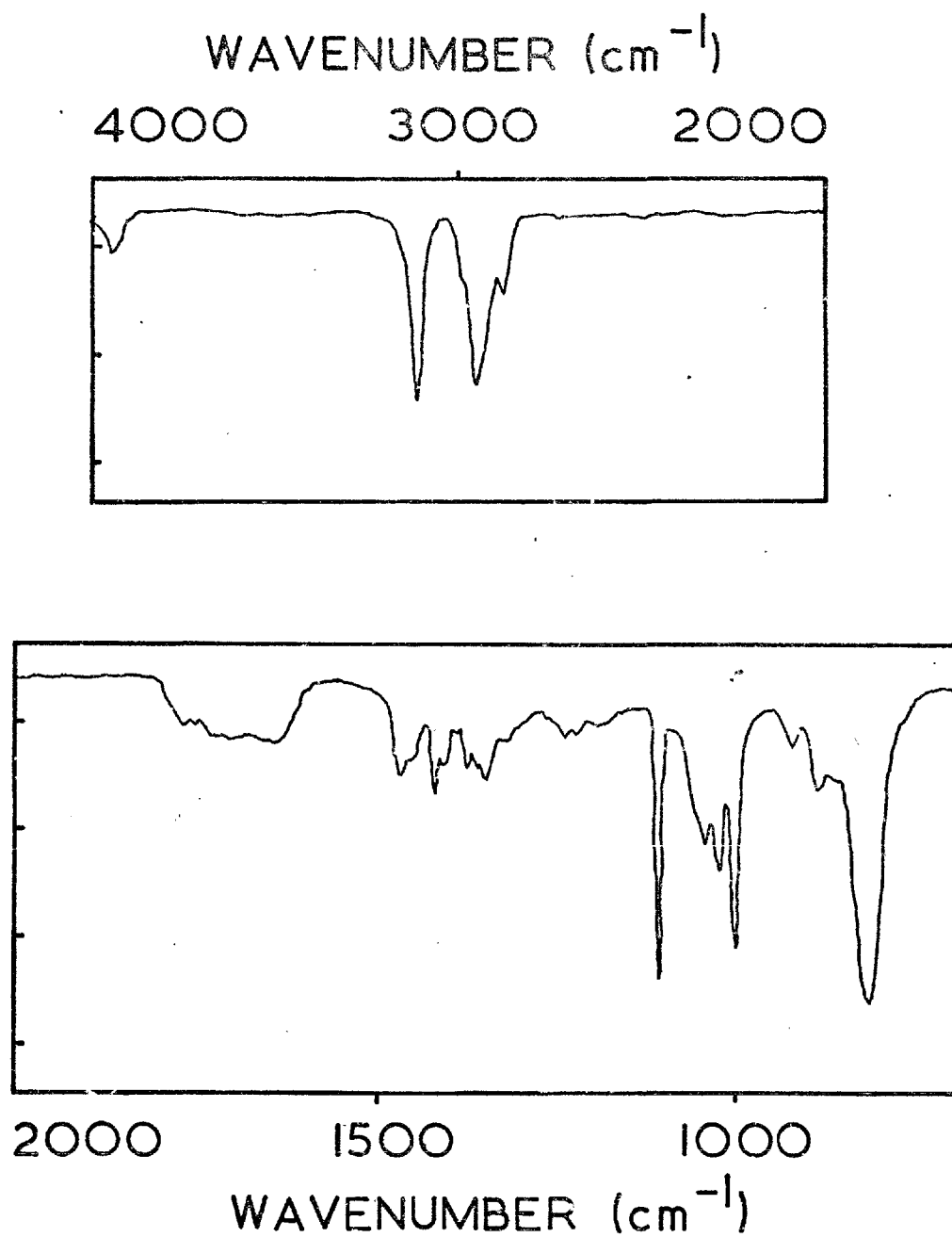
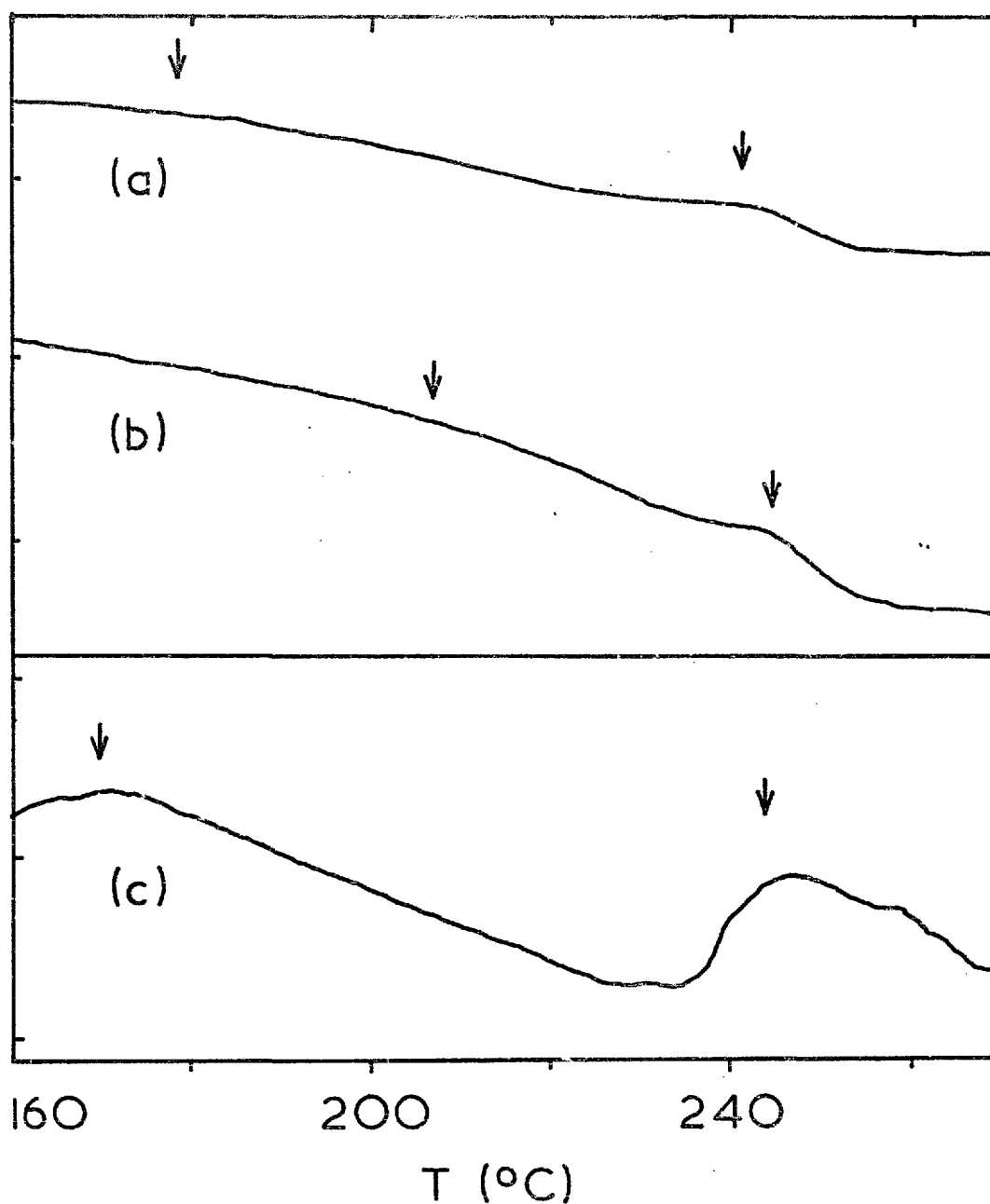


Fig. VII.9

Infrared spectrum of a film of polyvinylferrocene cast from carbon disulphide.



Figs. VII.10.a and VII.10.b

DSC curves for polyvinylferrocene ($\bar{M}_n = 7,760$), ΔT sensitivity $0.05^{\circ}\text{C in}^{-1}$ and heating rate (a) $7.7^{\circ}\text{C min}^{-1}$, (b) $14^{\circ}\text{C min}^{-1}$.

Fig. VII.10.c

DTA curve for the same polymer, ΔT sensitivity $0.1^{\circ}\text{C in}^{-1}$ and heating rate $14^{\circ}\text{C min}^{-1}$.

The transitions are indicated by arrows.

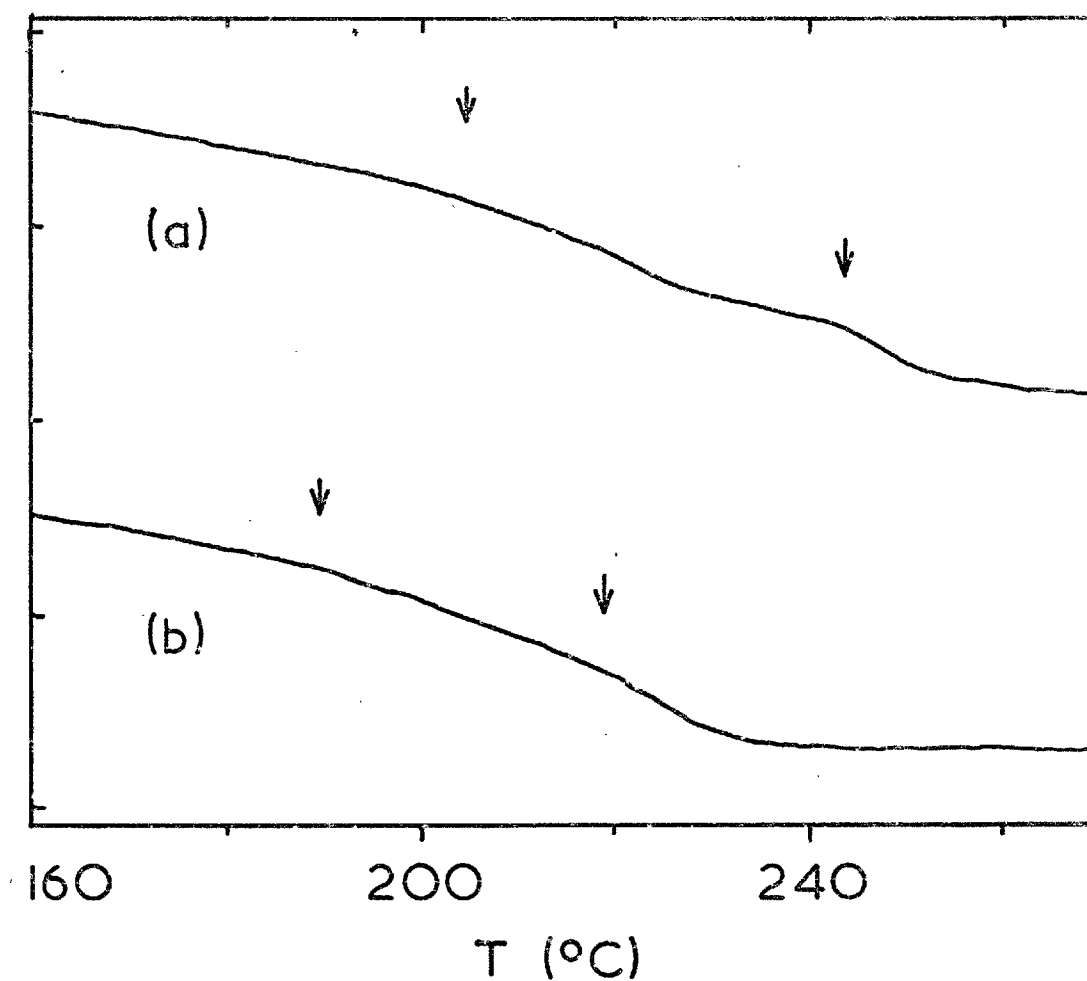


Fig. VII.11

DSC curves for polyvinylferrocene ($\bar{M}_n = 7,480$), ΔT sensitivity $0.05^{\circ}\text{C in}^{-1}$ and heating rate $14^{\circ}\text{C min}^{-1}$; (a) initial run and (b) recycle run after cooling to room temperature.

The transitions are indicated by arrows.

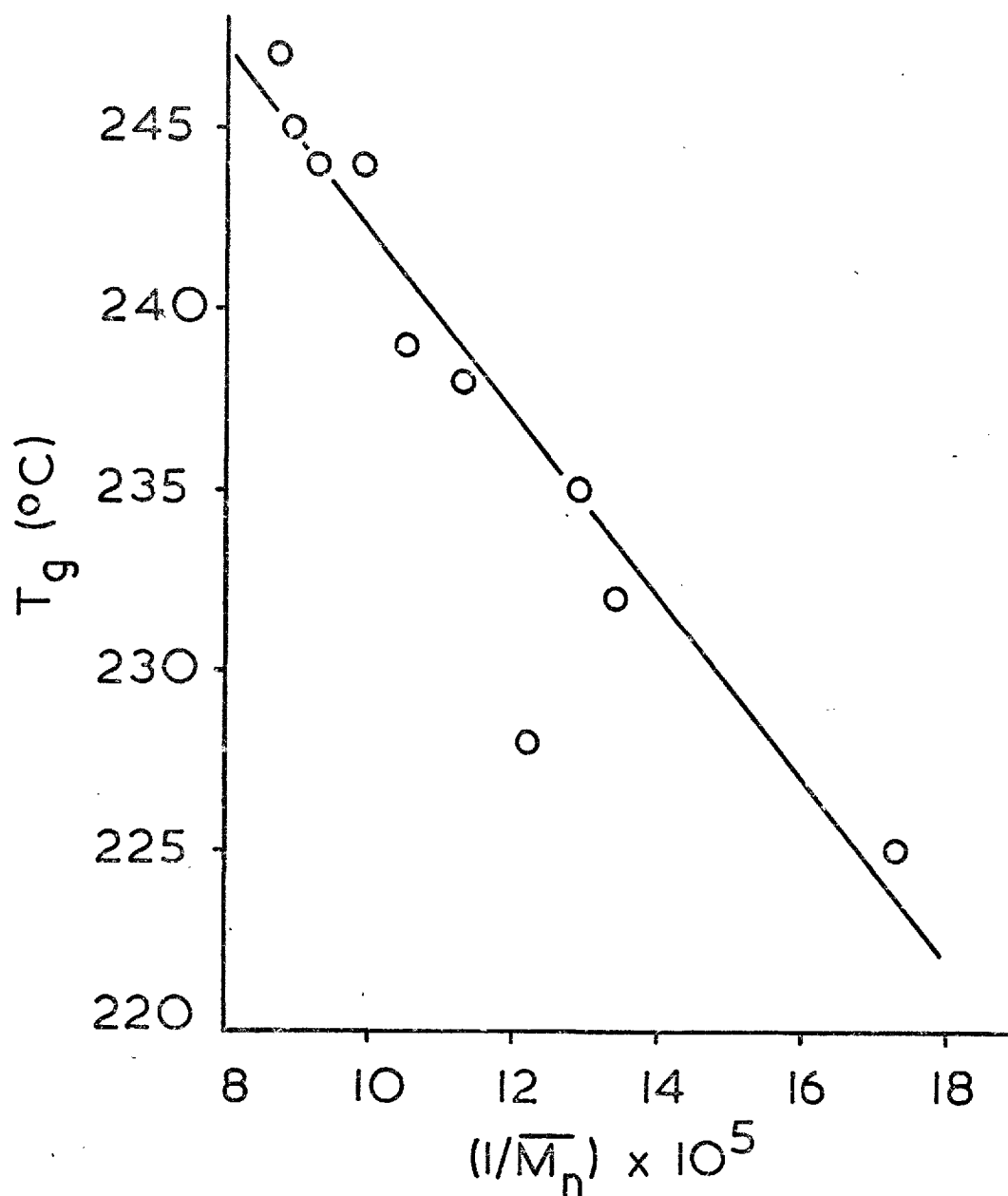


Fig. VII.12

The glass transition temperature, T_g , as a function of $1/\bar{M}_n$ for polyvinylferrocene. T_g values are those for zero heating rate and the line drawn was obtained by omitting the point $\bar{M}_n = 8,200$ from the fitting.

VIII The free-radical copolymerization of styrene and vinylferrocene and the properties of the copolymers formed

The free-radical copolymerization of styrene and vinylferrocene has been recorded on several occasions^{1,7-9,11-13,17}, and two of these reports^{11,17} contain a detailed discussion of the kinetic aspects of the copolymerization. However, the values presented in these reports are somewhat at variance, and no detailed study of the properties of the copolymer formed has been recorded.

A further study of this copolymerization was undertaken, therefore, in an attempt to clarify the kinetic aspects of the copolymerization, but primarily in order to provide copolymer of varying composition, suitable for a study of polymer properties with copolymer composition. Since vinylferrocene is known to give polymer of considerably lower degree of polymerization than polystyrene formed under comparable conditions, a preliminary study was carried out to assess the maximum level of vinylferrocene which could be incorporated into polystyrene, under standard polymerization conditions, without appreciably lowering the degree of polymerization of the polymer. This precaution was necessary because many polymer properties are strongly dependent on degree of polymerization. The preliminary investigation suggested that an upper limit of approximately 20 mole-percent vinylferrocene in the copolymer would be adequate, under the conditions employed.

VIII.A Kinetic aspects of the copolymerization of styrene and vinylferrocene

Styrene was copolymerized with varying amounts of vinylferrocene (0-41 mole-percent in the monomer feed) at 60°C in benzene solution with AIBN as initiator. The AIBN concentration and the total monomer concentration were held constant. Dilatometric measurements, made on the homopolymerization of styrene and the copolymerization with the highest vinylferrocene content, demonstrated that the polymerizations were linear with respect to time, at conversions of less than 10%. The conversions, with respect to total monomer weight, were determined gravimetrically. The compositions of the purified copolymers were determined by elemental analysis and the results are given in table VIII.1, together with details of the copolymerizations.

The relative reactivity ratios r_1 , for vinylferrocene, and r_2 , for styrene, were calculated from the composition data by the Fineman-Ross method (Section II.B). Of the two plots, based on equations II.26 and II.27, reproduced below, that of $(f - 1)/F$

$$\frac{(f - 1)}{F} = r_1 - \left(\frac{f}{F^2}\right)r_2 \quad (1)$$

$$\frac{F(f - 1)}{f} = \left(\frac{F^2}{f}\right)r_1 - r_2 \quad (2)$$

against f/F^2 ($F = M_1/M_2$, $f = m_1/m_2$) appears to be the better (Fig. VIII.1). A least mean squares analysis of the data for this plot gives a value for r_2 of 2.64 ± 0.42 and r_1 as 0.40 ± 0.80 . The plot of $(F/f)(f - 1)$ against (F^2/f) exhibits some scatter (Fig. VIII.2), this being largely due to the small gradient. The point with (F^2/f) as 0.557 is clearly anomalous and this was omitted from the least mean squares analysis of the data, which gave a value for r_2 of 2.49 ± 0.32 and for r_1

a value of 0.38 ± 0.32 . Thus, the mean values, given by the Fineman-Ross method, for r_1 and r_2 are 0.39 and 2.57, respectively. These may be compared with literature values, which are summarized in table VIII.2. A plot of m_1 against M_1 , including the line generated from the copolymer equation (II.24) by these values for the relative reactivity ratios, illustrates the fit of the latter to the experimental data (Fig. VIII.3).

The 10°C difference in polymerization temperature between this and previous studies will have had some effect on the values of r_1 and r_2 , but this probably would be small compared with the overall error limits. Although the maximum vinylferrocene content of the monomer feed used in this study was ca. 41%, and previous studies have covered the entire composition range, it should be noted that, in the plot of $(f - 1)/F$ against f/F^2 , higher vinylferrocene content polymerizations would have provided data only in a small region close to the intercept. Such data would have exerted little effect on the gradient of the plot, although the intercept may have been affected to a greater extent, because of its low value. A discussion of the relative reactivity ratios given in table VIII.2 has some validity, therefore, and it would seem that a value of r_2 in the region of 2.5 is the more correct of those previously determined. However, this study favours the higher of the previously determined values for r_1 .

The large discrepancy between the two sets of Q and e values (Section II.B) previously determined^{11,17} for vinylferrocene from its copolymerization with styrene (Table VIII.2) is due apparently not only to the difference in the values of r_1 and r_2 from which they were calculated, but also seems to arise, in part, from the manner in which they were calculated. The first stage in the calculation of these

values is the solution of equation II.32, given below.

$$r_1 r_2 = \exp\{-(e_1 - e_2)^2\} \quad (3)$$

Clearly, the solution proceeds via equation VIII.4 and there

$$(e_1 - e_2) = \pm(-\ln r_1 r_2)^{0.5} \quad (4)$$

are, therefore, two possible values for e_1 . Conventionally, the positive solution of this equation is taken, that is

$$e_1 = e_2 + (-\ln r_1 r_2)^{0.5} \quad (5)$$

However, it would appear that the negative solution was taken when Q and e values for vinylferrocene were calculated from values of r_1 and r_2 of 0.2 and 4 respectively, to give Q as 0.4 and e as -1.3 (styrene is the standard in the Q and e scheme and has^{11,2} $Q = 1.00$ and $e = -0.8$). If the positive solution is applied to these relative reactivity ratios, Q and e values for vinylferrocene of 0.2 and -0.3, respectively, are obtained. These values are considerably closer to the other previously determined values (Table VIII.2) than those obtained from the negative solution of equation VIII.4.

The Q and e values for vinylferrocene calculated from the reactivity ratios derived from this study are 0.39 and -0.8, respectively. These values would tend to suggest that vinylferrocene has a lower reactivity than styrene, but a similar polarity. However, Q and e values obtained for vinylferrocene should be treated with caution because it appears that this monomer does not fit the Q and e scheme¹¹, in that widely differing Q and e values have been obtained¹¹ for vinylferrocene from copolymerizations with a variety of monomers. Nevertheless, the Q and e values determined here were found to predict the behaviour of the vinylferrocene-vinyl acetate copolymerization quite accurately.

VIII.B Styrene-vinylferrocene copolymer properties

Two readily determined polymer properties are the limiting viscosity number in solution and the glass transition temperature.

Limiting viscosity numbers of the styrene-vinylferrocene copolymers in A.R. toluene were determined at 30°C (Section III.B.15). The values obtained are listed in table VIII.3 and are displayed as a function of copolymer composition in fig. VIII.4. In general, it has been shown that, for both block¹¹⁴ and random¹¹⁵ copolymers, as the content of the minor component of a copolymer is increased, the polymer chain in solution extends. This arises from repulsion between the unlike units in the copolymer and for copolymers of a given molecular weight, is reflected in an increase in limiting viscosity number. Although the number average molecular weights for the copolymers, listed in table VIII.3, are constant within experimental limits, these are based on GPC measurements, which in fact revealed a decrease in number average molecular size with increasing vinylferrocene content. The calculated number average molecular weights of the polymers remain nearly constant because of the much greater molecular weight, and hence Q factor (molecular weight per $\overset{\circ}{A}$ unit of extended chain length), of the vinylferrocene repeat unit with respect to the styrene repeat unit. The number average molecular weights of these polymers lie in a region which is too high for determination by vapour pressure osmometry, and yet are sufficiently low to allow permeation through the membrane of a membrane osmometer by the lower molecular weight fractions. Thus, in the absence of reliable molecular weight data, the discussion of the effect of the incorporation of vinylferrocene into polystyrene must be limited

to the obvious effect of a decrease in limiting viscosity number with increasing vinylferrocene content, probably resulting from a decrease in the degree of polymerization of the polymer.

The glass transition temperatures, T_g , of the copolymers were determined, under nitrogen, by DSC (Section III.B.18). The values obtained are listed in table VIII.3, and, with the exception of one anomalous value, exhibit a trend of increasing T_g with increasing vinylferrocene content in the copolymer. Such a trend is to be expected, since the T_g of vinylferrocene (Section VII.B) is much greater than that of styrene. Although the relationship between copolymer T_g and vinylferrocene content is apparently linear (Fig. VIII.5), this is probably fortuitous, since the degree of polymerization of the polymer seems to decrease with increasing vinylferrocene content and, as has been observed (Section VII.B), this would result in a lowering of T_g . Indeed, the value obtained for the T_g of polyvinylferrocene by extrapolating the line in fig. VIII.5 to 100% vinylferrocene content is ca. 150°C, which is well below the region defined by the study of vinylferrocene homopolymers (225-247°C, section VII.B).

VIII.C Summary

This study of the copolymerization of vinylferrocene and styrene gave values for the relative reactivity ratios for the two monomers of 0.39 and 2.57 respectively. These values assist in the assessment of two previously determined sets of values, which were somewhat disparate. The Q and e values for vinylferrocene, calculated from the relative reactivity ratios obtained here, are 0.39 and -0.8 respectively, indicating that vinylferrocene has a lower reactivity than styrene, but a similar polarity.

The limiting viscosity numbers of the copolymers, in toluene at 30°C, decreased with increasing vinylferrocene content, but this was attributed to a decrease in degree of polymerization, $\overline{DP}$, of the polymers with increasing vinylferrocene content.

The glass transition temperatures, T_g , of the copolymers increased with increasing vinylferrocene content, but not to the extent that would be expected from the T_g of polyvinylferrocene. Again, this was attributed to a decrease in $\overline{DP}$ of the polymers with increasing vinylferrocene content.

The ultraviolet and visible spectra and ^1H and ^{13}C nmr spectra of the copolymers, which exhibit some anomalies, have been presented and discussed in sections IV.A and IV.B respectively. The esr spectrum of one of the copolymers was discussed in section VII.A, and is similar to that obtained for polyvinylferrocene prepared free-radically in benzene¹⁴.

Table VIII.1

The AIBN-initiated copolymerization of styrene and vinylferrocene in benzene solution at 60°C

$$[\text{AIBN}] = (9.94 \pm 0.07) \times 10^{-3} \text{ mol dm}^{-3}$$

$$\text{Total monomer concentration} = 2.98 \pm 0.02 \text{ mol dm}^{-3}$$

VFcH in feed M_1 , mole%	^a Conversion %	^b VFcH in copolymer m_1 , mole%
0	10.1	0
9.50	9.97	3.92
15.3	9.36	5.54
20.0	9.01	8.65
24.7	8.67	12.2
30.5	8.08	15.6
^c 40.6	6.43	20.8

^a Conversion, based in total monomer weight, after 4 hr.

^b From elemental analysis.

^c $[\text{AIBN}] = 8.10 \times 10^{-3} \text{ mol dm}^{-3}$.

Table VIII.2

Relative reactivity ratios for the copolymerization of vinylferrocene (monomer 1) and styrene (monomer 2) in benzene

r_1	r_2	$^a Q_1$	$^a e_1$	Ref.
^{b,c} 0.39	2.57	0.39	-0.8	This work
^{d,e} 0.08	2.50	0.145	0.47	11
^{d,c} 0.08	2.50	-	-	11
^{d,f} 0.097	2.91	-	-	11
^d 0.2	4	0.4	-1.3	17

^a Based¹¹² on $Q_2 = 1.0$ and $e_2 = -0.8$.

^b Polymerization temperature 60°C.

^c From the Fineman-Ross treatment.

^d Polymerization temperature 70°C.

^e From a curve-fitting technique.

^f Using the integrated form of the copolymer equation⁵⁴ on copolymerizations taken to higher conversion.

Table VIII.3

Styrene-vinylferrocene copolymer properties

m_1 mole%	^a $[\eta]$ $100\text{cm}^3 \text{ g}^{-1}$	^b T_g $^{\circ}\text{C}$	^c $\bar{M}_n$
0	0.29	82	45,500
3.92	0.27	85	47,100
5.54	0.261	85	43,900
8.65	0.257	88	45,500
12.2	0.246	83	47,900
15.6	0.234	93	44,100
20.8	0.227	96.5	48,300

^a In toluene at 30°C .^b Determined by DSC at a heating rate of $2^{\circ}\text{C min}^{-1}$.^c Estimated from GPC analysis, using a Q factor of 41.4 for polystyrene¹¹³ and 88 for polyvinylferrocene¹⁰.

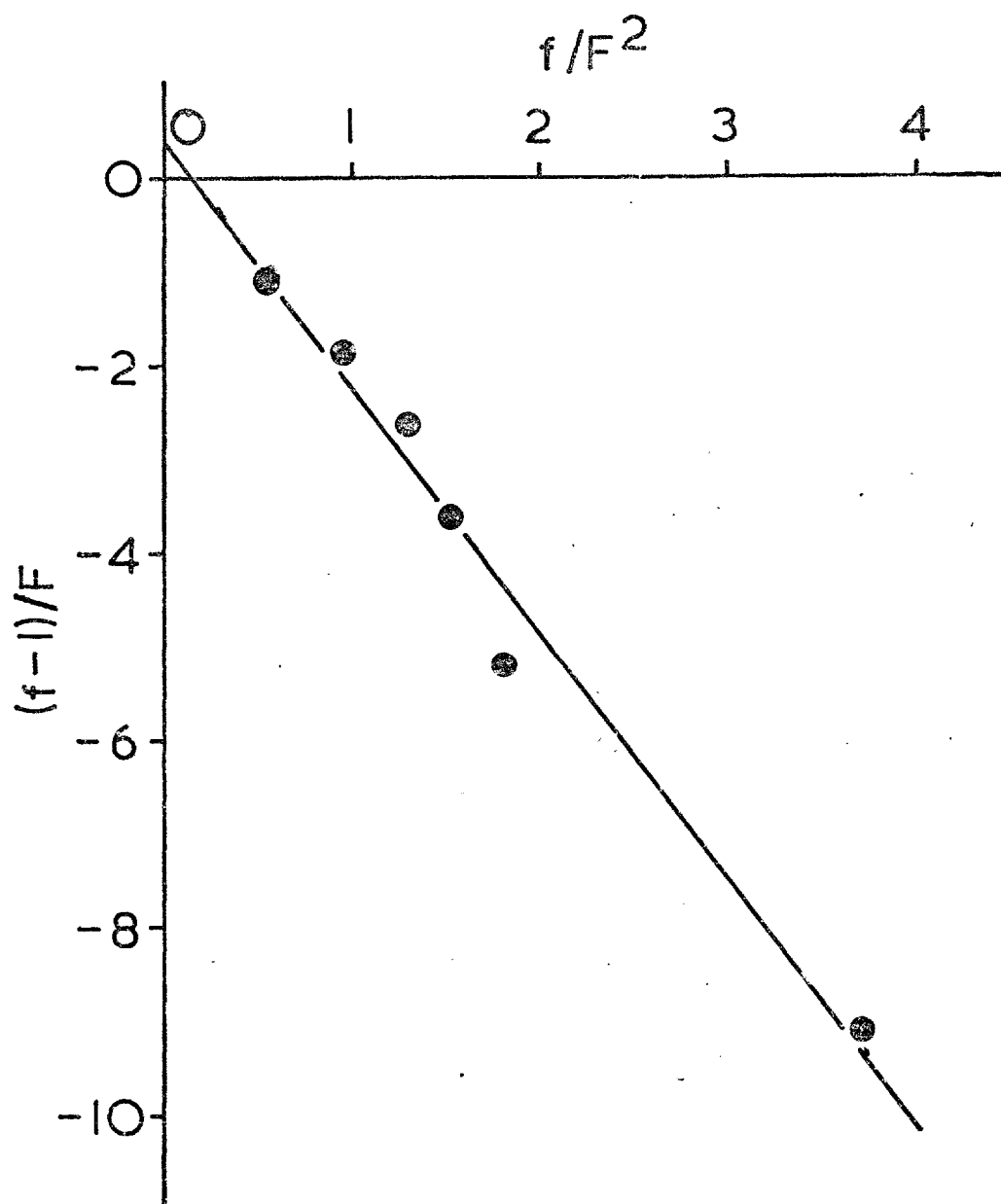


Fig. VIII.1

$(f - 1)/F$ as a function of f/F^2 for the copolymerization of styrene and vinylferrocene, where $F = M_1/M_2$ and $f = m_1/m_2$.

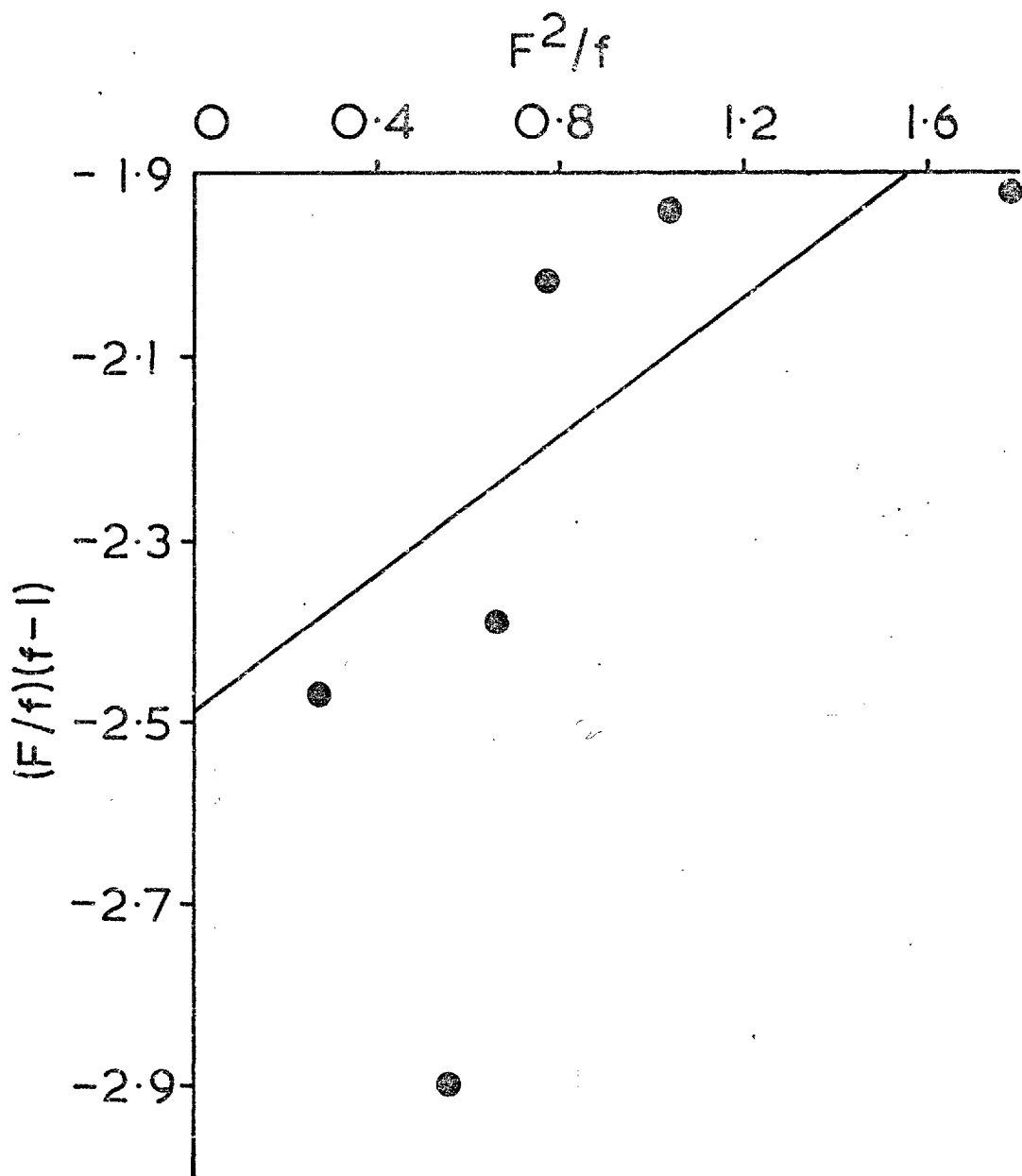


Fig. VIII.2

$(F/f)(f-1)$ as a function of F^2/f for the copolymerization of styrene and vinylferrocene, where $F = M_1/M_2$ and $f = m_1/m_2$. The point $F^2/f = 0.557$ is omitted in the fitting indicated in the plot.

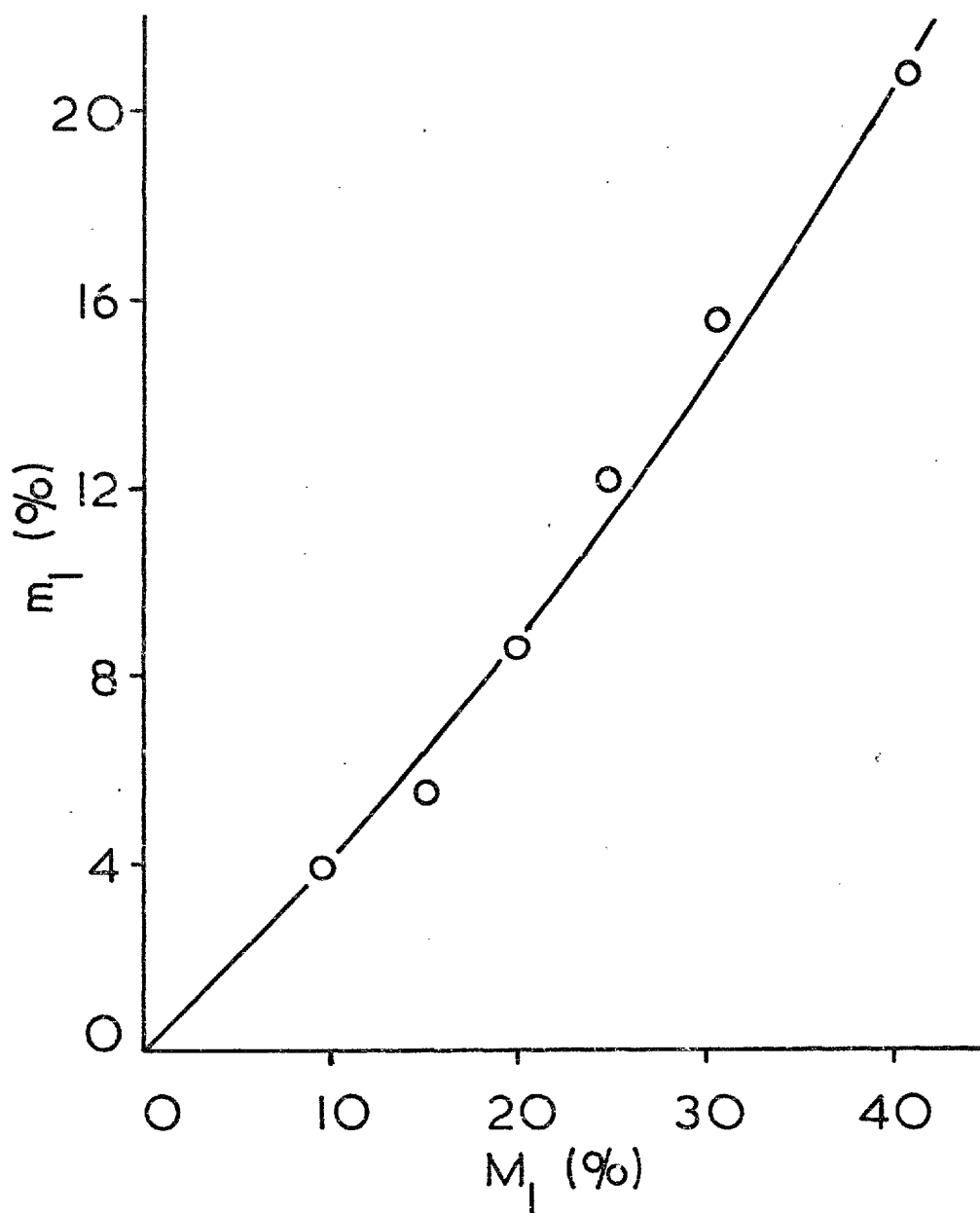


Fig. VIII.3

Mole-percent vinylferrocene in styrene-vinylferrocene copolymers, m_1 , as a function of mole-percent vinylferrocene in the monomer feed, M_1 . The line drawn is that generated using values of 0.39 and 2.57 for r_1 and r_2 , respectively, in the copolymer equation.

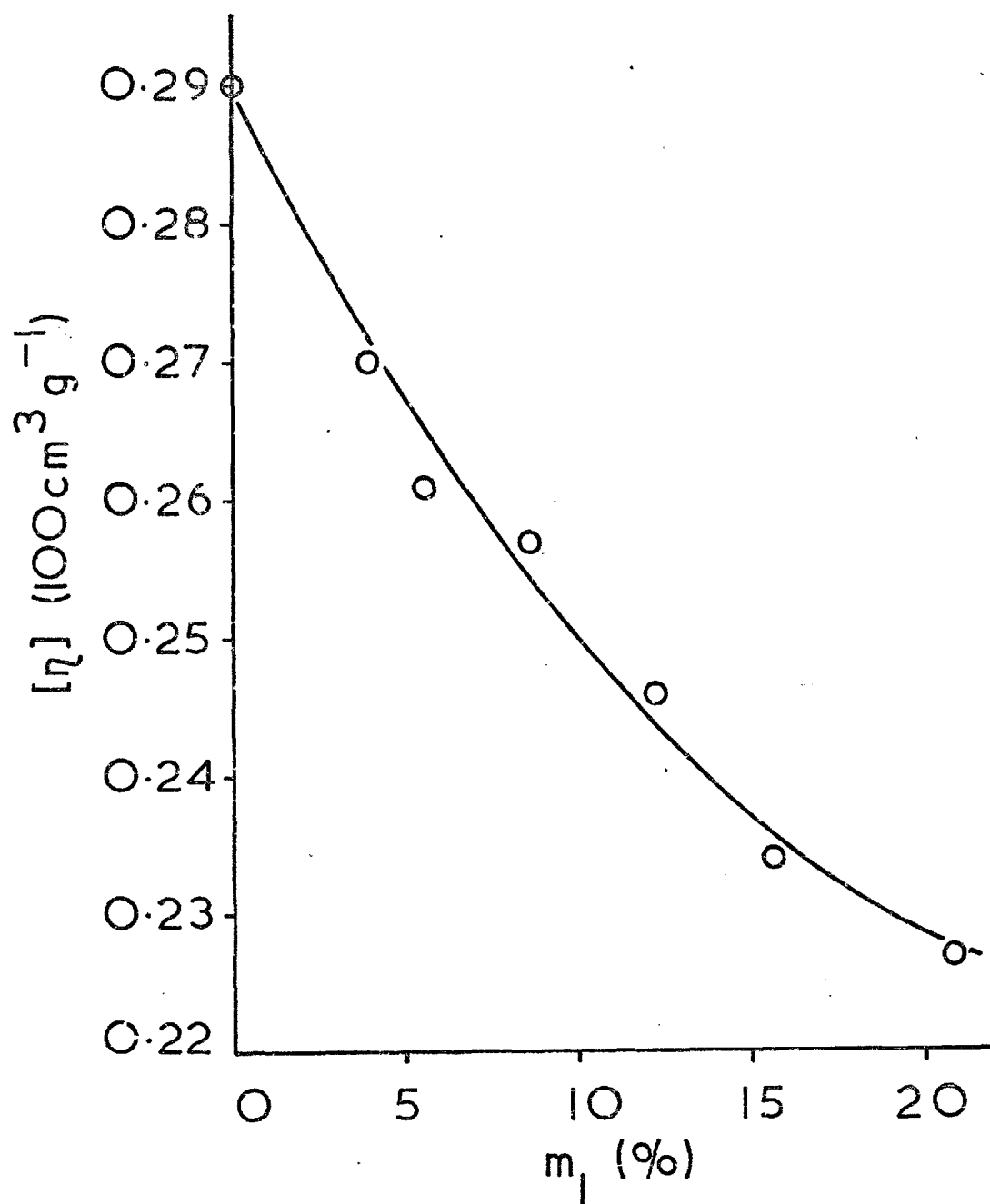


Fig. VIII.4

Limiting viscosity number, $[\eta]$, in toluene at 30°C , of styrene-vinylferrocene copolymers as a function of the vinylferrocene content of the polymer, m_1 , in mole-percent.

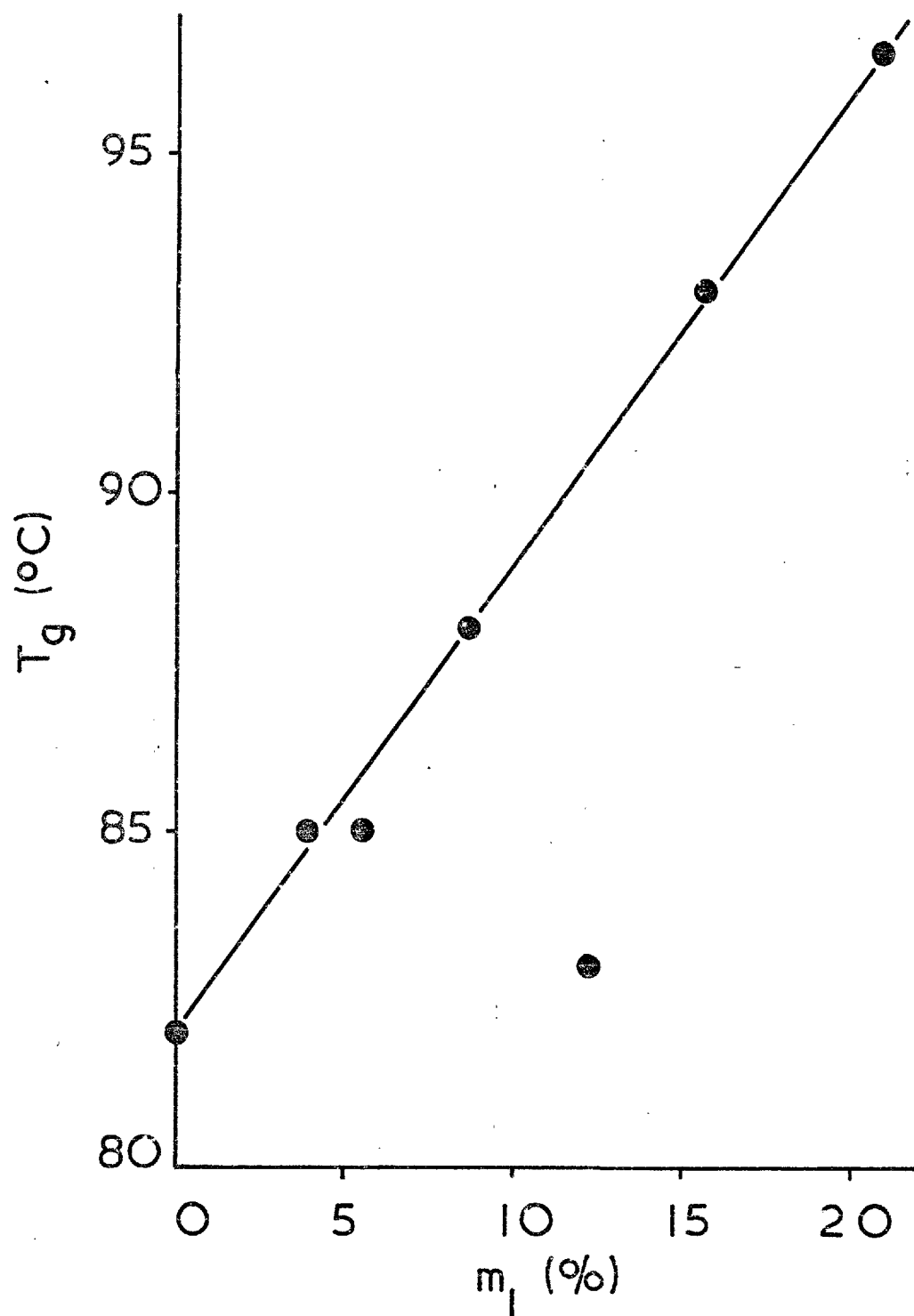


Fig. VIII.5

The glass transition temperature, T_g , of styrene-vinylferrocene copolymers as a function of the vinylferrocene content of the polymer, m_1 , in mole-percent.

IX The free-radical copolymerization of vinylferrocene and vinyl acetate

The AIBN-initiated copolymerization of vinylferrocene and vinyl acetate has been attempted previously¹¹ in benzene solution at 70°C, but with no success. With a vinylferrocene/vinyl acetate mole ratio of 0.48/1 and a reaction time of up to 147 hr, unreacted vinylferrocene was recovered on work-up, and a mole ratio of 0.206/1 also failed to produce copolymer.

However, the importance of this system prompted further investigation of the copolymerization. A preliminary attempt was made in benzene at 60°C, with vinylferrocene, vinyl acetate and AIBN concentrations of 1.8, 2.02 and 1.01×10^{-2} mol dm⁻³ respectively, and yielded yellow polymer in a 3% conversion after 7hr. Infrared spectra demonstrated that this polymer had a high vinylferrocene content, but absorptions at 1740 cm⁻¹ and 1245 cm⁻¹ indicated the presence of vinyl acetate repeat units, since these absorptions may be attributed to the carbonyl stretch and C-O stretch, respectively, in the acetate group.

However, benzene is not a good solvent for this system, because, in addition to the abnormal kinetics observed for the homopolymerization of vinylferrocene in benzene¹¹, this solvent is known to retard the polymerization of vinyl acetate¹¹⁶. Dioxane was chosen, therefore, as the solvent in a more extensive study of the copolymerization at 60°C, on the basis that it dissolves both homopolymers and does not interfere excessively with vinyl acetate polymerization. The vinylferrocene content of the feed was varied from 15 to 89 mole-percent, the total monomer concentration and AIBN concentration being held constant, and the reaction time was increased for the high vinylferrocene

content feeds. The homopolymerization of vinyl acetate was observed dilatometrically and found to be linear with respect to time, at low conversions, indicating high monomer purity. All of the copolymerizations gave low conversions (Table IX.1), and much of the solid isolated was subsequently insoluble in a variety of solvents, including carbon disulphide and chlorobenzene, which are solvents for both homopolymers. The fawn-brown colour of the copolymers, instead of the usual yellow colour of vinylferrocene-containing polymers, suggested that degradation had taken place.

The low yields and the presence of the insoluble residue prevented the normal procedure of purification of the copolymers followed by elemental analysis. The copolymers were analysed, therefore, by infrared spectroscopy. A series of solutions of mixtures of polyvinylferrocene and poly(vinyl acetate), of known composition, were prepared in carbon disulphide, and several films were cast from each of these solutions. Infrared spectra were obtained for these films in the region of 1300 cm^{-1} to 1050 cm^{-1} and the absorbances at 1240 cm^{-1} and 1105 cm^{-1} were determined, the baseline being taken to be the minimum observed at 1145 cm^{-1} . The absorption at 1240 cm^{-1} arises from the C-O stretch in the acetate group and the absorption at 1105 cm^{-1} is due to the antisymmetric ring breath in the ferrocene nucleus. Thus, the ratio of the absorbances of a homopolymer mixture or copolymer at these two frequencies, A_{1240} and A_{1105} , is a measure of the composition of the mixture or copolymer. A calibration plot of A_{1240}/A_{1105} against mole-percent poly(vinyl acetate) (Fig. IX.1) was constructed, therefore, from the data obtained for the homopolymer mixtures.

Carbon disulphide solutions of the vinylferrocene-vinyl

acetate copolymers were centrifuged to remove the insoluble residue prior to casting several films from each solution. Infrared spectra were obtained for the films in the region of 1300 cm^{-1} to 1050 cm^{-1} and the absorbance was determined at 1240 cm^{-1} and 1105 cm^{-1} , as for the films of the homopolymer mixtures. Infrared spectra in the region of 4000 cm^{-1} to 700 cm^{-1} (Fig. IX.2) contained only absorptions attributable to polyvinylferrocene (Fig. VII.9) and poly(vinyl acetate) (Fig. IX.3), thus indicating that the copolymer films were free from impurity. The copolymer compositions were determined from the calibration plot, and these are given in table IX.1.

The Fineman-Ross method was applied to the monomer feed/copolymer composition data in order to estimate values for the relative reactivity ratios (Section II.B), r_1 and r_2 for vinylferrocene and vinyl acetate respectively. The two relevant equations (II.26 and II.27) are reproduced below. The plot of

$$\frac{(f - 1)}{F} = r_1 - r_2 \left(\frac{f}{F^2} \right) \quad (1)$$

$$\frac{F(f - 1)}{f} = r_1 \left(\frac{F^2}{f} \right) - r_2 \quad (2)$$

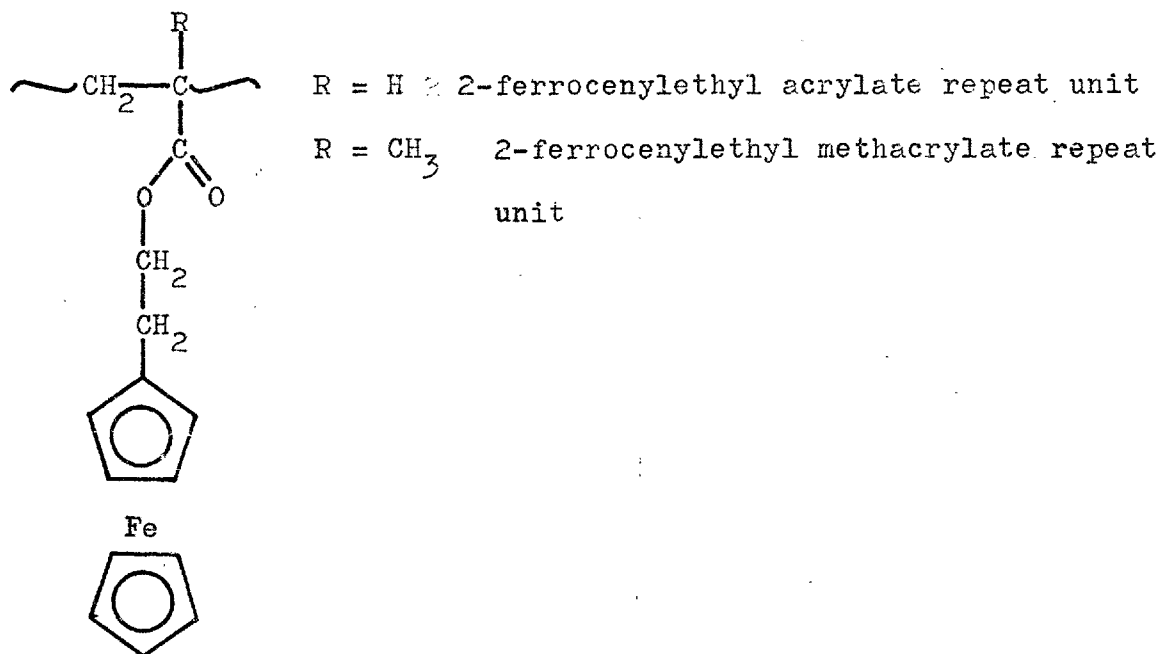
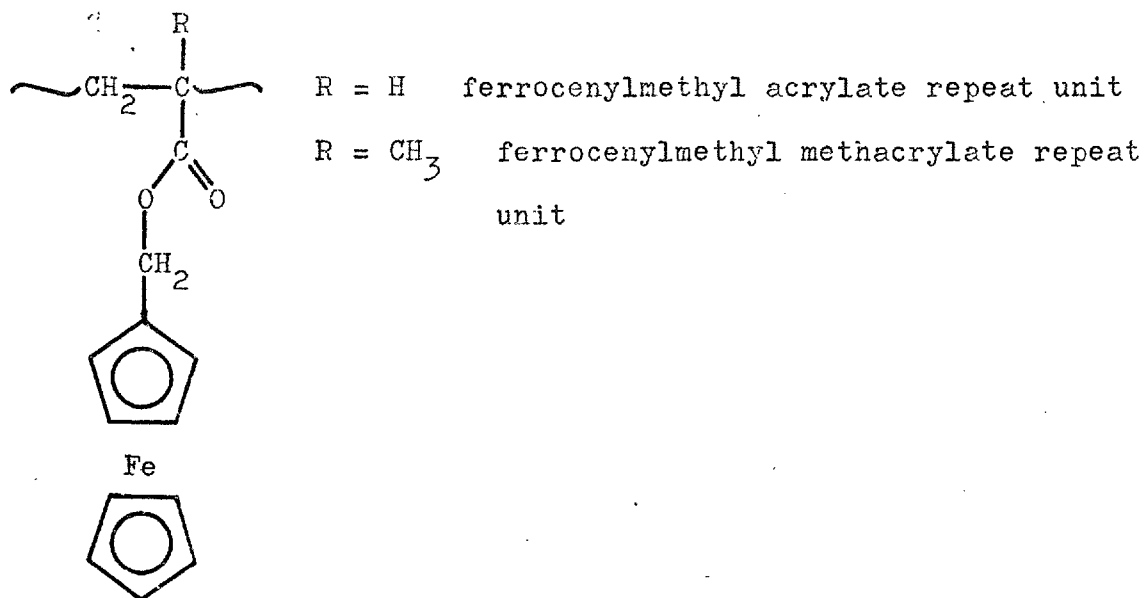
$(f - 1)/F$ against f/F^2 ($F = M_1/M_2$, $f = m_1/m_2$) exhibited scatter, primarily about a value of $(f - 1)/F$ of 14, due to a very small gradient. The plot of $(F/f)(f - 1)$ against F^2/f indicated that the analysis values for the two lowest vinyl acetate content were somewhat high with respect to vinyl acetate; this also being apparent in a plot of copolymer composition against monomer feed composition (Fig. IX.5). However, the remaining four points lie on a straight line in the former plot (Fig. IX.4), and a least mean squares analysis of this data gives a value for r_1 of 14 ± 4 and for r_2 of 0 ± 0.2 . The fit of these values to the experimental data is demonstrated in fig. IX.5

by the line generated from the copolymer equation (II.24) using these values.

The behaviour of this system is similar to that observed for the styrene-vinyl acetate copolymerization (styrene, $r_1 = 55 \pm 10$, vinyl acetate, $r_2 = 0.01 \pm 0.01$ at 60°C ¹¹⁷). If the Q and e scheme is applicable to vinylferrocene, this finding would be expected in view of the similarity between the Q and e values for styrene and those obtained in section VIII.A for vinylferrocene, from the copolymerization with styrene. In fact, the relative reactivity ratios predicted for the copolymerization of vinylferrocene and vinyl acetate from these Q and e values for vinylferrocene and literature values¹¹² for Q and e for vinyl acetate ($Q = 0.026$, $e = -0.22$) are r_1 of 9.4 and r_2 of 0.076.

The fawn-brown colour of the copolymers, and the presence of a residue, which was insoluble in solvents for both the homopolymers and the copolymers, suggested that degradation had taken place, either during the polymerization or on isolation of the copolymer. The flow time of a ferrocene/poly(vinyl acetate) solution in dioxane in a vacuum viscometer was unaltered after 18 hr at 60°C . Although this clearly demonstrates that the polymer was not degraded by ferrocene under these conditions, it cannot preclude degradation of a vinylferrocene-vinyl acetate copolymer under the same conditions, since, in the copolymer, the vinylferrocene and vinyl acetate repeat units are not only in intimate contact but also are bonded to each other. This latter condition might be the more important in view of the reported successful copolymerization^{30,32} of vinyl acetate with ferrocene-containing acrylates and methacrylates. As can be seen from the structures given

below, the ferrocene nucleus in the repeat unit from these



monomers is well removed from the polymer backbone, and hence from any comonomer repeat unit.

Thermal analysis, by DSC (Section III.E.18), of samples cast from centrifuged solutions failed to locate a glass transition for any of the copolymers. The traces obtained indicated that thermal degradation occurred, even under nitrogen, before the T_g was reached.

Table IX.1

The AIBN-initiated copolymerization of vinylferrocene and vinyl acetate in dioxane at 60°C

Total monomer concentration = $3.06 \pm 0.08 \text{ mol dm}^{-3}$

$[\text{AIBN}] = (4.9 \pm 0.12) \times 10^{-3} \text{ mol dm}^{-3}$

VFcH in feed, M_1 mole%	Reaction time hr	Conversion a %	^b $\frac{A_{1240}}{A_{1105}}$	VFcH in copolymer, m_1 mole%
15.0	3	0.74	0.483	77
30.3	9	1.6	0.356	86.9
42.0	9	1.7	0.234	92.6
59.9	9	2.1	0.148	95.7
75.1	14	2.1	0.122	96.5
88.8	14	2.2	0.078	97.8

^a Based on total monomer weight, and including insoluble material.

^b Mean value from infrared spectra of films.

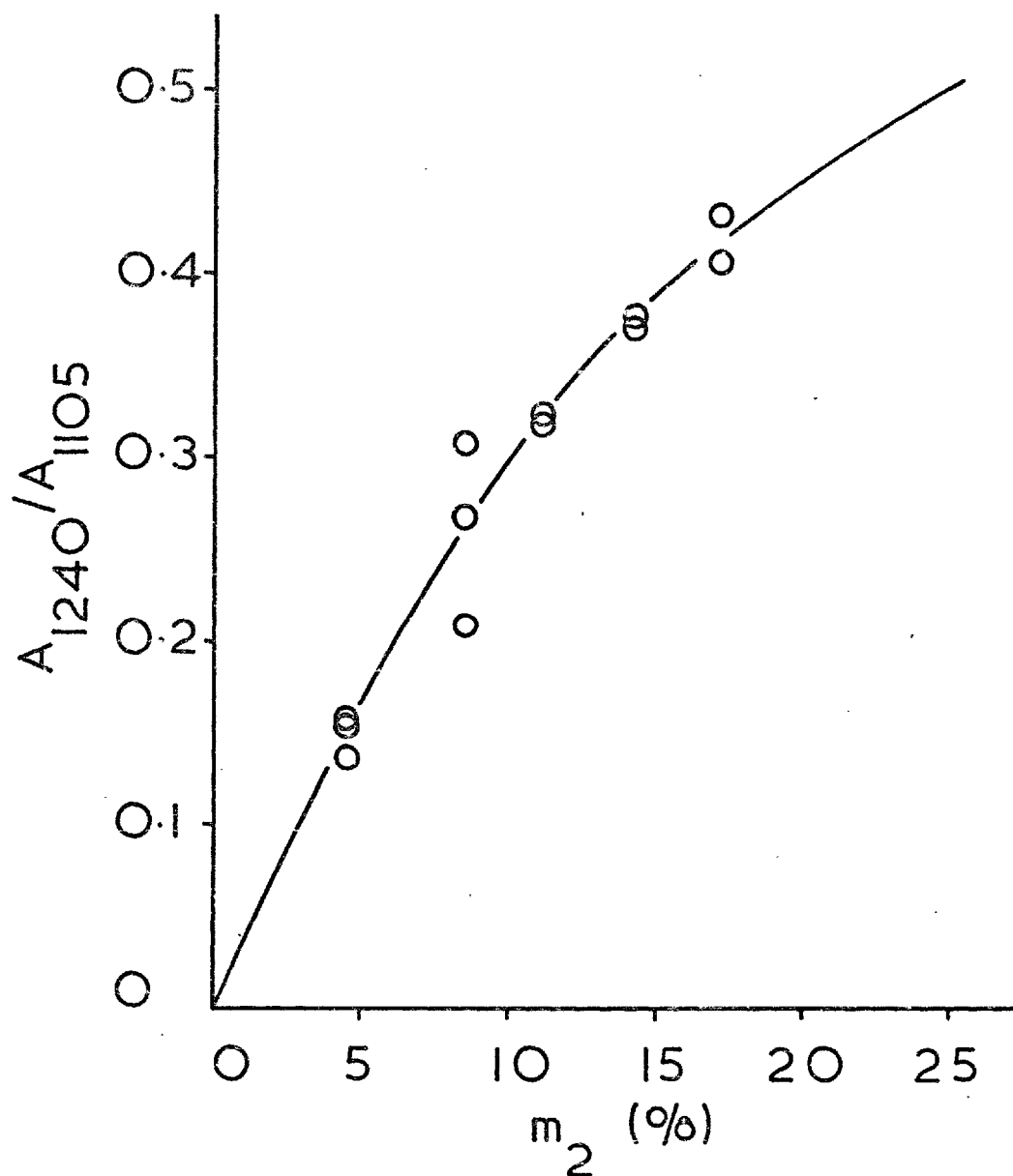


Fig. IX.1

A_{1240}/A_{1105} in the infrared spectra of polyvinylferrocene/poly(vinyl acetate) mixtures as a function of poly(vinyl acetate) content, m_2 , in mole-percent.

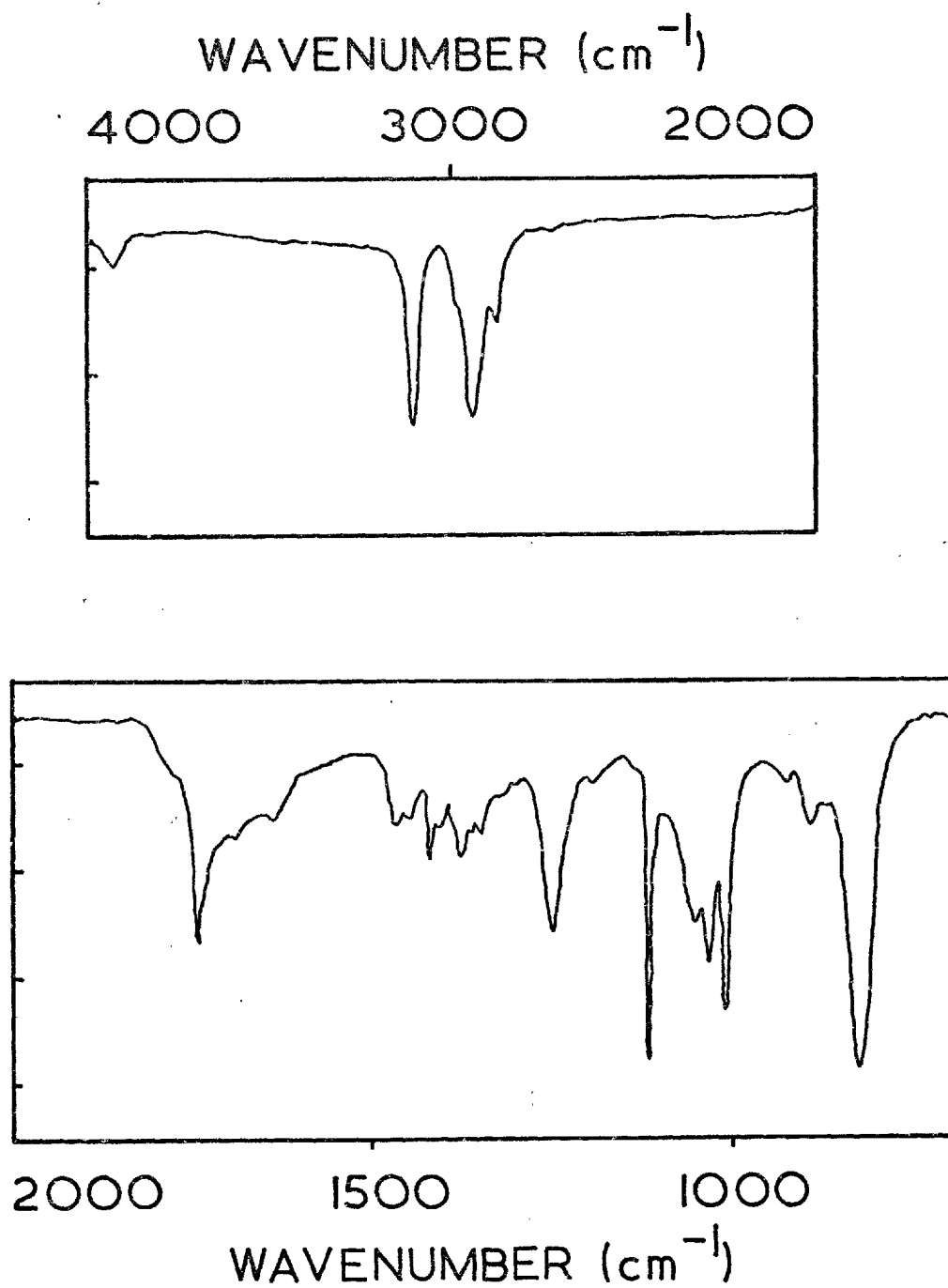


Fig. IX.2

Infrared spectrum of a vinylferrocene-vinyl acetate copolymer (86.9 mole-percent vinylferrocene) film, cast from carbon disulphide.

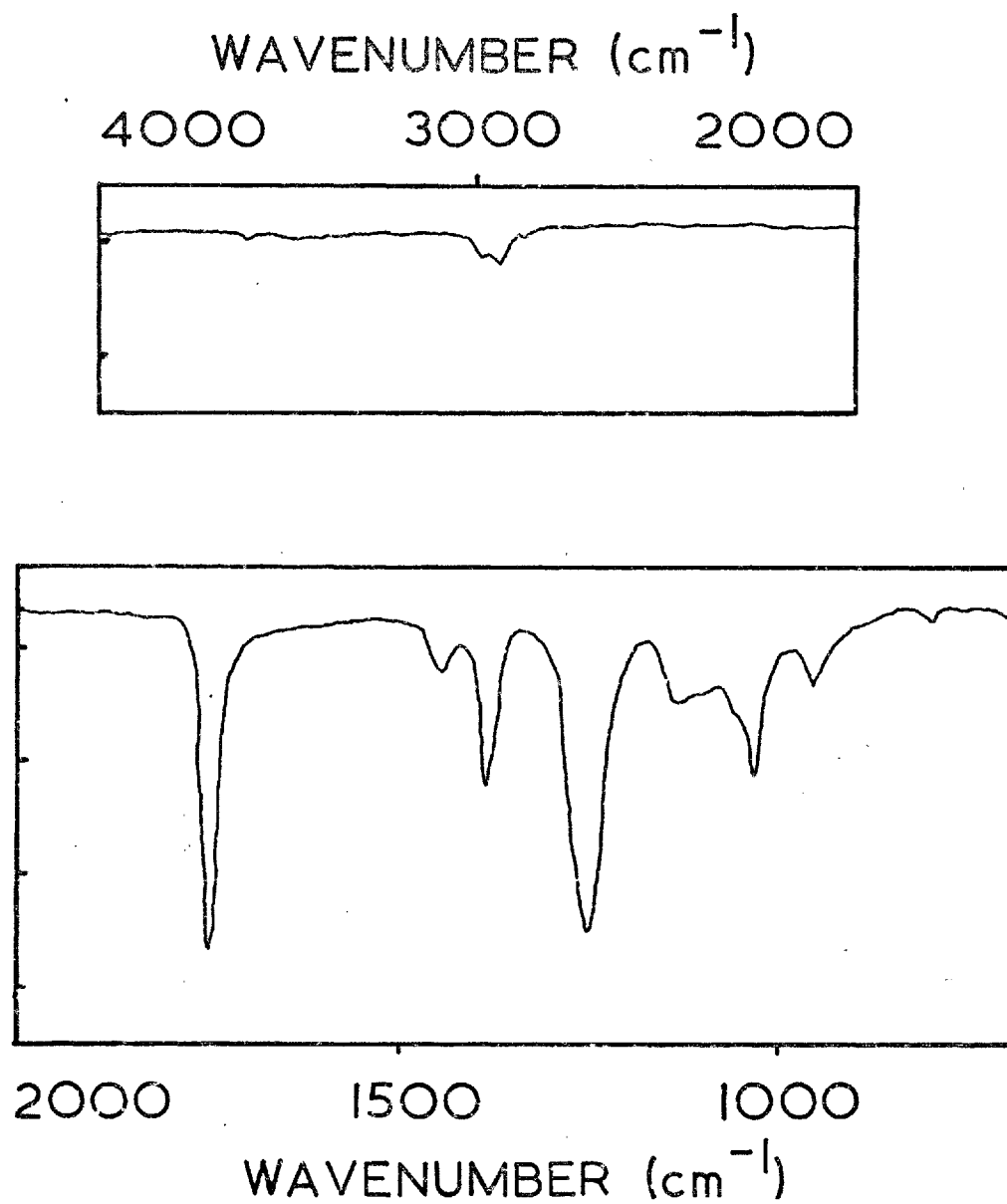


Fig. IX.3

Infrared spectrum of a poly(vinyl acetate) film, cast from chlorobenzene.

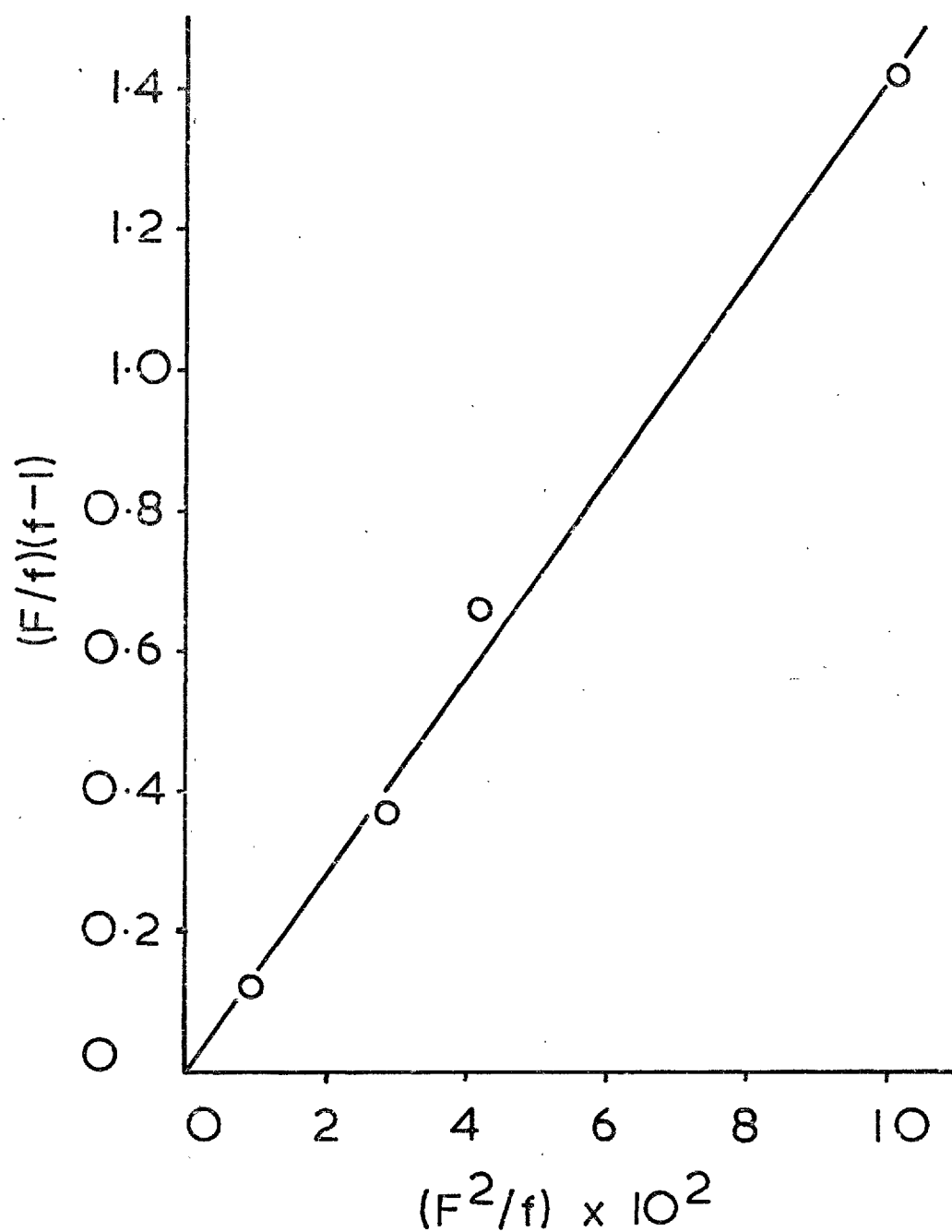


Fig. IX.4

$(F/f)(f - 1)$ as a function of F^2/f for the copolymerization of vinylferrocene and vinyl acetate, where $F = M_1/M_2$ and $f = m_1/m_2$.

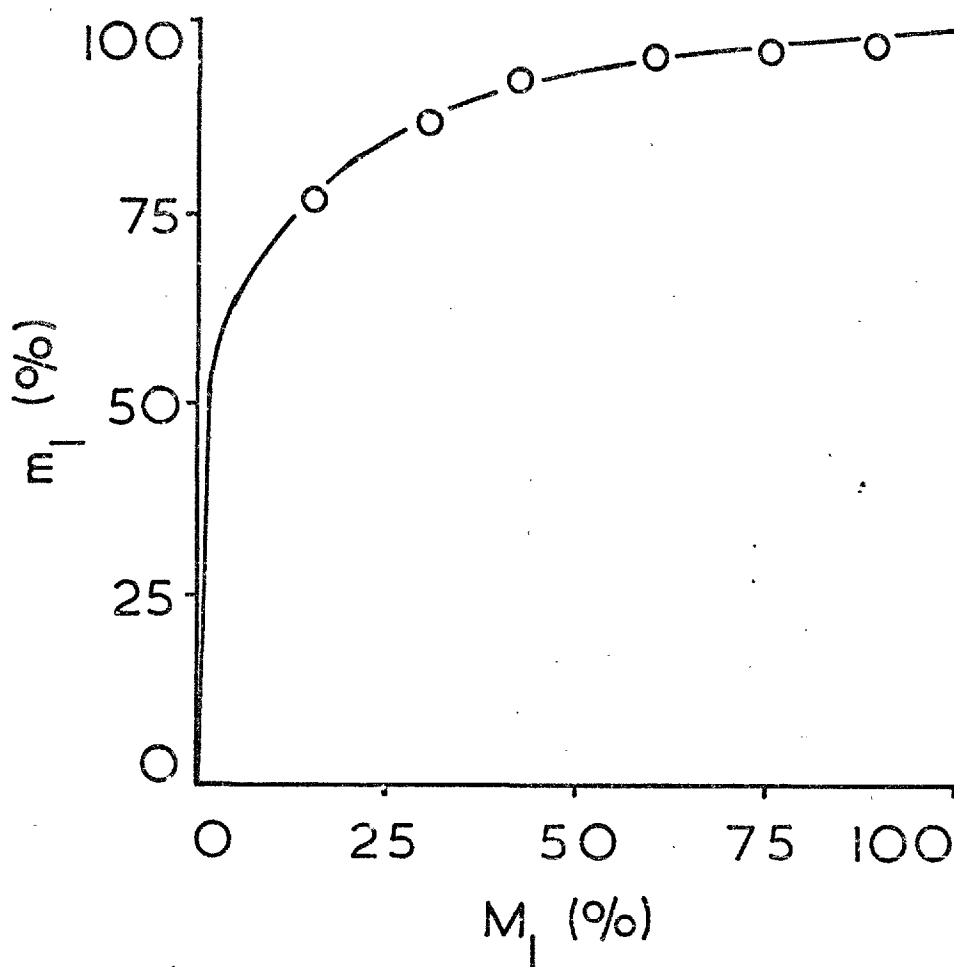


Fig. IX.5

The vinylferrocene content of vinylferrocene-vinyl acetate copolymers, m_1 mole-percent, as a function of the vinylferrocene content of the monomer feed, M_1 mole-percent. The line drawn is obtained by using $r_1 = 14$ and $r_2 = 0$ in the copolymer equation.

X The polymerization of vinylferrocene by heterogeneous
Ziegler-Natta catalysts

Recently, there has been a report²⁴ of vinylferrocene polymerization by homogeneous Ziegler-Natta catalysts. The polymerizations were carried out at 60°C in chloroform solution, and catalysts of the form $\text{AlEt}_3/\text{TM}(\text{acac})_2$ and $\text{AlEt}_2\text{Cl}/\text{TM}(\text{acac})_2$, TM being Ni, Co or VO, gave yields of 20-75% over a period of 6-24 hr. However, the polymers formed would seem to be of low molecular weight, since substantial amounts were methanol soluble. Catalysts of the form $\text{Al}(\text{i-Bu})_3/\text{TM}(\text{acac})_2$ were found to be inefficient under the same conditions.

In an attempt to prepare high molecular weight polymer, a study of the polymerization of vinylferrocene by a variety of commonly used heterogeneous Ziegler-Natta catalysts was undertaken.

X.A The homopolymerization of vinylferrocene by
heterogeneous Ziegler-Natta catalysts

Vinylferrocene was polymerized in benzene at 60°C by catalysts formed by combinations of either AlEt_3 or AlEt_2Cl with one of the following transition metal compounds: TiCl_3 , TiCl_4 , VCl_3 , VOCl_3 . A dilatometric study of a polymerization in the presence of $\text{AlEt}_3/\text{TiCl}_3$, the monomer solution being added to the catalyst immediately after the latter had been mixed, suggested that a catalyst ageing period of 30 min. would be adequate. The performance of all of the catalyst mixtures was assessed then, using a standard method (Section III.B.10), polymer yields being determined by gravimetric analysis.

The results are listed in table X.1 and demonstrate that

the catalysts fall into two distinct categories, low yield and high yield. The conversions given for the high yield catalysts are approximate because of difficulties experienced in isolating polymers from these systems. This difficulty arose when the polymerization mixture from these systems was poured into methylated spirits, since under these conditions the polymer predominately formed a gum. In contrast, the polymer formed by the low yield catalysts was isolated as a powder in methylated spirits.

The behaviour of the high yield systems is similar to that observed for vinylferrocene polymerization by TiCl_3 alone. With a vinylferrocene concentration of $2.5 \times 10^{-2} \text{ mol dm}^{-3}$, 100% conversion was attained in less than 20 min. at 60°C . Again, the polymer formed in this polymerization was isolated as a gum in methylated spirits. The polymerization probably proceeded by a cationic mechanism, with traces of water acting as co-catalyst. The formation of a gum in methylated spirits suggests that the polymer was of very low molecular weight, which is typical of cationic polymerizations of vinylferrocene²². Thus, it seems possible that polymerization in the presence of the high yield catalysts also proceeded via a cationic mechanism. Certainly, TiCl_4 has been used as a catalyst in the cationic polymerization of vinylferrocene²².

The sharp change in conversion would tend to suggest a different polymerization mechanism in the presence of the low yield catalysts. Also, polymer prepared in the presence of the $\text{AlEt}_3/\text{TiCl}_3$ catalyst had a limiting viscosity number of $0.030 \text{ 100cm}^3 \text{ g}^{-1}$ in tetrahydrofuran at 30°C , from which a viscometric average molecular weight, $\bar{M}_v$, of 4,350 may be calculated, using values¹⁵ of $7.2 \times 10^{-5} \text{ 100cm}^3 \text{ g}^{-1}$ and 0.72 for K and a,

respectively, in the Mark-Houwink equation (Equation III.16). Furthermore, the formation of isotactic polystyrene in the presence of vinylferrocene in the $\text{AlEt}_3/\text{TiCl}_3$ catalysed copolymerization of vinylferrocene and styrene (Section X.B) clearly demonstrates the presence of Ziegler-Natta type catalyst sites in the polymerization. Thus, it would seem that the low yield catalysts promote polymerization of vinylferrocene by a Ziegler-Natta mechanism. The precise mechanism of this mode of polymerization has been the subject of much study and debate, and several extensive reviews have been made of this subject¹¹⁸.

The conversion obtained even with $\text{AlEt}_3/\text{TiCl}_3$, the more active of the two catalysts giving Ziegler-Natta type polymerization, is extremely low for this type of polymerization. Indeed, even styrene, which is itself not one of the more active monomers toward such catalysts, gave ten times the yield obtained for vinylferrocene under the same conditions. The low activity of vinylferrocene toward these catalysts may be due to the large pendant ferrocene nucleus hindering the access of further monomer to the active site.

The infrared and ^1H nmr spectra of polymer prepared with the $\text{AlEt}_3/\text{TiCl}_3$ catalyst were identical to those obtained for free-radically prepared polyvinylferrocene (Section VII.B).

X.B The homopolymerization of styrene and copolymerization of styrene and vinylferrocene with $\text{AlEt}_3/\text{TiCl}_3$ as catalyst

A benzene solution of styrene was polymerized at 60°C using the standard method employed for vinylferrocene in the previous section (X.A), with $\text{AlEt}_3/\text{TiCl}_3$ as catalyst ($[\text{St}] = 1.35 \text{ mol dm}^{-3}$, $[\text{AlEt}_3] = 0.128 \text{ mol dm}^{-3}$, $[\text{TiCl}_3] = 5.5 \times 10^{-2} \text{ mol dm}^{-3}$). A 43% conversion was obtained in 1 hr. The polystyrene formed was insoluble in toluene, but dissolved in warm chlorobenzene. This suggests that the polymer had a high isotactic content. Thermal analysis, by DSC, confirmed the presence of isotactic polymer, since the DSC trace (Fig. X.1.a) exhibited not only the endothermic dip associated with the glass transition (90°C) but also an exothermic peak (159°C , max. 178°C) followed by an endothermic peak (218°C). These last two features are characteristic of isotactic polystyrene¹¹⁹. The exothermic peak is due to crystallization of the isotactic polymer and the endothermic peak is caused by the subsequent melting of the crystals at the higher temperature. The values obtained for the temperature at which the rate of crystallization is a maximum, T_c^{max} , (178°C) and for the melting point, T_m , (218°C) are in reasonable agreement with literature values¹¹⁹ of ca. 175°C and 240°C respectively.

A benzene solution of styrene and vinylferrocene was polymerized at 60°C by the standard method ($[\text{VFcH}] = 1.08 \text{ mol dm}^{-3}$, $[\text{St}] = 1.1 \text{ mol dm}^{-3}$, $[\text{AlEt}_3] = 0.105 \text{ mol dm}^{-3}$, $[\text{TiCl}_3] = 4.5 \times 10^{-2} \text{ mol dm}^{-3}$). After 1 hr, the conversion, with respect to total monomer weight, was 9%. Part of the polymer formed, which was yellow in colour, was soluble in toluene to give a yellow solution, the remainder being

insoluble. The insoluble polymer was extracted repeatedly with A.R. toluene until the solution was no longer coloured. The residual insoluble polymer was white in colour. This white polymer was found to be soluble in warm chlorobenzene, which suggests that it was isotactic polystyrene. An infrared spectrum of this polymer contained only absorptions due to polystyrene. Thermal analysis, by DSC, confirmed that the polymer had a high isotactic content, the DSC trace (Fig. X.1.b) being very similar to that obtained for the isotactic polystyrene prepared in the homopolymerization of styrene (Fig. X.1.a). It gave $T_c^{\max}$ as 159°C and T_m as 212°C .

The infrared spectrum of the toluene soluble polymer from the copolymerization contained absorptions due to both styrene and vinylferrocene repeat units. Elemental analysis gave the vinylferrocene content of this polymer as 27.2 mole-percent. However, ultraviolet and visible spectra of a toluene solution of the polymer gave a value for A_{444}/A_{326} , which is equivalent to $\epsilon_{444}/\epsilon_{326}$, of 1.07. This demonstrates the presence of true copolymer, since the value for homopolymer mixtures is 1.39 (Section IV.A). Using the plot of $\epsilon_{444}/\epsilon_{326}$ against mole-percent vinylferrocene in the copolymer (Section IV.A, fig. IV.6), constructed from data for free-radically prepared styrene-vinylferrocene copolymers, this value indicates a copolymer composition of 15 mole-percent vinylferrocene. This suggests that either polyvinylferrocene was formed as well as styrene-vinylferrocene copolymer or that there was considerable formation of homopolymer blocks in the latter. Thus, it would seem probable that when a mixture of styrene and vinylferrocene is polymerized by $\text{AlEt}_3/\text{TiCl}_3$, under these conditions, both homopolymers are formed in addition to the copolymer. Such

behaviour is not unusual in Ziegler-Natta catalysed copolymerizations¹²⁰, a particular example¹²¹ being the polymerization of mixtures of styrene and 4-methylpent-1-ene or 3-methylbut-1-ene, with $\text{VOCl}_3/\text{Al}(\text{i-Bu})_3$ as catalyst. Here, the presence of both homopolymers and copolymer in the reaction products was attributed to the presence of different active sites in the catalyst.

X.C Summary

Polymerization of vinylferrocene, in benzene at 60°C, by catalysts formed from a combination of either AlEt_2Cl and one of TiCl_3 , TiCl_4 , VCl_3 and VOCl_3 or AlEt_3 and one of TiCl_4 and VOCl_3 proceeds to 100% conversion within 1 hr. The polymer formed was isolated as a gum in methylated spirits, and was therefore probably of very low molecular weight. Since some of the components of these catalysts can act as catalysts or co-catalysts in the cationic polymerization of vinylferrocene, a cationic mechanism may be operating in the presence of these combination catalysts.

Catalysts formed by the combination of AlEt_3 with either TiCl_3 or VCl_3 gave very low conversions, under these conditions, and the polyvinylferrocene formed was of higher molecular weight than that obtained with the other combination catalysts. There is no reason to doubt that these polymerizations proceeded by a Ziegler-Natta mechanism, particularly since this mechanism was operating in a styrene/vinylferrocene copolymerization. The low conversion is possibly caused by the bulky ferrocene nucleus of the terminal unit of a growing polymer chain hindering the approach of monomer molecules to the active site.

The $\text{AlEt}_3/\text{TiCl}_3$ catalyst gave isotactic polystyrene in a styrene homopolymerization. The polymerization of a mixture of styrene and vinylferrocene by this catalyst gave isotactic polystyrene, copolymer and possibly polyvinylferrocene.

Table X.1

Vinylferrocene polymerization by heterogeneous Ziegler-Natta catalysts in benzene at 60°C

Polymerization time = 1 hr

[VFcH] mol dm ⁻³	Alkyl aluminium and conc. mol dm ⁻³	^a TM compound and conc. mol dm ⁻³ x 10 ²	^a $\frac{[Al]}{[TM]}$	Conv. %
1.4	AlEt ₃ , 0.134	^b TiCl ₃ , 5.8	2.3	4
1.4	AlEt ₃ , 0.134	VCl ₃ , 6.4	2.1	1
1.4	AlEt ₃ , 0.134	TiCl ₄ , 6.4	2.1	100
1.4	AlEt ₃ , 0.134	VOCl ₃ , 6.3	2.1	100
1.6	AlEt ₂ Cl, 0.137	^b TiCl ₃ , 5.8	2.4	100
1.6	AlEt ₂ Cl, 0.137	VCl ₃ , 6.4	2.1	100
1.6	AlEt ₂ Cl, 0.137	TiCl ₄ , 6.4	2.1	100
1.6	AlEt ₂ Cl, 0.137	VOCl ₃ , 6.3	2.2	100

^a TM represents transition metal.

^b More correctly, δ -TiCl₃.1/3AlCl₃.

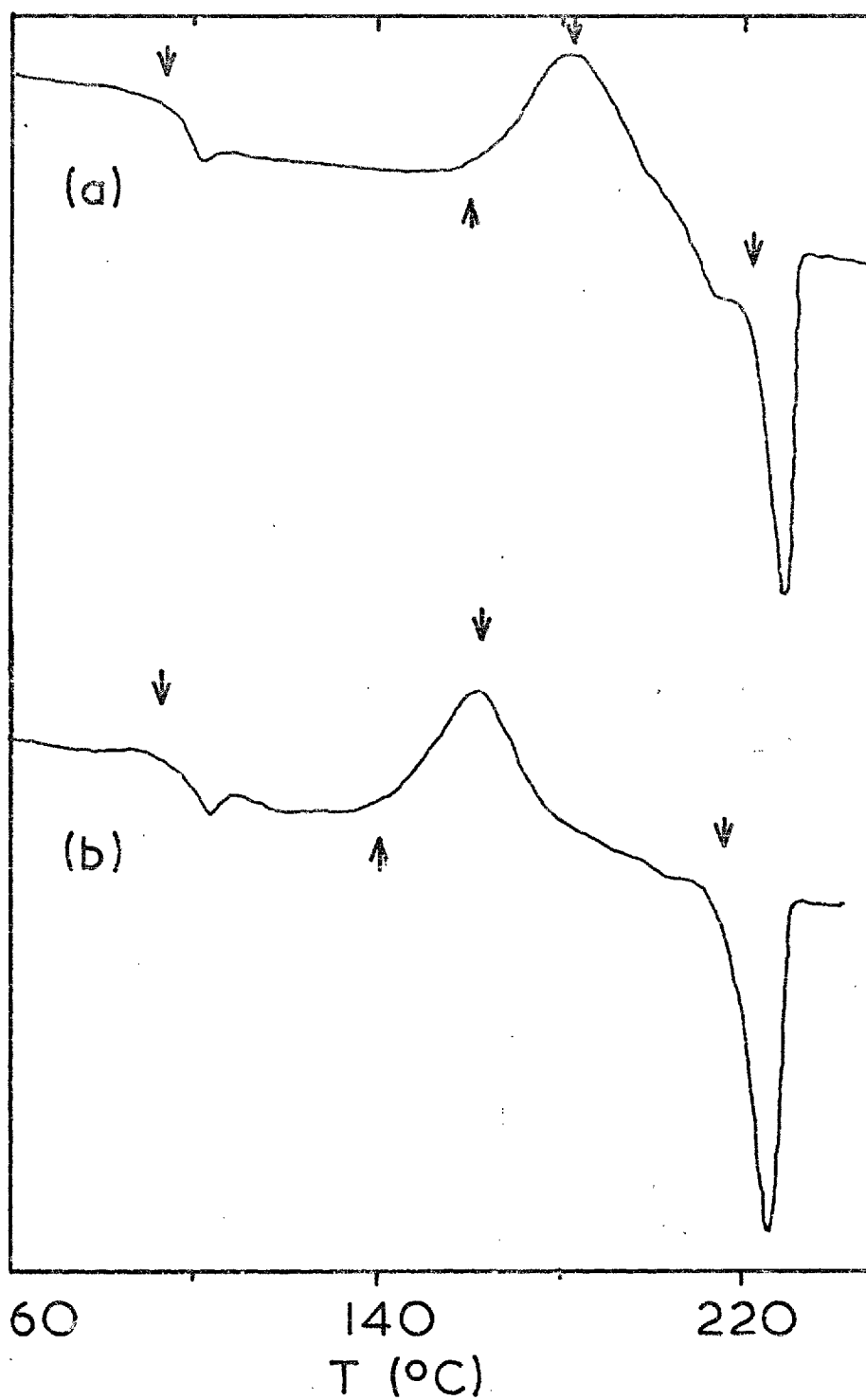


Fig. X.1

DSC curves for (a) isotactic polystyrene and (b) the toluene insoluble polymer from the Ziegler-Natta copolymerization of styrene and vinylferrocene, heating rate $10^{\circ}\text{C min}^{-1}$ and ΔT sensitivity $0.05^{\circ}\text{C in}^{-1}$.

The transitions are indicated by arrows.

XI The anionic polymerization of vinylferrocene

The anionic polymerization of vinylferrocene by both *n*-butyllithium and methyllithium has been recorded¹²², but no details were given. More detailed reports have been made concerning the anionic polymerization of acryloylferrocene³⁸ and 1-ferrocenyl-1,3-butadiene^{34,35,37}. The most comprehensive study³⁷ was carried out on the polymerization of 1-ferrocenyl-1,3-butadiene by *n*-butyllithium in toluene at room temperature. Complete conversion was only attained when low monomer to initiator ratios were employed, and the molecular weights of the polymers formed were consequently low. Additionally the dispersity indices ($\bar{M}_w/\bar{M}_n$) of these polymers were relatively high for anionically prepared polymers. Analysis of the molecular weight data led to the suggestion that both the initiator and the poly(1-ferrocenyl-1,3-butadienyl) anion transferred to the ferrocene nucleus, thereby terminating the polymerization.

As a part of an investigation of the methods available to prepare high molecular weight linear polyvinylferrocene in a controlled manner, a study of the anionic polymerization of vinylferrocene over a wide range of conditions was undertaken.

XI.A The anionic homopolymerization of vinylferrocene

The anionic polymerization of vinylferrocene was attempted in cyclohexane, decahydronaphthalene and tetrahydrofuran solution with *n*-butyllithium or cumylpotassium as initiator (Section III.B.8). The polymerization temperature was varied from -75°C to 60°C. The conditions of the polymerizations and the conversions obtained are summarized in table XI.1.

As in the anionic polymerization of 1-ferrocenyl-1,3-

butadiene, it would appear that transfer to the ferrocene nucleus is the dominant feature of the anionic polymerization of vinylferrocene. In the absence of transfer, anionic polymerizations in polar solvents, such as tetrahydrofuran, proceed rapidly to 100% conversion, the polymerization being slower in non-polar solvents. Polymer anions in such polymerizations are known as 'living' polymers and give polymer with a low dispersity index. Transfer terminates the polymer anion before complete conversion is attained and therefore produces polymer with a lower molecular weight than predicted from a knowledge of the monomer to initiator ratio, assuming that complete and instantaneous initiation took place. Also, the dispersity index of the polymer obtained from the system as a whole is higher than that of polymer formed in a 'living' polymerization. However, 100% conversion may still be achieved if the anion formed as a result of the transfer reaction is capable of initiating further polymerization. If the anion formed by transfer is incapable of initiating polymerization, the number of propagating species declines with time and the polymerization may fail to reach 100% conversion. Again, the dispersity index of polymer formed in such a system is greater than that for polymer formed in a 'living' polymerization.

The suggestion³⁷ that transfer to the ferrocene nucleus occurred in the anionic polymerization of 1-ferrocenyl-1,3-butadiene was based on the reported¹²³ lithiation of ferrocene by n-butyllithium. Thus, it would seem probable that such a reaction would compete with initiation and propagation in the vinylferrocene polymerization and, although lithiated ferrocene has been reported¹²⁴ as initiating butadiene polymerization, it is possible that these species are not capable of initiating vinylferrocene polymerization. However, the infrared spectra

of two of the polymers terminated with carbon dioxide did not contain absorptions due to the carboxyl group. If there had been anions on the polymer chain when the reaction mixture was terminated with carbon dioxide, carboxyl groups would have been formed and the strong carbonyl absorption should have been detected in the infrared spectrum of the polymer. It would appear, therefore, that transfer from the polyvinylferrocenyl anion occurs primarily, if not exclusively, to monomer under the conditions employed in these polymerizations (Table XI.1).

The results obtained may be explained by the change in the relationship between transfer and initiation and propagation as the polymerization conditions vary. With *n*-butyllithium as initiator the observed temperature effect of polymer formation only at higher temperatures may be accounted for by the reported¹²³ decrease in the lithiation of ferrocene as the reaction temperature was increased. Thus, it would seem that at low temperatures lithiation of the ferrocene nucleus occurred exclusively, whereas at higher temperatures initiation of polymerization was able to compete effectively. However, subsequent transfer by the polyvinylferrocenyl anion to the ferrocene is indicated by the low conversions obtained for these polymerizations. With cumylpotassium as initiator, initiation occurred over the entire temperature range studied. There have been no reported studies of the metalation of ferrocene by cumylpotassium and, therefore, the temperature dependence of this reaction is unknown. However, the low conversions observed and the absence of carboxyl groups in polymers from reactions terminated with carbon dioxide suggest that metalation of the ferrocene nucleus of the monomer does occur. The results for these systems are best accommodated if

this reaction is favoured, over initiation and propagation, by higher temperatures, although the low yield at -75°C does not readily fit this scheme.

This study, carried out over a wide range of reaction conditions, suggests that anionic polymerization cannot be used to obtain high molecular weight, low dispersity polyvinylferrocene.

XI.B The anionic random copolymerization of vinylferrocene and styrene

Vinylferrocene and styrene were copolymerized in cyclohexane ($[VFcH] = [St] = 0.4 \text{ mol dm}^{-3}$) at 60°C , with n-butyllithium as initiator ($[total \text{ monomer}]/[In] = 38$). A 25% conversion, based in total monomer weight, was obtained after 3 hr. Elemental analysis gave the vinylferrocene content of the polymer as 7.86 mole-percent. GPC analysis demonstrated that this was a copolymer with a dispersity index of 1.48 and, using Q factors of 41.4 and 88 for polystyrene¹¹³ and polyvinylferrocene¹⁰ respectively, the number average molecular weight was estimated to be 20,000. Data from visible and ultraviolet spectra of solutions of the polymer are given in table IV.4 and the value of $\epsilon_{444}/\epsilon_{324}$ of 0.918 confirms that it is a random copolymer (Section IV.A).

The considerably higher molecular weight than would be predicted from the monomer to initiator ratio suggests that transfer competed with initiation. The low conversion and relatively high dispersity index also suggest the occurrence of termination by transfer, as would be expected from the study of the anionic homopolymerization of vinylferrocene (Section XI.A). In view of the results obtained in the latter study and since styrene is known to form living polymers, this transfer presumably involves metalation of the ferrocene nucleus of vinylferrocene to give a species incapable of initiating further polymerization.

The low vinylferrocene content (7.86 mole-percent) of the copolymer, obtained from an equimolar mixture of vinylferrocene and styrene, suggests that vinylferrocene is considerably less reactive than styrene toward anionic propagation.

XI.C Summary

The anionic polymerization of vinylferrocene under a wide range of reaction conditions gave zero or low conversion, the highest conversion being 43% for the n-butyllithium initiated polymerization in cyclohexane at 60°C.

Comparison with a study³⁷ of the anionic polymerization of 1-ferrocenyl-1,3-butadiene and results obtained here suggest transfer to the ferrocene nucleus of the monomer from both the initiator anion and the polyvinylferrocenyl anion. Thus, high molecular weight, low dispersity polyvinylferrocene cannot be obtained by anionic polymerization.

Copolymerization of an equimolar mixture of vinylferrocene and styrene with n-butyllithium as initiator gave a low vinylferrocene content copolymer (7.86 mole-percent). This suggests a lower reactivity for vinylferrocene than styrene toward anionic propagation.

Table XI.1

The anionic homopolymerization of vinylferrocene

$$[\text{VFcH}] = 0.4 \text{ mol dm}^{-3}$$

Polymerization time = 1 hr

Initiator	Solvent	Temperature °C	$\frac{[\text{VFcH}]}{[\text{In}]}$	Conv. %
n-BuLi	cyclohexane	60	18	^a 43
n-BuLi	^b decalin	28	60	0
n-BuLi	decalin	0	60	0
n-BuLi	^c THF	22	60	1
n-BuLi	THF	0	60	0
n-BuLi	THF	-40	60	0
n-BuLi	THF	-75	60	0
CumylK	THF	22	24	1.5
CumylK	THF	0	24	3.5
CumylK	THF	-40	24	^d 18.5
CumylK	THF	-75	24	^d 5

^a Conversion after 2 hr, $[\text{VFcH}] = 0.7 \text{ mol dm}^{-3}$ and, from GPC analysis, $\bar{M}_n = 3,710$ and $\bar{M}_w/\bar{M}_n = 1.58$, using values¹⁵ for K and a of $7.2 \times 10^{-5} \text{ 100cm}^3 \text{ g}^{-1}$ and 0.72, respectively, in the calibration conversion.

^b Decahydronaphthalene.

^c Tetrahydrofuran.

^d No carbonyl absorptcion in the infrared spectrum.

XII The polymerization of vinylferrocene with
manganese(III) acetylacetonate as initiator

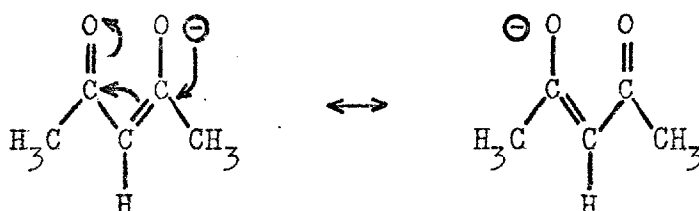
It has been established¹²⁵ that some metal chelates can act as free-radical initiators in vinyl polymerization. The most commonly used initiator of this kind is manganese(III) acetylacetonate ($\text{Mn}(\text{acac})_3$), primarily because it has been found to be of relatively high activity. In inert solvents, for example benzene, the dependence of the rate of polymerization on monomer concentration has been shown¹²⁵ to be greater than unity for all monomers studied. In the presence of a wide range of solvents and additives, such as ethyl acetate¹²⁵, cyclohexanone¹²⁶ and phenanthroline¹²⁷, the rate of polymerization is increased and, where there has been a full kinetic study, a decrease in the order of dependence of the rate of polymerization on monomer concentration has been observed. Such observations have led to the suggestion¹²⁵⁻¹²⁷ that monomer and/or solvent participate in the initiation step. Such participation is generally taken to involve coordination of the monomer or solvent molecules with the $\text{Mn}(\text{III})$ ion followed by dissociation to give a free-radical and $\text{Mn}(\text{acac})_2$.

$\text{Mn}(\text{acac})_3$ has been used²⁰ successfully as an initiator in the copolymerization of butadiene and vinylferrocene in toluene at 120°C . However, there has been no report of this initiator being used in the homopolymerization of vinylferrocene.

When a study of the homopolymerization of vinylferrocene by $\text{Mn}(\text{acac})_3$ was undertaken, repeated attempts in benzene solution at 80°C failed to produce polymer after 53.5 hr ($[\text{VFCH}] = 1.24\text{--}3.1 \text{ mol dm}^{-3}$, $[\text{Mn}(\text{acac})_3] = 5 \times 10^{-3}\text{--}2 \times 10^{-2} \text{ mol dm}^{-3}$). A further attempt in dioxane at 60°C also failed.

However, a copolymerization of vinylferrocene and styrene in dioxane ($[\text{VFcH}] = 2.91 \text{ mol dm}^{-3}$, $[\text{St}] = 2.89 \text{ mol dm}^{-3}$, $[\text{Mn}(\text{acac})_3] = 1.05 \times 10^{-2} \text{ mol dm}^{-3}$) at 60°C gave a low yield of copolymer (2.3% conversion based on total monomer weight) after 93.5 hr.

However, polymerization in the presence of styrene, a monomer which participates in the initiation process, cannot be taken to indicate that the inclusion of an additive, such as phenanthroline¹²⁷, will enable $\text{Mn}(\text{acac})_3$ to be effective as an initiator for the homopolymerization of vinylferrocene. Such a suggestion does not take account of the slow thermal dissociation of $\text{Mn}(\text{acac})_3$ in benzene¹²⁵. This requires that some polymerization should take place even in the absence of monomer participation in the initiation process. It is possible, therefore, that the radicals formed from $\text{Mn}(\text{acac})_3$ do not initiate vinylferrocene polymerization, but may react with it in some other manner, as is the case with benzoyl peroxide^{9,39}. The reaction between vinylferrocene and the latter initiator is probably the same as that between ferrocene and benzoyl radicals, in which ferrocene is oxidised to the ferricenium cation and the benzoyl radical is reduced to the stable benzoate anion^{128,129}. A similar reaction between vinylferrocene and an acetylacetonate radical is feasible. The ferrocene nucleus could be oxidised to the ferrocenium state, thereby reducing the acetylacetonate radical to the corresponding anion, which may be resonance stabilised, as can be seen from the structures given below.



XIII Conclusion and suggestions for further work

The existing evidence for ferrocene-olefin and ferrocene-aromatic interactions, and the anomalous kinetics observed for the bulk thermal polymerization of styrene in the presence of ferrocene derivatives, suggest that further study of the bulk thermal polymerization of vinyl monomers in the presence of ferrocene derivatives may substantiate the presence of these effects. Such study could also provide information concerning the nature of these interactions. Since ferrocene and a ketone apparently act as a source of initiating radicals, any monomer containing a carbonyl group, such as the acrylic and methacrylic esters, would be unsuitable for a study of this nature. Also, monomers which give polymer that is insoluble in the monomer, such as acrylonitrile, would not be suitable for these studies, because of the heterogeneous nature of the polymerization, which results in the polymerizations being non-linear with respect to time. However, in view of the previous study of ferrocene-diene systems, an investigation of the bulk thermal polymerization of these monomers in the presence of ferrocene might be fruitful.

Further study of the ferrocene/cyclohexanone system is necessary to elucidate the mechanism of the formation of initiating radicals from these two compounds. Polymerizations in the presence of high concentrations of these two components, but at low monomer concentration, could give polymer of low molecular weight, suitable for end-group analysis.

The marked difference between the kinetics of the free-radical homopolymerization of vinylferrocene in benzene solution and dioxane solution suggest that investigation of this

polymerization in a variety of solvents is desirable. Also, a study of the homopolymerization in aromatic solvents, with the benzene nucleus substituted by groups of varying electron donating or withdrawing ability, might assist in defining the role of benzene in the proposed monomolecular termination step. A study of the homopolymerization in a mixed solvent system, such as dioxane and benzene, might provide further information on this aspect of the free-radical homopolymerization of vinylferrocene. The present study indicates that the other techniques available for the homopolymerization of vinylferrocene are not capable of yielding high molecular weight, linear polyvinylferrocene. Indeed, it would appear that the best method available for the preparation of high molecular weight polyvinylferrocene is bulk free-radical polymerization to high conversion, but the polymer formed will be highly branched.

The observation of two transitions in the study of the thermal behaviour of polyvinylferrocene, the second being assigned as the glass transition and the first as being due to the rotation of the unsubstituted cyclopentadiene ring, suggests that further study of the thermal behaviour of ferrocene-containing homopolymers is necessary.

Another aspect of thermal behaviour, thermal degradation, of homopolymers and copolymers derived from ferrocene-containing vinyl monomers has yet to be investigated. Also, although resistance toward photodegradation has often been cited as a potential property of these polymers, no systematic investigation has yet been made. Some study of these two properties is required, therefore.

XIV Glossary

A	absorbance
acac	acetylacetonate
AIBN	2,2'-azobisisobutyronitrile
n-BuFcH	n-butylferrocene
C_m	chain transfer to monomer constant
C_s	chain transfer to species S (solvent) constant
CXON	cyclohexanone
$\overline{DP}$	degree of polymerization
DPPH	diphenylpicrylhydrazyl
DSC	differential scanning calorimetry
DTA	differential thermal analysis
DX	dioxane
ϵ	extinction coefficient
esr	electron spin resonance
EtFcH	ethylferrocene
GPC	gel permeation chromatographic
HFcH	ferrocene
I	rate of initiation
In	initiator
k_d	velocity constant for initiator decomposition
k_{fm}	velocity constant for chain transfer to monomer
k_{fs}	velocity constant for chain transfer to species S (solvent)
k_i	overall velocity constant for the formation of initiating radicals from styrene
k_p	velocity constant for propagation
k_t	velocity constant for termination by reaction of two polymer radicals

k_{tc}	velocity constant for termination by polymer radical combination
$\bar{M}_n$	number average molecular weight
mp	melting point
$\bar{M}_v$	viscometric average molecular weight
$\bar{M}_w$	weight average molecular weight
M.W.	molecular weight
$[\eta]$	limiting viscosity number
nmr	nuclear magnetic resonance
η_r	relative viscosity
η_{sp}	specific viscosity
OFN	dried oxygen-free nitrogen
$R\cdot$	polymer radical
$R_c\cdot$	initiating radical
R_p	rate of polymerization
St	styrene
T_g	glass transition temperature
THF	tetrahydrofuran
VFcH	vinylferrocene

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