THE FREE RADICAL CYCLOPOLYMERIZATION OF NON-CONJUGATED DIENES AT ONE ATMOSPHERE AND ~~AT~~ UNDER HIGH PRESSURES

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by

JAMES PATRICK JOHN HIGGINS, B.A.Sc.

Department of Chemical Engineering and Chemical Technology
Imperial College of Science and Technology
London S. W. 7

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ABSTRACT

Many non-conjugated dienes are known to polymerize by an alternating inter-intramolecular reaction mechanism that is now commonly known as cyclopolymerization. This thesis describes the free radical homopolymerization of several of these monomers and, for the first time, investigates the effects of high pressure on cyclopolymerization.

The monomers examined were the symmetrical 1,6 dienes diallyl ether, acrylic anhydride, diallylamine,hydrochloride and diallyl cyanamide; the unsymmetrical 1,6 diene allyl methacrylate; the unsymmetrical 1,5 diene vinyl methacrylate; and the symmetrical 1,4 diene vinyl sulfone. Also, some comparative experiments were carried out with indene in bulk and styrene in solution.

Where possible, the effects of pressure on the overall rate of polymerization, the degree of cyclization, the activation energy and the volume of activation were determined. Good results were achieved for the cyclopolymerizations of the 1,6 dienes allyl methacrylate, diallyl cyanamide and acrylic anhydride. In a few cases it was possible to deduce the probable individual termination reaction mechanism by comparison of the experimental results with derived theoretical expressions. Less satisfactory results were obtained using diallyl ether, vinyl methacrylate and vinyl sulfone.

The rate of cyclopolymerization was usually found to be greatly increased by pressure, but in the cyclopolymerization of acrylic anhydride in dimethylformamide solution, the rate was found to decrease slightly for pressures up to 2500 atm. pressure. It was also found that pressure increased both the molecular weight and the degree of cyclization in the cyclopolymers.

It was considered that microgel formation and other heterophase effects were factors in those cyclopolymerizations which yielded high molecular weight polymers. It was shown that, in certain solvents, soluble cyclopolymers could be obtained at monomer concentrations and conversions not previously achieved.

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PART I

INTRODUCTORY REMARKS

High pressures are known to have a large accelerating effect on the rate of free radical polymerization[1]. Many cyclization reactions, especially those which involve the formation of a new covalent bond, are accompanied by volume contraction and are thus thermodynamically favoured by pressure[2]. Recently, it was discovered that certain non-conjugated dienes could be 'cyclopolymerized' to yield soluble polymers by a mechanism involving an intramolecular cyclization step as part of the polymerization process[3].

The work described in this thesis is an investigation of the mechanism and kinetics of the free radical cyclopolymerization of several 1,5 and 1,6 dienes and the effect of high pressure on such polymerizations.

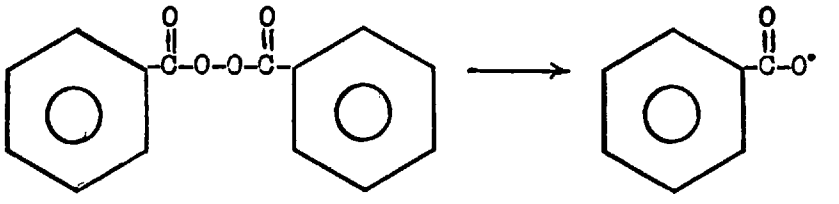
SECTION I

FREE RADICAL POLYMERIZATION

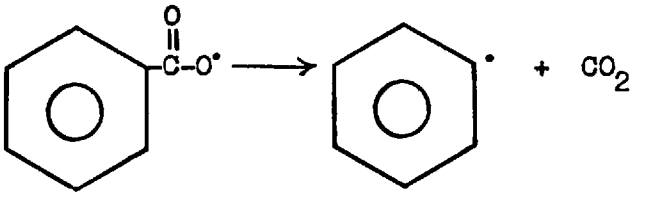
A. GENERAL ASPECTS OF FREE RADICAL POLYMERIZATION

Addition polymerization by a free radical chain mechanism was first proposed by Staudinger[4,5] and may be considered to consist of three stages: initiation, propagation and termination. Although thermal or self-initiation is possible, the addition of free radical-producing initiators is far more practical and conducive to reproducible results. These initiators, such as organic peroxides, azo- and diazo-compounds, decompose under thermal or photochemical influence to give radicals.

Two of the most common initiators which decompose to give free radicals are benzoyl peroxide (Bz_2O_2)

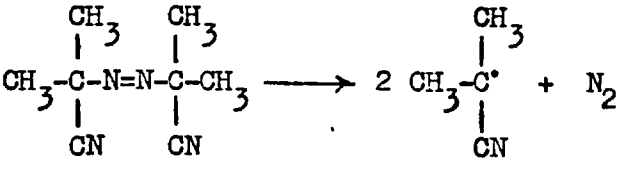


(1-1)



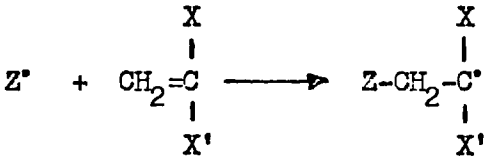
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and azobisisobutyronitrile (AIBN)



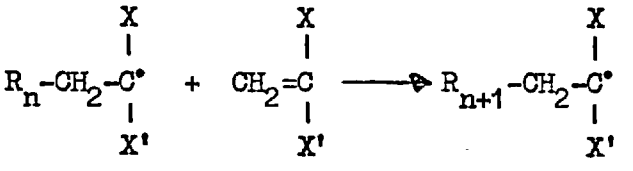
(1-3)

Initiation occurs when the initiator radical ($Z^{\bullet}$) adds to the double bond of a vinylic monomer.



(1-4)

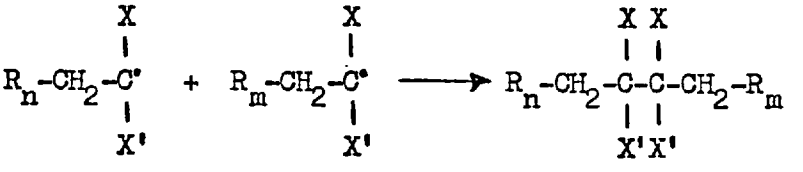
In this step the initiator radical transfers its active centre (the unpaired electron) to form a new radical with a net gain in resonance stabilization. Once this process has been accomplished the propagation reaction merely consists of the successive addition of monomer molecules to the growing chain. The active centre shifts to each newly added monomer molecule which in turn becomes capable of adding another monomer molecule, etc. If R_n represents a growing chain of n repeating units the propagation reaction is:



(1-5)

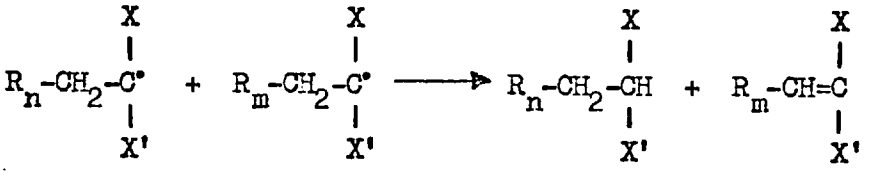
The growing polymer chains may be terminated by biradical reactions or by transfer. The two biradical termination reactions are coupling and disproportionation.

(ii) Coupling:



(1-6)

(ii) Disproportionation



(1-7)

In each case the activity of the two active polymer radicals is mutually satisfied; in coupling by the formation of a stable electron pair and in disproportionation by the transfer of a hydrogen atom. Although these biradical termination reactions are quite different and can substantially influence the molecular weight of the polymer, both processes lead to radical destruction and the same kinetic effect.

B. KINETIC SCHEME OF FREE RADICAL POLYMERIZATION

(i) Assumptions:

Three important simplifying assumptions are frequently made in kinetic treatments of free radical polymerization[6]. They are as follows:

(a) Radical reactivity is independent of the radical size, for all but the shortest radicals, so that a single rate constant may be applied to all the reactions in which large radicals participate.

(b) The average kinetic chain length (υ) is great. This amounts to putting the total rate of reaction of monomer equal to the rate of reaction of monomer in the propagation steps alone, neglecting by comparison, any consumption of monomer in initiation or transfer reactions.

(c) A 'stationary state'[7] is attained. This may be defined as the phase of the reaction in which the net rate of change of concentration of radical intermediates is very much less than both their rate of production and their rate of destruction. In practice it will be taken that their rates of change of concentration are zero.

In addition, we shall make a fourth assumption:

(d) Since only the early stages of the polymerization will be considered, the concentrations of all the reactions may be taken as being equal to their initial values.

All four of the above assumptions will be referred to in generalized terms as the stationary state assumptions in this work.

(ii) Simplified Kinetic Scheme

In the general case the decomposition of an initiator (In) yields two radicals:

$$In \xrightarrow{k_d} 2Z^{\bullet} \qquad (i)$$

Initiation occurs when monomer (M) is added to the initiating radical:

$$Z^{\bullet} + M \xrightarrow{k_i} R^{\bullet} \qquad (ii)$$

where $R^{\bullet}$ represents a growing polymer radical. Chain propagation then occurs and any rate effects arising from the initiator residue rapidly vanish with increasing monomer units:

$$R^{\bullet} + M \xrightarrow{k_p} R^{\bullet} \qquad (iii)$$

Biradical termination may occur by coupling (rate k_{tc}) and/or by disproportionation (rate k_{td}). Since both of these processes have the same kinetic effect, we may represent the rate constant for termination as:

$$k_t = k_{tc} + k_{td} \qquad (1\text{-}8)$$

$$2R^{\bullet} \xrightarrow{k_t} P \quad (+ P) \qquad \text{(iv)}$$

Termination by chain transfer usually does not affect the overall kinetic rate and will be considered later in this section. Using the stationary state assumptions we have:

$$\frac{d[Z^{\bullet}]}{dt} = I - k_i[Z^{\bullet}][M] = 0 \qquad (1\text{-}9)$$

$$\frac{d[R^{\bullet}]}{dt} = k_i[Z^{\bullet}][M] - k_t[R^{\bullet}]^2 = 0 \qquad (1\text{-}10)$$

where I represents the rate of decomposition of initiator.

$$I = 2fk_d[In] \qquad (1\text{-}11)$$

and f is the initiator efficiency and is defined as:

$$f = \frac{\text{rate of initiation of polymerization chains}}{2(\text{rate of decomposition of initiator})} \qquad (1\text{-}12)$$

This term is usually between 0.5 and 1.0 as some of the initiator radicals may recombine with each other[8].

From equations (1-9) and (1-10):

$$[R^{\bullet}] = (I/k_t)^{\frac{1}{2}} \qquad (1\text{-}13)$$

From assumption (b) above it is seen that the rate of polymerization (R_p) is given by the rate of disappearance of monomer ($-d[M]/dt$) in the propagation step alone:

$$R_p = k_p[R^{\bullet}][M] \qquad (1\text{-}14)$$

Hence:

$$R_p = k_p(2fk_d/k_t)^{\frac{1}{2}}[In]^{\frac{1}{2}}[M] \qquad (1\text{-}15)$$

C. CHAIN TRANSFER IN POLYMERIZATION

(i) Influence of Chain Transfer

In many vinyl polymerizations, especially when they are carried out in solution, the average degree of polymerization (the average number of monomer units per polymer molecule) is found to be somewhat lower than that calculated on the basis of the above kinetic scheme, although the actual polymerization rates are in reasonable agreement. Flory[9] suggested that this phenomenon might be explained by radical mechanisms in which the reactions were as follows:

$$R_n\text{-}CH_2\text{-}\overset{\displaystyle X}{\underset{\displaystyle X'}{\overset{|}{\underset{|}{C^{\bullet}}}}} \quad SX'' \xrightarrow{k_{tr}} R_n\text{-}CH_2\text{-}\overset{\displaystyle X}{\underset{\displaystyle X'}{\overset{|}{\underset{|}{C}}}}\text{-}X'' + S^{\bullet} \qquad (1\text{-}16)$$

$$S^{\bullet} + M \xrightarrow{k_p} R^{\bullet} \qquad (1\text{-}17)$$

where SX'' is a chain transfer agent molecule and X'' is a radical-extractable group. The product of the reaction is 'dead' polymer and a new radical, which if it is active enough, may initiate a new chain by adding monomer. The chain transfer agent may be monomer, polymer, initiator or solvent. Usually the new radical is almost as active as the chain radicals, so little or no change in the overall rate of polymerization will be observed.

(ii) Kinetics of Chain Transfer

The molecular weight of polymer produced in the presence of

chain-transfer agents is always lower than that in the absence of such agents. Flory[10] has related the average molecular chain length ($\overline{DP}$) to transfer with the following theoretical equation:

$$\frac{1}{\overline{DP}} = C_M + C_s\frac{[S]}{[M]} + \frac{k_t R_p}{k_p^2[M]^2} + C_I\frac{k_t R_p^2}{2fk_d k_p^2[M]^3} \qquad (1\text{-}18)$$

Here the subscripts M, S and I refer to monomer, solvent and initiator respectively, and the chain-transfer constants are defined by:

$$C_M = \frac{k_{tr,M}}{k_p}; \quad C_s = \frac{k_{tr,s}}{k_p}; \quad C_I = \frac{k_{tr,I}}{k_p} \qquad (1\text{-}19)$$

(iii) Degradative Chain Transfer

A type of chain transfer which merits special consideration is that exhibited by certain compounds such as allyl derivatives (CH_2=CH-CH_2-X). Propagation occurs in the normal manner as follows:

$$R^{\bullet} + CH_2{=}CH{-}CH_2{-}X \longrightarrow R{-}CH_2{-}\dot{C}H{-}CH_2{-}X \qquad (1\text{-}20)$$

In general, however, since allylic monomers are relatively unreactive, the chain-transfer reaction, in which an alpha hydrogen is extracted from the monomer, competes with the propagation reaction.

$$R^{\bullet} + CH_2{=}CH{-}CH_2{-}X \longrightarrow RH + CH_2{\cdots}CH{\cdots}CH{-}X \qquad (1\text{-}21)$$

The resulting allylic radical is resonance-stabilized and does not readily add monomer at atmospheric pressure, although it may terminate by a bimolecular reaction. Reactions of this type where the transfer radical is too unreactive to regenerate a new chain are

called autoinhibition or degradative chain transfer (DCT) reactions[11-13]. For compounds in which DCT predominates the rate of polymerization and the degree of polymerization are relatively low and the rate varies approximately as the first power of initiator concentration. Nozaki[14] has suggested that some olefins with α-methylenic hydrogens, such as octene-1, propylene and isobutylene, may also be characterized by this effect.

(iv) Simplified Kinetics of Polymerization with Termination by Degradative Chain Transfer

In polymerizations where termination by degradative transfer reactions predominate, the production of radicals, initiation and propagation are as shown before, but the termination reaction now becomes:

$$R^{\bullet} + M \xrightarrow{k_D} RH + M^{*} \qquad (v)$$

where the star indicates a resonance-stabilized allyl radical, whose propagation rate is essentially zero. Such radicals may disappear by bimolecular termination.

$$M^{*} + M^{*} \longrightarrow \text{unreactive product} \qquad (vi)$$

Assuming a stationary state:

$$\frac{d[R^{\bullet}]}{dt} = k_i[Z^{\bullet}][M] - k_D[R^{\bullet}][M] = 0 \qquad (1\text{-}22)$$

In this case:

$$[R^{\bullet}] = (I/k_D[M]) \qquad (1\text{-}23)$$

Substituting equation (1-23) into equation (1-14) we have:

$$R_p = \frac{2fk_dk_p}{k_D}[In] \qquad (1\text{-}24)$$

By assumption (b) of the simplifying assumptions it is seen that the amount of monomer used up in the termination reaction is negligible compared to that used up in the propagation reaction. Thus the theoretical derivation shows the overall rate of polymerization to be proportional to the first power of the initiator concentration, and this is in agreement with the experimental results for the polymerization of allylic monomers.

D. ACTIVATION ENERGY

The parameter k_p^2/k_t is particularly significant as it gives a measure of the relative importance of the propagation and termination reactions. From equation (1-15):

$$\frac{k_p^2}{k_t} = \frac{2R_p^2}{I[M]^2} \qquad (1\text{-}25)$$

This may be obtained from the experimental rate of polymerization at a particular monomer concentration and from the rate of initiation, which may be evaluated independently.[15]. Expressing rate constants according to the Arrhenius equation:

$$k_p = A_p \exp(-E_p/RT) \qquad (1\text{-}26)$$

where E_p and A_p represent the energy of activation and the frequency factor for chain propagation, respectively.

Combining equation (1-26) with the corresponding expression for k_t:

$$k_p/k_t^{\frac{1}{2}} = (A_p/A_t^{\frac{1}{2}}) \exp\left\{-(E_p - \tfrac{1}{2}E_t)/RT\right\} \qquad (1\text{-}27)$$

It is seen that the value of $(E_p - \frac{1}{2}E_t)$ may be obtained from the slope of a plot of $\ln(k_p/k_t^{\frac{1}{2}})$ vs. the reciprocal of the absolute temperature (1/T). R is the gas constant. In the same manner the overall activation energy (E_T) may be evaluated from a plot of $\ln(R_p/[In]^{\frac{1}{2}}[M])$ vs. 1/T. In the case of polymerization with biradical termination (equation 1-15):

$$E_T = \tfrac{1}{2}E_d + (E_p - \tfrac{1}{2}E_t) \qquad (1\text{-}28)$$

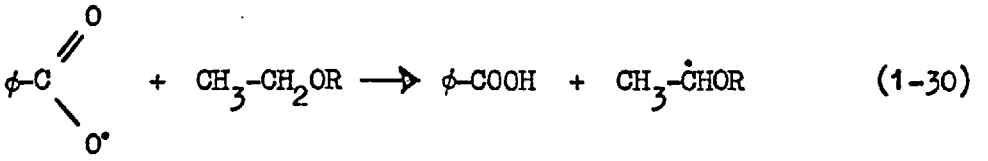
where E_d is the activation energy for the spontaneous decomposition of the initiator. The activation energies for the spontaneous decomposition of both Bz_2O_2 and AIBN have been found to be approximately 30 kcal./mole[16]. The value of E_d for tert-butyl perbenzoate is about 34.5 kcal./mole[17]. In cases where termination is by degradative chain transfer we may evaluate $(E_p - E_D)$. From equation (1-24):

$$E_T = E_d + (E_p - E_D) \qquad (1\text{-}29)$$

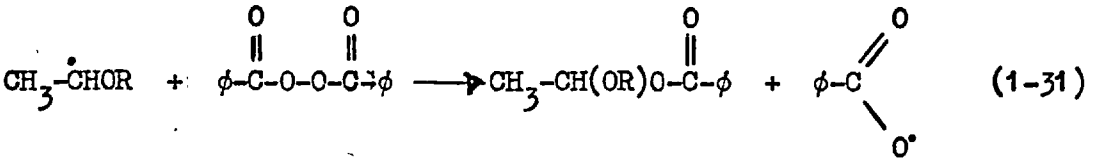
E. INDUCED DECOMPOSITION OF INITIATORS

It has been observed that in the decomposition of many initiators the apparent unimolecular rate constant increases with peroxide concentration[18]. This effect is known as induced decomposition and may give rise to $\frac{1}{2}$, first, 3/2 or second order kinetics of decomposition depending on the specific reaction mechanism.

In several types of solvent a much more rapid induced decomposition occurs. Bartlett and Nozaki[19] have shown that the decomposition of benzoyl peroxide at 80°C is unimolecular and has a half-life of less than 5 minutes in ethyl ether, and just under 15 minutes in isopropyl and butyl ethers, compared with 4-6 hours in 'unreactive' solvents. They suggest, as the major chain, the sequence:



(1-30)



(1-31)

where the symbol ϕ represents a phenyl group. A similar effect is observed in dioxan.

In the presence of polymerizable olefins the induced decomposition rate is depressed but may still occur to a moderate extent. A very rapid induced decomposition occurs, however, in the polymerizations of maleic anhydride[20] and allyl acetate[11], and in maleic anhydride-allyl acetate co-polymerizations[21].

SECTION II

HETEROPHASE AND DIENE POLYMERIZATION

A. INTRODUCTION

Since cyclopolymerization reactions are often of a heterophase nature it is necessary to review the effects of polymer separation on the mechanism and kinetics of vinyl polymerization. This section will examine gel and heterogeneous polymerizations and attempt to show that these reactions are different aspects of the same phenomenon.

Gel polymerization will refer to those often apparently homogeneous polymerizations where the polymer appears in a translucent or transparent gel at some stage in the reaction. Heterogeneous polymerization will refer to those truly precipitative polymerizations where the polymer separates from the reaction medium and either precipitates as a visible granular solid, or remains dispersed in the mixture forming a cloudy suspension.

B. GEL POLYMERIZATION

(i) Cross-linking and Gelation[22]

Gelation occurs when the cross-linking of polymer molecules forms a network which extends through the polymerization mixture. There are two cases in which the cross-linking of polymer chains can occur in vinyl polymerization. The first is by the further activation of polymer chains by a process such as chain transfer. This leads to the growth of chain branches, which, if biradical termination by combination occurs, can lead to cross-linking. The second is in the polymerization or copolymerization of a diene. In the initial stages of the polymerization of a diene the polymer is linear and unbranched.

However, each diene unit which enters into a polymer chain contains one unreacted double bond which may be initiated to produce side chains or incorporate 'dead' polymer molecules into the growing chain. Since each chain contains many unreacted double bonds the size and complexity of these cross-linked molecules rapidly increases and they may come to extend through the whole volume of the material being polymerized. With respect to normal molecular dimensions such a structure is practically infinitely large and is usually called an 'infinite network.' The formation of an infinite network causes the gelation of the reaction mixture and the narrow range of conversions over which it forms is referred to as the 'gel point' (θ_c). In cases where the initial chains are long, incipient gelation corresponds to an average of only one cross-linked unit per primary chain initially present[22]. The statistical aspects of cross-linking has been developed by Stockmayer[23,24] and by Flory[25] who has developed the following relation between the weight average degree of polymerization ($\bar{y}_w$) of the initial chains and the gel point:

$$\frac{1}{\bar{y}_w} = -2\frac{k_x}{k_p}\left\{1 + \frac{1}{\theta_c}\ln(1 - \theta_c)\right\} \qquad (2\text{-}1)$$

where k_x is the effective mean rate constant for the reaction of double bonds in a diene polymer to form cross-links.

(ii) Autoacceleration

In normal homogeneous polymerizations experimental plots of percent conversion versus duration of the polymerization reaction are linear at low conversions and the polymerization rate falls off gradually at higher conversions. In many heterophase polymerizations,

however, results of quite a different character are found. Norrish and Smith[26] found that for the polymerization of methyl methacrylate in bulk and solvents such as heptane (which is a precipitant for the polymer), that above 10-20% conversion the rate of polymerization rose very rapidly. Similar, but less severe, effects were found in poor solvents (such as amyl acetate). Polymerization was normal in good solvents. These rapid rate increases were associated with the precipitation (as a gel) of the polymer and the effect is known as 'autoacceleration.' This deviation from first order kinetics is found with many monomers[27,28] and a simultaneous increase in the molecular weight occurs. Polymerizations where the polymer is precipitated or where gelation occurs at some stage of the reaction, usually exhibit autoacceleration although this phenomenon does not always accompany such reactions. Autoacceleration is most marked in the polymerization of acrylic and substituted acrylic compounds[15].

Autoacceleration often occurs in apparently homogeneous polymerizations before the inception of gelation. Flory[29] has attributed such rate increases to growing radicals becoming entrapped in gel droplets of small size. Eilers[30] and Walling[31] have depicted these 'microgel' particles as spherical, highly swollen masses suspended in the reaction medium.

(iii) Effect of Gelation on Rate Constants

Trommsdorf[32] polymerized methyl methacrylate in the presence of various proportions of cellulose tripropionate and showed that the gel point occurred at lower conversions as the viscosity of the reaction medium increased. He and other authors[26,27] concluded that the increased rates and higher molecular weights associated with

gelation could only be explained by a decrease in the termination rate.

This decrease in the apparent value of k_t is attributed to the increasing viscosity of the reaction medium (i.e. the increase in the number and size of the gel particles) as the concentration of polymer increases. This decreases the rate of diffusion of the growing polymer radicals and thereby restricts the biradical termination reaction. The rate of diffusion of the relatively much smaller monomer molecules is not affected so k_p is unchanged. This results in a rate increase. If the effects of such a rate increase are cumulative (i.e. higher rates cause greater amounts of gelation which further reduces the effective value of k_t) then autoacceleration results.

Evidence supporting this theory was advanced by Burnett and Melville[33] who polymerized vinyl acetate in both ethyl acetate, a good solvent for the polymer, and in n-hexane, a precipitant. In the latter case autoacceleration and gelation occurred and it was found that k_t decreased substantially after autoacceleration began, while k_p remained virtually constant. The inception and extent of the gel stage in the heterophase polymerization depended on the initiator concentration and the temperature. At higher temperatures autoacceleration was eliminated.

(iv) Radical Entrapment

In gel polymerization it is possible for growing polymer radicals to become occluded when polymer coalesces in microgel particles. Such radicals might eventually become trapped in the gel. This would constitute an effective monoradical termination and would

increase the value of the catalyst exponent in the rate equation above the normal value of 0.5. Ingram et al[34] have examined gels of polymethacrylonitrile and polymethyl methacrylate using electron spin resonance (ESR) techniques and have found absorptions indicating small amounts of radical occlusion. Fraenkel et al[35] used ESR to examine the gels produced in the free radical polymerization of non-conjugated dienes (glycol dimethacrylate, vinyl methacrylate, divinyl benzene, and glycol diacrylate) in the temperature range 60°-100°C and found trapped radical concentrations as high as 10^{-4} - 10^{-3} moles/l. in some cases. These results indicate that in some instances of gel polymerization, the physical entrapment of radicals can occur but in most cases, however, no evidence for the occlusion of radicals in gels can be found[36].

C. HETEROGENEOUS POLYMERIZATION

(i) Types of Heterogeneous Polymerization

In heterogeneous polymerization the propagating free radicals pass from one phase to another. Emulsion and suspension polymerization, 'popcorn' polymerization and all vapor-phase polymerizations are examples[37]. Polymerizations which are normally homogeneous may be made heterogeneous by the addition of a liquid miscible with the monomer, but which acts as a precipitant for the polymer[38,39]. The bulk polymerizations of all halogen- and pseudo-halogen-substituted ethylenes such as vinyl bromide, vinylidene chloride and acrylonitrile (vinyl cyanide) are heterogeneous.

For the purposes of this work, only those heterogeneous polymerizations where the polymer passes from a liquid phase to a visible solid phase, will be considered. The bulk polymerization of

acrylonitrile is an example of a heterogeneous polymerization which exhibits severe occlusion, and it will be reviewed for comparison with gel polymerization.

(ii) The Bulk Polymerization of Acrylonitrile[37,40]

Acrylonitrile is a monomer which polymerizes to produce a polymer which is insoluble in the monomer and in most common organic solvents, with the exception of NN-dimethylformamide (DMF). The bulk polymerization is heterogeneous with polymer separating as a granular solid or dispersing through the reaction mixture as a milky suspension depending on the particular polymerization parameters. Its polymerization is homogeneous and normal in DMF solution[41], but is autocatalytic to at least 20% conversion in bulk[40]. The catalyst exponent in the rate equation was found to 0.9 for the heterogeneous polymerization compared to the normal value of 0.5 found for the DMF solution polymerization. Examination of the photochemical after-effect indicates that the polymer produced in the bulk reaction possesses a residual activity.

When a mixture of acrylonitrile and catalyst is irradiated at 25°C and photochemically prepolymerized to about 20% conversion, allowed to stand in the dark and then heated to 60°C, a novel result known as the 'fast reaction' occurs. As the temperature approaches 60°C a very rapid reaction occurs which may consume a further 10% of the monomer in 2-3 minutes. Thereafter the reaction proceeds normally.

Bamford and Jenkins[40] have attributed these results to mechanically trapped radicals in the precipitated polyacrylonitrile. The sensitizing action of the photopolymer depends on the possibility of making these radicals accessible to a reagent without promoting too

facile mutual destruction of them. The concentration of the trapped radicals was found by both chemical[42] and physical (ESR)[43] methods to be about 10^{-4} moles/l. which indicates that from 1-10% of the radicals formed are trapped in the precipitate.

Various theories[42,44,45] have been proposed to explain the anomalous kinetics of the bulk polymerization of acrylonitrile and the activity of the precipitated polymer; the best of these is the occlusion theory[42].

(iii) The Occlusion Theory of Heterogeneous Polymerization[42]

(a) Degree of Occlusion

The occlusion theory supposes that many, if not all, of the polymer radicals are precipitated from the liquid phase during growth and that these active radicals are occluded in polymer aggregates.

As a polymer radical grows it will at some stage become insoluble in the monomer and will be precipitated in a non-solvent environment where it will exist in a tightly coiled configuration. There will be a finite probability that the active end of such a radical will be shielded by the coils. The formation of aggregates from polymer radicals and 'dead' polymer will further reduce the reactivity of polymer radicals. This coalescence will be the major factor in occlusion although in an unswollen polymer of high molecular weight, coiling will also contribute to the reduction in radical reactivity. In a swollen polymer coiling will be of little significance.

The degree of occlusion determines the accessibility of polymer radicals and cannot be defined precisely, but indicates the magnitude of the polymer barrier which protects a given radical from reagent

molecules (usually monomer).

(b) Effect of Occlusion on Rate Constants

When the formation of polymer aggregates traps polymer radicals, these radicals are unable to act freely for steric reasons. This results in a reduction of the velocity coefficients for all polymer radical reactions, except transfer to polymer.

Propagation and transfer to monomer may be decreased if the concentration of monomer at the active end of an occluded polymer radical is reduced due to the decreased rate of diffusion of monomer in the aggregate. If k_p^* represents the effective rate constant for propagation then:

$$k_p^* = k_p [M]_o / [M] \qquad (2\text{-}2)$$

where $[M]_o$ is the effective monomer concentration at the site of reaction in an aggregate particle. The effect of aggregation can be seen from results for the polymerization of acrylonitrile. For the heterogeneous bulk polymerization of this monomer at 60°C, $k_p^* = 84.1.$/mole/sec.[42]. For the homogeneous polymerization of acrylonitrile at 60°C in DMF solution $k_p = 1960$ l./mole/sec.[46]. Thus, from equation (2-2) the monomer concentration in a polymer aggregate is:

$$[M]_o = [M] \times (k_p^*/k_p)$$

$$= 15.2 \times (84/1910)$$

$$\simeq 0.6 \text{ moles/l.}$$

This 25-fold decrease in monomer concentration (assuming that

the rate of propagation in DMF solution is equal to the intrinsic rate of polymerization) gives an estimate of the degree to which occlusion may affect the concentration of monomer at the site of polymerization in the aggregate.

Biradical termination will be even more affected by occlusion[40] as it requires the juxtaposition of the active ends of two polymer radicals in order to occur. For occluded radicals this would occur only in that very small fraction of cases where the active ends were on the surface of polymer particles. Because of this there will be a greater decrease in the effective value of k_t than in k_p and the effect of moderate degrees of occlusion will be to increase the rate of reaction. In the cases where termination is by transfer the effect of occlusion on the rate of reaction will depend on the relative rates of diffusion of monomer and transfer agents in the aggregates[47].

(c) Effect of Occlusion on Overall Kinetics

The behaviour of heterogeneous systems is determined by the number of polymer aggregate particles and their sizes. The former determines the rate at which particles become occluded and the latter the efficiency of the polymer barrier. As the reaction proceeds the number and size of the aggregates increase and the termination coefficient decreases.

This leads to a progressive increase in reaction rate (autoacceleration). Higher catalyst concentrations increase both the number and the size of the aggregates and thus the elevation in rate is greater than would normally be expected. The effect of occlusion is always to increase the catalyst exponent in the rate equation above the normal value of 0.5 found with biradical termination.

Transfer agents facilitate biradical termination[47] by the formation of small mobile radicals which can escape from the aggregate and undergo mutual termination. Similarly, non-degradative transfer to monomer produces small mobile radicals, but the egress of these radicals from the aggregate may be impeded by subsequent growth, biradical termination with another polymer radical occluded in the same aggregate particle, or by transfer to 'dead' polymer[37].

At high degrees of occlusion both termination and propagation may be impeded to such an extent that reaction is prevented. In the polymerization of acrylonitrile it has been shown[42] that only about 1% of the radicals formed are trapped so the anomalous kinetics found in the polymerization of that monomer must be due primarily to variations in radical reactivity with degree of occlusion and not to radical burial.

D. COMPARISON OF GEL AND HETEROGENEOUS POLYMERIZATIONS

As may be seen from the above reviews even extreme cases of gel polymerization and heterogeneous polymerization exhibit many similarities such as autoacceleration, decreased values of k_t and radical entrapment. The differences between the two seem to be due more to the nature of the particular reaction medium-polymer system than to anything fundamental. In the poor- or non-solvent environment of heterogeneous polymerization the polymer molecules are tightly coiled and coalesce in relatively dense aggregates. These give the solution a milky appearance if they do not precipitate and the onset of heterophase polymerization is apparent. The reaction medium in gel polymerization is a much better, but still not ideal, solvent for the polymer and the polymer molecules are loosely coiled, and are

suspended in solution as highly swollen microgel particles. As these 'droplets' are initially small and transparent the inception of heterophase polymerization is not immediately apparent. Microgel particles may become heavy enough to precipitate from solution or large enough to come into contact with each other. The resulting cross-linking may cause an apparently homogeneous polymerization medium to abruptly undergo gelation.

Propagation and monomer transfer are not appreciably hindered in gel polymerization[26] and the same is true with many heterogeneous polymerizations[37] although as seen with the bulk polymerization of acrylonitrile, they may be. In both cases biradical termination is hindered by a decrease in the rate of diffusion of the polymer radicals. Autoacceleration, if it occurs at all, usually begins much earlier in heterogeneous polymerization, probably due to the effect of the coiling of polymer molecules.

In some cases of both gel polymerization and heterogeneous polymerization the occlusion of polymer radicals can be significant[34,35] but usually radical entrapment is negligible[48,49]. Whether it occurs at all seems to depend on the configuration of the polymer chains and the ease of transfer from monomer to polymer.

The differences between the two types are, therefore, attributed to the greater densities of aggregates in heterogeneous polymerization, and this in turn is due to the tight coiling of the polymer molecules. This is a result of the nature of the polymerization medium-polymer system.

In some instances the kinetic equations derived in Section I may be applied to heterophase polymerizations, (especially in their early stages, and if autoacceleration does not occur to any appreciable

extent) but in most cases the physical effects caused by the coalescence of polymer molecules cause the kinetics to be much more complex than those found for homogeneous polymerization.

E. DIENE POLYMERIZATION

(i) Relative Reactivities of Double Bonds in Dienes

Monomers with two double bonds can arbitrarily be divided into conjugated 1,3 dienes and non-conjugated 'divinyl' compounds[50]. Except in cases when complete cyclization occurs or when the entrance of one of the double bonds into polymerization leaves the second so unreactive that it will not enter into polymerization reactions, polymerization of these monomers will eventually lead to branched or cross-linked polymers.

If the two double bonds in the monomer are close to each other, the reaction of one of them may sterically shield the other from reaction or at least (especially in the case of 1,3 dienes) have an effect on the reactivity of the remaining double bond. However, if the two double bonds are more widely separated in the monomer, then the reaction of one of them will have little or no effect on the other. Examples of the dependance of the reactivity of the remaining double bond when one double bond enters into polymerization are given in Table 2-1 for symmetrical and unsymmetrical dienes.

TABLE 2-1

Dependance of Reactivity	Symmetrical	Unsymmetrical
Independant	acrylic anhydride	allyl methacrylate
Intermediate	o-divinyl benzene	vinyl methacrylate
Interdependant	butadiene	chloroprene

This work will be mainly concerned with monomers of the first (independant) type.

(ii) Intra-Chain Cyclization and the Gel Point

It has been found that the gel points with many non-conjugated diene polymers occur at substantially higher conversions than those predicted according to equation (2-1). Walling[31] has found that the results of the copolymerization of methyl methacrylate and ethylene dimethacrylate agree approximately with equation (2-1) at low dimethacrylate concentrations but poorly at higher concentrations. Holt and Simpson[51] studied the polymerization of fourteen diallyl esters and their work was a strong basis for considering that the lack of agreement between the theory of gelation and experiment was due to intramolecular cyclization. The work of these and other authors[52] led to the re-evaluation of the theory of gelation to take cyclization reactions into account.

SECTION III

THE MECHANISM OF THE CYCLOPOLYMERIZATION OF NON-CONJUGATED DIENES

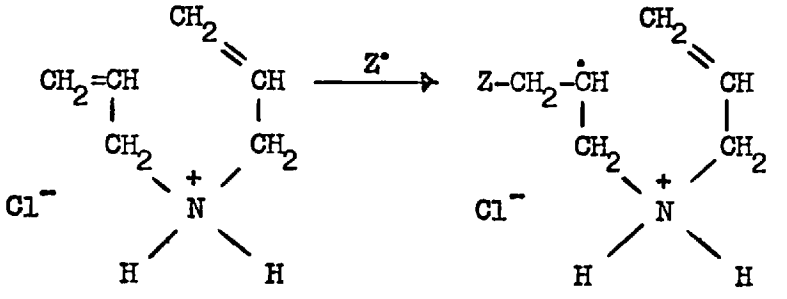
A. INTRODUCTION

As was noted in the previous section, the polymerization of non-conjugated dienes usually yields polymers which are three-dimensional networks since the double bonds polymerize independantly of one another. It has been recognized, however, that these compounds need not always polymerize to yield insoluble polymers as some of them may polymerize by using up only one of their double bonds or may undergo a cyclization reaction in which both double bonds participate.

G.B. Butler and his co-workers found that diallyl quaternary ammonium salts could be polymerized in aqueous solution to yield soluble gel-free polymers[53] which showed little or no residual unsaturation[54].

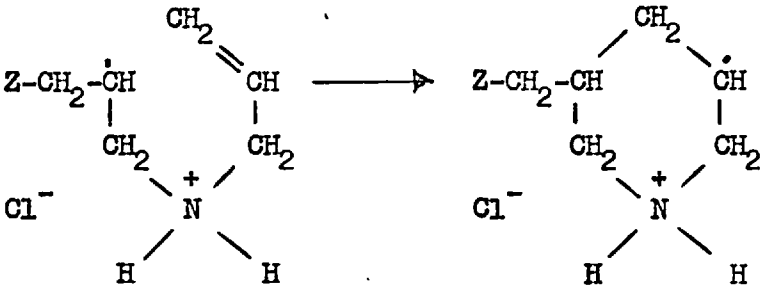
An alternating intra-intermolecular propagation mechanism[54], in which both of the double bonds were consumed, was proposed to explain these results.

Initiation:



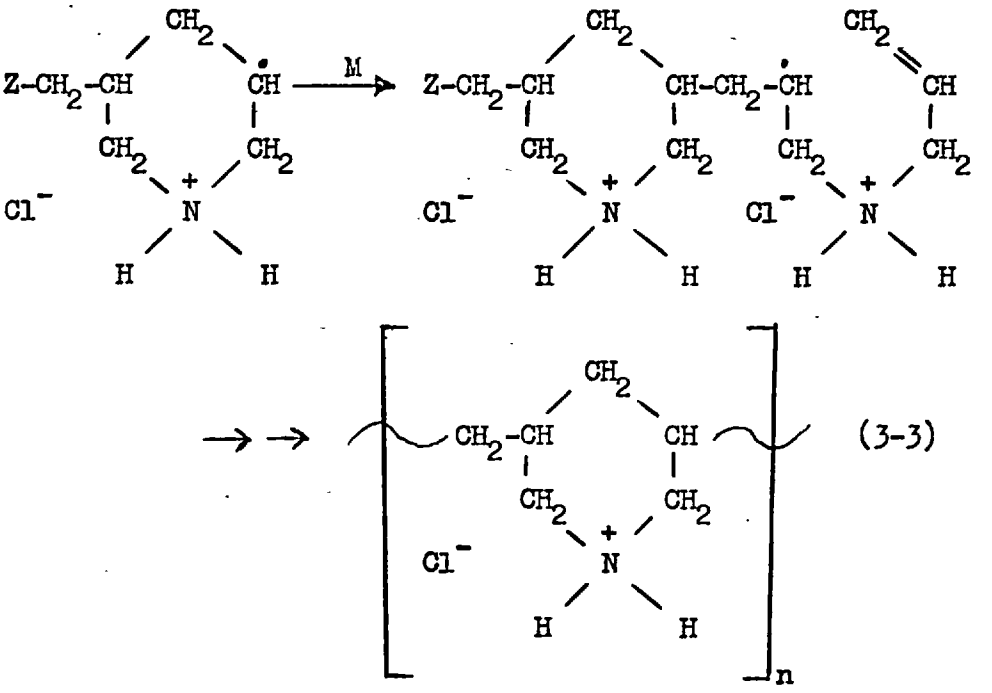
(3-1)

Intramolecular Propagation:



(3-2)

Intermolecular Propagation:



(3-3)

for diallylammonium chloride (diallylamine hydrochloride).

The reactions are a normal intermolecular propagation and then a further intramolecular cyclization, between the radical and the double bond present in the same recurring unit, forming a cyclized radical. The overall result of this 'cyclopolymerization' is a soluble polymer with cyclic recurring units along the backbone of the chain.

Originally the term cyclopolymerization was restricted to the polymerization of non-conjugated dienes having double bonds in the

terminal positions and capable of short-range cyclization reactions. Recently, however, it has been extended to cover other types of polymerization in which short-range cyclization reactions occur. Examples are the polymerization of dialdehydes[55-57], diisocyanates[58], diepoxides[59], monomers containing non-conjugated carbon-carbon triple bonds[60] and cyclic monomers, such as 4-vinyl cyclohexene[61], whose propagation reaction involves a transannular cyclization reaction. These novel types of cyclopolymerization are outside the scope of this work and are examined by Butler[62] in his review of the current status of the field.

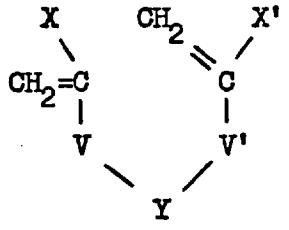
In general cyclopolymerization may be characterized as producing polymers which are soluble and essentially linear (at least at low conversions and/or at high dilutions) and which contain at least a moderate proportion of cyclized units which are formed by an intramolecular cyclization process.

B. THE CYCLOPOLYMERIZATION PROCESS

The cyclic nature of the repeating units in the polymers of non-conjugated dienes was first confirmed by Butler et al[63] who characterized the degradation products of poly(diallylammonium bromide) by chemical means. Marvel and Vest[64] polymerized 2,6 dimethylene pimelic acid and its methyl ester by free radical methods. They confirmed the formation of cyclohexane rings by partially dehydrogenating the soluble polymers and then finding, for these treated polymers, ultra-violet absorption peaks which are characteristic of aromatic rings. Evidence claiming the existence of cyclic recurring units in polymers of non-conjugated dienes formed by Ziegler[65], anionic[66] and cationic[67] methods has also been published.

Many non-conjugated dienes have now been found to form cyclopolymers by free radical methods. A few examples are the symmetrical dienes acrylic anhydride[68,69], methacrylic anhydride[70], divinyl formal[71] and diallylcyanamide[72]; and the unsymmetrical dienes n-allyl-acrylamide[73], trans-vinyl cinnamate[74], and allyl methacrylate[75].

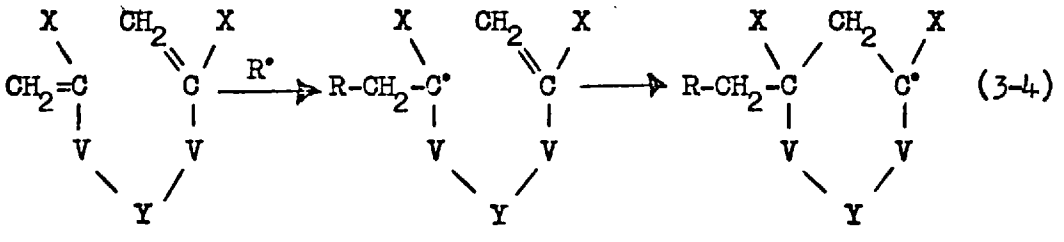
It has been demonstrated[76] that cyclopolymerization is quite general for monomers of the type:



I

where V and Y may represent such groups as $-\dot{C}H_2$, $-\dot{C}{=}O$, $-\dot{N}H$, $-\dot{O}$, etc., and X may represent such groups as -H, $-CH_3$, -COOH, etc.

Treating structure I as a symmetrical diene, the cyclopolymerization reactions may be represented as:



(3-4)

I Intermolecular II Intramolecular III

In many cases of cyclopolymerization structure II radicals, as well as structure III radicals, may propagate by adding monomer and this leads to polymer chains with unsaturated pendant groups. The extent of this 'residual unsaturation' will depend on the relative magnitudes of

intermolecular propagation (rate k_p) and intramolecular cyclization (rate k_c).

C. THE EFFECT OF MONOMER STRUCTURE ON THE DEGREE OF CYCLIZATION

An examination of the results from work on condensation and polycondensation systems is a useful starting point for examining the effect of monomer structure on the tendency to form cyclic recurring units.

Carothers and his co-workers[77,78] examined the effect of the size of the rings produced on the yield of cyclic monomers formed from esterifying various alkene glycols and aliphatic dicarboxylic acids and found that the variation of the degree of cyclization with the number of ring atoms (N) is given by the following series of N: $5,6 \gg 7,8 < 10 > 13 < 15$.

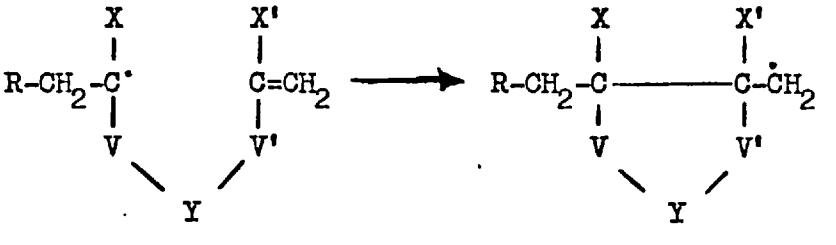
Stoll et al[79,80] investigated the acid catalysed condensation of various aliphatic ω-hydroxy acids to form lactones and polyesters. Cyclization was found to be at a maximum when N = 5, and at a minimum when N = 8, 9.

In these and other cases[81] there is a marked dependance of ease of cyclization on ring size. These results can be explained on the basis of steric hindrance to ring closure and possible deformation of valence bond angles[78]. Five- and six-membered rings consisting primarily of carbon atoms are favoured as they can form with little or no strain. However, when N = 7 to 12 the carbon atoms must have their substituent hydrogen atoms turned inwards towards the centre of the ring to effect ring closure. Hydrogen repulsion will, therefore, make such configurations unlikely. If carbonyl or ether oxygen is substituted

for methylene groups in the ring then the number of interfering hydrogen atoms is reduced and these ring sizes are formed with greater ease. Rings larger than about 12 members do not usually have steric limitations but as N becomes larger the probability of intermolecular reaction also becomes larger until it becomes dominant for N > 18. Ziegler and Luttringhaus[82] have determined the relative rates of ring closure in a series of bromocatechol ethers for $6 < N < 14$ and found the six-membered ring forms twice as fast as the seven-membered ring and the relative rates then decrease by smaller increments as N increases from 8 to 14.

The influence of monomer structure on the degree of cyclization in vinyl cyclopolymerization shows much the same results. Marvel and his co-workers[65,83] studied the Ziegler polymerization of α-ω dienes $\{CH_2=CH(CH_2)_nCH=CH_2$ where n varied from 2 to 18$\}$ and found the variation of degree of cyclization with ring size to be given by the following series of N; 5, 6 >>> 7 >> 8, 9 < 10 < 11, 15 < 17, 21. For dienes of the type $CH_2=CH(\phi)(CH_2)_n(\phi)CH=CH_2$ where n = 2,3,4 they report[84] that rings of 6 members are formed more readily than those of 5 or 7 members.

In general, 1,6 dienes will cyclopolymerize to form six-membered recurring units (see equation 3-4) but the presence of a bulky substituent group may cause five-membered rings to form:

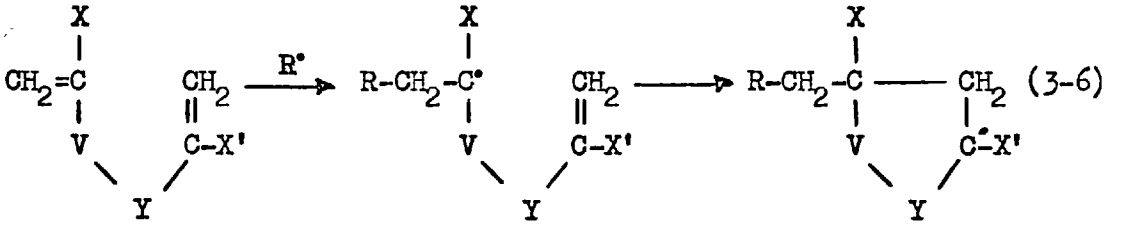


(3-5)

II IV

Marvel and Vest[64,85] found for the polymerization of dimethyl-2-2'-dimethylene adipate and pimelate that, while the pimelate derivative gave a high proportion of cyclization to six-membered rings, the adipate gave a lower proportion of recurring units which had 5 rather than 6 members. A recent paper by Kawai and his co-workers[86] has shown when using the telomerization of divinyl formal as a model of cyclopolymerization, structures with five-membered rings are formed. This confirms an earlier supposition by Minoura and Mitoh[71].

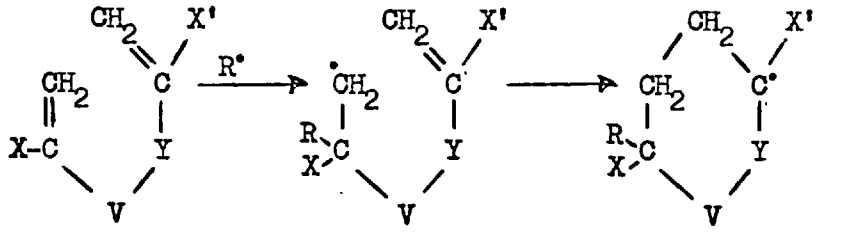
Barnett and Butler[87] have shown that polymers of allyl and methallyl crotonate contain recurring units of 5 members. It has been reported that allyl methacrylate[88] and acrylic anhydride[89] can form cyclic recurring units of both 5 and 6 members. A somewhat analagous situation can occur with 1,5 dienes. In general, these monomers, such as vinyl-trans-cinnamate[74], cyclize to form five-membered rings. Representing a typical 1,5 diene by structure V the reaction is:



(3-6)

V VI VII

However, in some cases the cyclization can proceed in such a way as to produce six-membered recurring units:

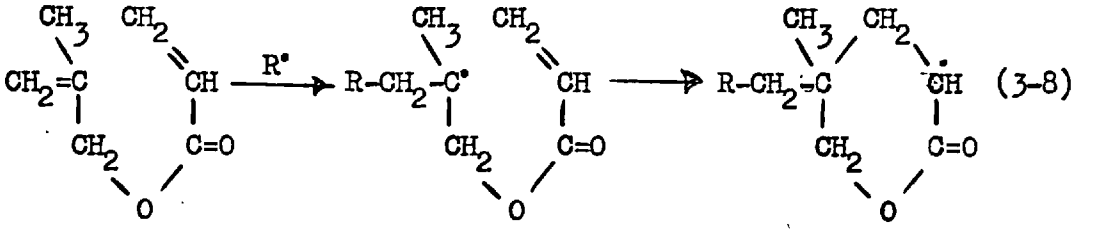


(3-7)

V VIII IX

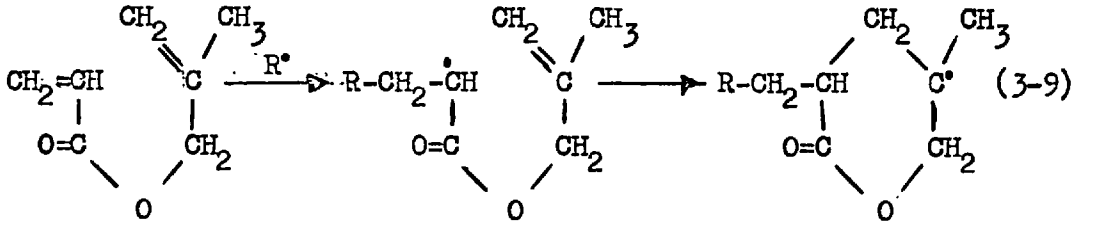
Vinyl methacrylate[90] is an example of such a 1,5 diene.

Unsymmetrical non-conjugated dienes may cyclopolymerize to form cyclic structures of two different configurations depending on which of two dissimilar functional groups of the monomer is added to the growing chain in the intermolecular step. For a 1,6 diene such as methallyl acrylate (X) the two modes of reaction may be represented by:



(3-8)

X XI XII



(3-9)

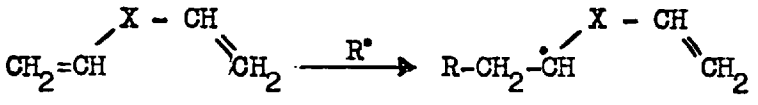
X XIII XIV

The proportions of the above radicals which will be found in the cyclopolymer will depend on the relative reactivities of the two functional groups and of the radicals formed when they react.

D. THE CYCLOPOLYMERIZATION OF 1,4 DIENES

The cyclopolymerization of 1,4 dienes[91] is a special case as cyclization of the monomer radical (or ion) to a four-membered ring is sterically inhibited. However, a dimer radical (or ion) can cyclize more readily. If the 1,4 diene monomer is represented by $CH_2=CH-X-CH=CH_2$ where X represents CH_2, CO, SO_2, etc., then the reaction may be represented by the following steps:

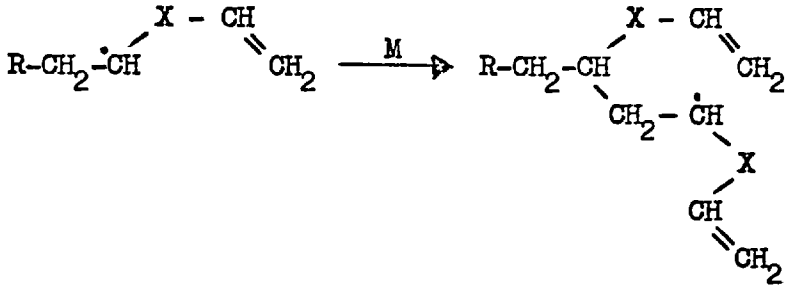
(a) Intermolecular:



(3-10)

XV XVI

(b) Dimerization:

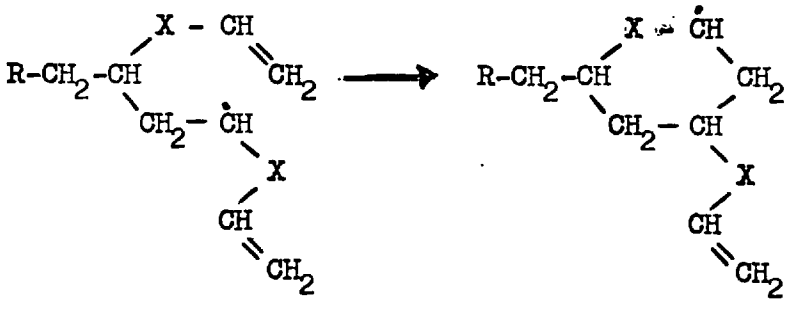


(3-11)

XVI XVII

The dimer radical may then cyclize normally.

(c) Cyclization:

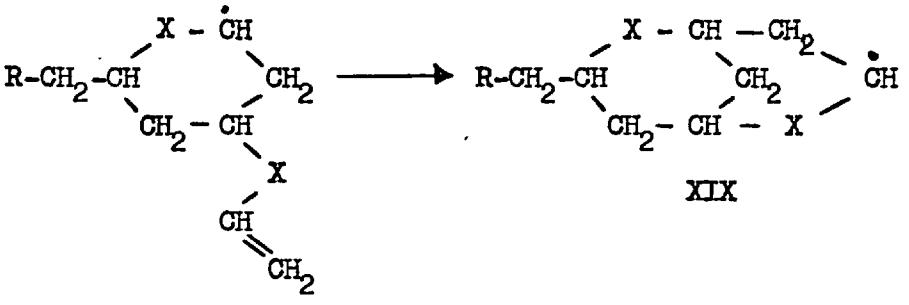


(3-12)

XVII XVIII

The cyclization reaction is then usually followed by a secondary cyclization to form a bicyclic structure.

(d) Secondary Cyclization:



(3-13)

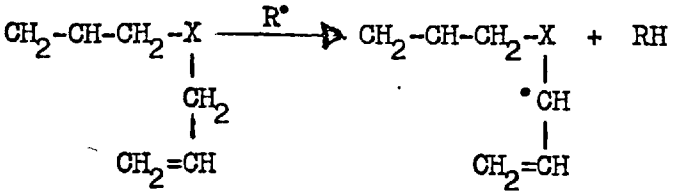
XIX

Structure XIX then propagates as above to form the cyclopolymer.

E. DEGRADATIVE CHAIN TRANSFER REACTIONS WITH NON-CONJUGATED DIENES

Many of the non-conjugated dienes which undergo cyclopolymerization contain one or two allyl groups which are capable of taking part in degradative chain transfer reactions. Mikulasova and Hrivik[92] studied the radical bulk polymerization of monoallyltrimethyl silane and diallyldimethyl silane and found that both monomers undergo polymerization characteristic of allylic compounds: the rate is proportional to the first power of initiator concentration and the $\overline{DP}$ is very low. Diallylcyanamide[72] was polymerized in solution with somewhat similar results and it was suggested that its mode of termination was monomolecular.

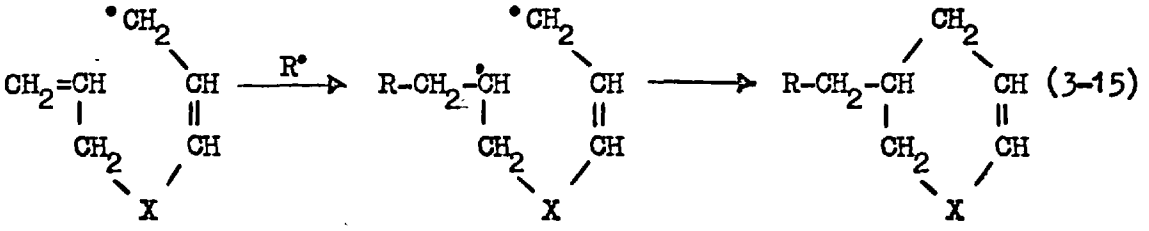
If structure XX represents a symmetrical diallyl compound then the DCT reaction may be represented:



(3-14)

XX XXI

If the reactivity of the remaining allyl group is not adversely affected by the resonance-stabilized allyl radical (RSAR), then a radical such as structure XXI may engage in a further DCT reaction via the unreacted allyl group or in a normal propagation reaction. In the latter case this would yield polymer molecules with pendant resonance-stabilized allyl radicals and a polymer radical with an active end of this type might terminate by cyclization.

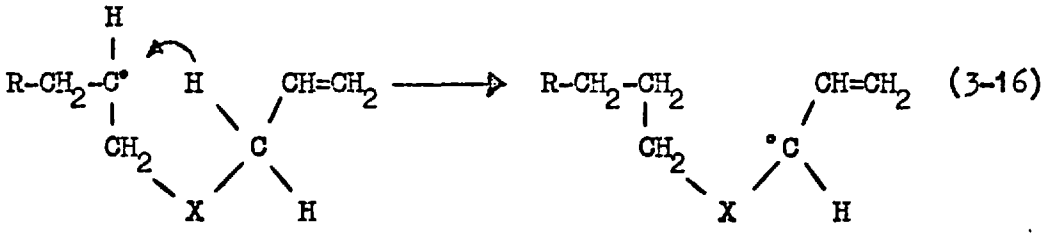


(3-15)

XXI XXII XXIII

1,4 cyclization is unlikely due to steric hindrance.

Another possible mode of 'degradative' termination in dienes is an intramolecular reaction in which a hydrogen atom is extracted from the γ-carbon atom of the noncyclized (structure II) type) radical.



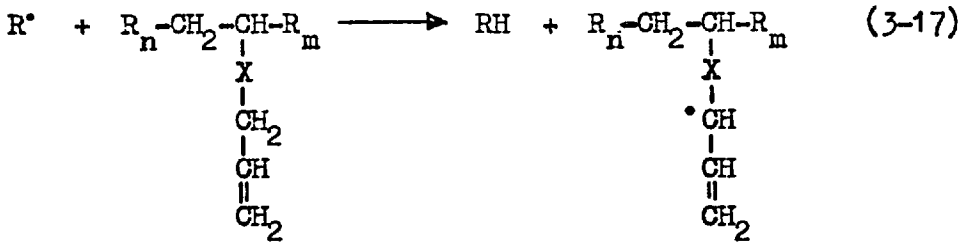
(3-16)

II XXIV

Since the RSAR on structure XXIV will not readily add monomer this reaction effectively terminates the growing chain.

Other possible DCT reactions are the extraction, by radicals,

of hydrogen atoms from allyl groups pendant on chain radicals or polymer molecules.



(3-17)

Biradical combination reactions between RSARs pendant on adjacent chains would lead to cross-linking and gelation if the polymer chains were long. Small rapidly diffusing radicals, such as those formed by solvent transfer, could also react with pendant RSARs and this would tend to suppress this type of cross-linking.

SECTION IV

THE KINETICS OF CYCLOPOLYMERIZATION

A. INTRODUCTION

The free radical cyclopolymerization of a diene molecule may yield polymer with five- or six-membered recurring units in the chains as well as pendant groups and chain branches due to intermolecular reactions. Additional complexity may be introduced by degradative chain transfer reactions and by cross-linking. The mechanism and kinetics of such cyclopolymerizations are thus very complex and a general theory for all cyclopolymerization reactions is not feasible.

However, with the use of various simplifying assumptions, semi-empirical expressions may be derived to relate to experimental results.

B. SIMPLE CYCLOPOLYMERIZATION

A simple example of cyclopolymerization is that in which a symmetrical diene which contains two identical double bonds undergoes linear cyclopolymerization involving rings of one size only, and in which biradical termination occurs[93]. Representing the noncyclized radical (type II, page 29) by $R_1^\bullet$ and the cyclized radical (type III) by $R_2^\bullet$ the elementary reactions may be represented as follows:

$$In \xrightarrow{k_d} 2Z^\bullet \qquad \text{(i)}$$

$$Z^\bullet + M \xrightarrow{k_i} R_1^\bullet \qquad \text{(ii)}$$

$$R_1^\bullet \xrightarrow{k_c} R_2^\bullet \qquad \text{(iii)}$$

$$R_1^\bullet + M \xrightarrow{k_1} R_1^\bullet \qquad \text{(iv)}$$

$$R_2^{\bullet} + M \xrightarrow{k_2} R_1^{\bullet} \qquad \text{(v)}$$

$$R_1^{\bullet} + R_1^{\bullet} \xrightarrow{\alpha^2 k_t} P \qquad \text{(vi)}$$

$$R_1^{\bullet} + R_2^{\bullet} \xrightarrow{\alpha k_t} P \qquad \text{(vii)}$$

$$R_2^{\bullet} + R_2^{\bullet} \xrightarrow{k_t} P \qquad \text{(viii)}$$

where α is a constant used to simplify the mathematics.

At one atmosphere pressure the biradical termination involving $R_1^{\bullet}$ radicals may be regarded as unlikely in many instances as this noncyclized radical has a relatively long pendant group on the β-carbon, while the cyclized radical ($R_2^{\bullet}$) does not have this steric hindrance to reaction. The relative effect of such a β-carbon substituent in the acrylate series may be seen from a comparison of k_p, k_t, E_p and E_t values for methyl and butyl acrylate[93-96].

TABLE 4-1

Absolute Rate Constants and Activation Energies for Methyl and Butyl Acrylates

	k_p (l./mole/sec. @ 30°C)	$10^{-6} k_t$	E_p (kcal./mole)	E_t
Methyl Acrylate	720	2.2	4.7	~ 0
Butyl Acrylate	14	0.009	2.1	~ 0

As the E_p values for the two monomers are not greatly different, the 50-fold variation in the k_p values must be largely due to steric hindrance. In the case of the termination constants the effect of the bulky substituent on the β-carbon is to cause a 220-fold variation.

Thus, it is seen that in many cases of cyclopolymerization, termination will proceed predominantly by the reaction of cyclized radicals. Assuming a stationary state, the kinetic derivation for the case of $R_2^\bullet + R_2^\bullet$ termination proceeds as follows:

$$\frac{d[Z^\bullet]}{dt} = I - k_i[Z^\bullet][M] = 0 \qquad (4\text{-}1)$$

$$\frac{d[R_1^\bullet]}{dt} = k_i[Z^\bullet][M] - k_c[R_1^\bullet] + k_2[R_2^\bullet][M] = 0 \qquad (4\text{-}2)$$

$$\frac{d[R_2^\bullet]}{dt} = k_c[R_1^\bullet] - k_2[R_2^\bullet][M] - k_t[R_2^\bullet]^2 = 0 \qquad (4\text{-}3)$$

Adding equations (4-1) to (4-3) and taking roots:

$$[R_2^\bullet] = (I/k_t)^{\frac{1}{2}} \qquad (4\text{-}4)$$

Using the long kinetic chain assumption:

$$k_c[R_1^\bullet] = k_2[R_2^\bullet][M] \qquad (4\text{-}5)$$

The rate of polymerization is given by:

$$R_p = k_1[R_1^\bullet][M] + k_2[R_2^\bullet][M] \qquad (4\text{-}6)$$

Solving for R_p using equations (4-4) and (4-5):

$$R_p = (k_c + k_1[M])(k_2/k_c)(I/k_t)^{\frac{1}{2}}[M] \qquad (4\text{-}7)$$

In a similar manner the rate expressions for the other two biradical termination reactions ($R_1^\bullet + R_2^\bullet$ and $R_1^\bullet + R_1^\bullet$) may be determined and the results are tabulated in Table 4-2.

TABLE 4-2

Rate Expressions for Simple Cyclopolymerization	
Biradical Termination Reaction	R_p
$R_2^\bullet + R_2^\bullet$	$(k_c + k_1[M])\left\{\frac{2fk_d[In]}{k_t}\right\}^{\frac{1}{2}} \times \frac{k_2}{k_c}[M]$
$R_1^\bullet + R_2^\bullet$	$(k_c + k_1[M])\left\{\frac{2fk_dk_2[In][M]}{k_ck_t}\right\}^{\frac{1}{2}}$
$R_1^\bullet + R_1^\bullet$	$(k_c + k_1[M])\left\{\frac{2fk_d[In]}{k_t}\right\}^{\frac{1}{2}}$

In some cases more than one biradical termination reaction may occur at the same time. Assuming a stationary state and proceeding as before:

$$\frac{d[R_1^\bullet]}{dt} = k_i[Z^\bullet][M] - k_c[R_1^\bullet] + k_2[R_2^\bullet][M] - \alpha k_t[R_1^\bullet][R_2^\bullet] - \alpha^2 k_t[R_1^\bullet]^2 = 0 \qquad (4\text{-}8)$$

$$\frac{d[R_2^\bullet]}{dt} = k_c[R_1^\bullet] - k_2[R_2^\bullet][M] - \alpha k_t[R_1^\bullet][R_2^\bullet] - k_t[R_2^\bullet]^2 = 0 \qquad (4\text{-}9)$$

Adding equations (4-1), (4-8) and (4-9) and taking roots:

$$\alpha[R_1^\bullet] + [R_2^\bullet] = (I/k_t)^{\frac{1}{2}} \qquad (4\text{-}10)$$

Using equations (4-5) and (4-10):

$$[R_1^\bullet] = \frac{k_2(I/k_t)^{\frac{1}{2}}[M]}{k_c + \alpha k_2[M]} \qquad (4\text{-}11)$$

and

$$[R_2^\bullet] = \frac{k_c(I/k_t)^{\frac{1}{2}}}{k_c + \alpha k_2[M]} \qquad (4\text{-}12)$$

Thus:

$$R_p = k_2\frac{(k_c + k_1[M])}{(k_c + \alpha k_2[M])} \times (I/k_t)^{\frac{1}{2}}[M] \qquad (4\text{-}13)$$

From the above equations it is obvious that if the $R_1^\bullet$ and $R_2^\bullet$ radicals were equally reactive (if $k_1 = \alpha k_2$) then the rate expression would be expected to be identical with that found for normal vinyl polymerization.

The overall rate expression for simple cyclopolymerization with biradical termination will be of the form:

$$R_p = K[In]^{\frac{1}{2}}[M]^{\kappa} \qquad (4\text{-}14)$$

where K is a constant at a particular polymerization temperature and pressure and $1.0 < \kappa < 2.0$.

From the results given in Table 4-2 it is possible to deduce the probable biradical termination mechanism from experimental rate determinations at varying monomer concentrations and fixed initiator concentration. This is shown in Table 4-3. The slope to intercept ratio (R) obtained from the approximate straight line relationship will equal k_1/k_c.

TABLE 4-3

Straight Line Relationships in Simple Cyclopolymerization with Biradical Termination		
Experimental κ	Straight Line From a Plot of	Probable Biradical Termination Mechanism
1.0 to 2.0	$R_p/[M]$ vs. $[M]$	$R_2^\bullet + R_2^\bullet$
1.0 to 1.5	$R_p/[M]^{\frac{1}{2}}$ vs. $[M]$	$R_1^\bullet + R_2^\bullet$
1.0	R_p vs. $[M]$	$R_1^\bullet + R_1^\bullet$

If two or three of the possible biradical termination reactions occur simultaneously to significant extents, straight line relationships for none or more than one of the above cases may occur, but a coincidental straight line relationship for only one of the cases cannot be ruled out. Such a case would, however, be unlikely, and if the appropriate plot from experimental results yields a straight line with a slope to intercept ratio approximately equal to the experimental value of k_1/k_c, it will argue strongly for a specific termination mechanism.

If the rate of cyclization is very high relative to the rate of intermolecular propagation, then the noncyclized radical will cyclize before it can propagate and linear propagation will proceed only by the addition of monomer to the cyclized radical. In such a case it may be shown that the rate expression is identical to that found with normal vinyl polymerization and will be represented by:

$$R_p = k_2(I/k_t)^{\frac{1}{2}}[M] \qquad (4\text{-}15)$$

C. SIMPLE CYCLOPOLYMERIZATION WITH TERMINATION BY DEGRADATIVE CHAIN TRANSFER

In the simple cyclopolymerization of a symmetrical diene, when the dominant mode of termination is by degradative chain transfer, the termination reactions may be represented[93] as follows:

1. Intermolecular (see equation 3-14)

$$R_1^\bullet + M \xrightarrow{k_{t1}} P + M^* \qquad \text{(ix)}$$

$$R_2^\bullet + M \xrightarrow{k_{t2}} P + M^* \qquad \text{(x)}$$

2. Intramolecular (see equation 3-16)

$$R_1^\bullet \xrightarrow{k_D} R_1^* \qquad \text{(xi)}$$

where the star indicates a stabilized radical whose propagation rate will be regarded as essentially zero.

The initiation, cyclization and propagation reactions are identical to those in the previous part. In the case of $R_1^\bullet + M$ termination, assuming a stationary state, we have:

$$\frac{d[R_1^\bullet]}{dt} = I - k_c[R_1^\bullet] + k_2[R_2^\bullet][M] - k_{t1}[R_1^\bullet][M] = 0 \qquad (4\text{-}16)$$

$$\frac{d[R_2^\bullet]}{dt} = k_c[R_1^\bullet] - k_2[R_2^\bullet][M] = 0 \qquad (4\text{-}17)$$

Adding equations (4-16) and (4-17):

$$[R_1^\bullet] = (I/k_{t1}[M]) \qquad (4\text{-}18)$$

therefore:

$$[R_2^\bullet] = (k_c I/k_{t1} k_2 [M]^2) \qquad (4\text{-}19)$$

Using equation (4-6) the rate of polymerization is found to be:

$$R_p = (k_c + k_1[M]) \times (I/k_{t1}[M]) \qquad (4\text{-}20)$$

In a similar method rate expressions for the cases where termination is $R_2^\bullet$ + M and $R_1^\bullet$ (intramolecular) may be found and these results are given in the following table:

TABLE 4-4

Rate Expressions for Simple Cyclopolymerization with DCT Termination	
DCT Termination Reaction	R_p
$R_1^\bullet$ + M	$(k_c + k_1[M]) \times \dfrac{2fk_d[In]}{k_{t1}[M]}$
$R_2^\bullet$ + M	$(k_c + k_1[M]) \times \dfrac{2fk_dk_2[In]}{k_ck_{t2}}$
$R_1^\bullet$ (intramolecular)	$(k_c + k_1[M]) \times \dfrac{2fk_d[In]}{k_D}$

The derivations of the above expressions assume that the kinetic chains are long.

In a similar manner a relation in which all three types of degradative termination were occurring could be derived. It is seen that a straight line relationship between experimental R_p vs. [M] results would suggest either $R_2^\bullet$ + M or $R_1^\bullet$ (intramolecular) termination, while a straight line relation from a $R_p[M]$ vs. [M] plot would suggest $R_1^\bullet$ + M termination. In the former case, if the $\overline{DP}$ varied with [M] then

$R_2^{\bullet}$ + M termination would be indicated, and if it did not then $R_1^{\bullet}$ (intramolecular) would be the probable termination mechanism. The slope to intercept ratio from the appropriate plot should again equal k_1/k_c.

If the dominant mode of termination is by the $R_1^{\bullet}$ (intramolecular) mechanism then it is possible that the non-cyclized radical might engage only in intramolecular reactions (i.e. cyclization and termination), and linear propagation would then proceed only by addition of monomer to the cyclized radical. In such a case[93] it may easily be shown that:

$$R_p = \frac{2fk_dk_c[In]}{k_D} \qquad (4\text{-}21)$$

if the kinetic chain length is long.

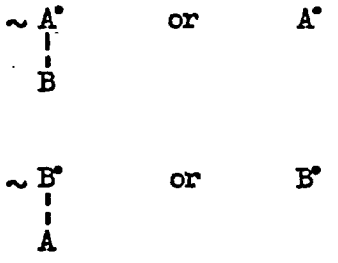
D. SIMPLIFIED KINETICS FOR THE CYCLOPOLYMERIZATION OF UNSYMMETRICAL 1,5 AND 1,6 DIENES

The kinetic study of non-conjugated dienes with non-equivalent double bonds may be divided into two categories. The first will be taken to encompass those unsymmetrical dienes whose kinetics will be expected to be effectively identical with those of symmetrical dienes. This category will include those dienes in which the monomer double bonds differ so significantly that the reactivity of one of the functional groups (towards cyclopolymerization reactions) is effectively zero relative to that of the other functional group. It will also include those monomers which have functional groups of essentially the same reactivity.

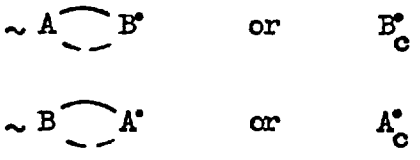
The second category[97] will encompass all other unsymmetrical 1,5 and 1,6 dienes. In these the double bonds will differ, but not to extreme amounts, in reactivity. In such a monomer, if all the reactions involving each functional group and the radicals generated from each functional group were taken into account, there would be 2 initiation, 4 cyclization, 12 propagation, 12 cross-linking and 27 termination reactions possible.

In order to examine a simplified case it will be assumed that cyclizations via a particular functional group lead to rings of one size only. Also, terminations by degradative chain transfer and all reactions involving double bonds pendant on chains will be neglected. In this case, there are 2 initiation, 2 cyclization, 8 propagation and 10 termination reactions. If, as with simple cyclopolymerization, it is considered that biradical termination reactions involving noncyclized radicals are unlikely, the number of possible termination reactions is reduced to three.

In the following derivation, monomer will be represented by A--B where A and B represent the two dissimilar functional groups[98]. The noncyclized radicals formed in the intermolecular step (of the types illustrated by structures XI and XIII on page 33) will be represented by:

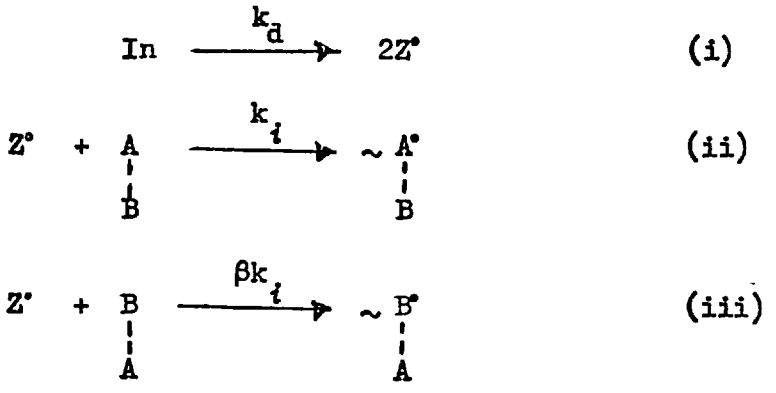


The cyclized radicals formed in the intramolecular step (of the types illustrated by structures XII and XIV) will be represented by:



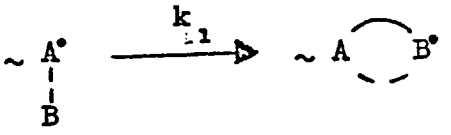
The reactions are:

(a) Initiation

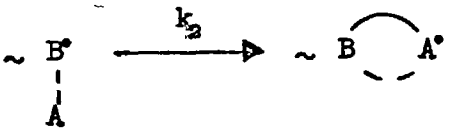


where β is a constant.

(b) Cyclization

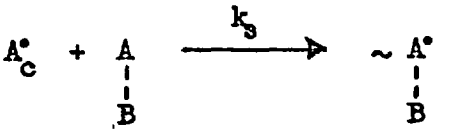


(iv)



(v)

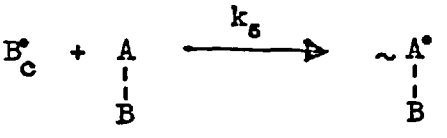
(c) Propagation I



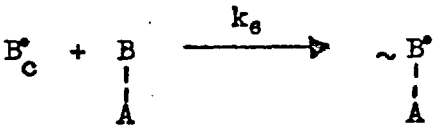
(vi)



(vii)

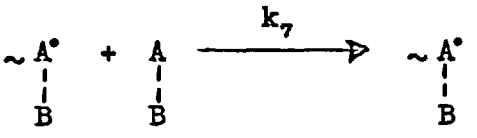


(viii)

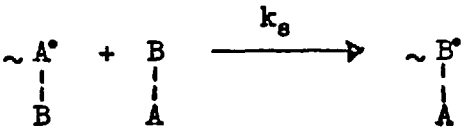


(ix)

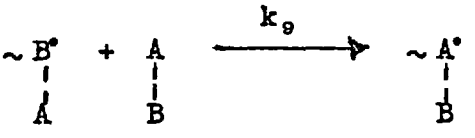
(d) Propagation II



(x)



(xi)



(xii)

$$\sim B^{\bullet} \begin{matrix}|\\A\end{matrix} + B \begin{matrix}|\\A\end{matrix} \xrightarrow{k_{10}} \sim B \begin{matrix}|\\A\end{matrix}^{\bullet} \qquad \text{(xiii)}$$

(e) Termination

$$B_c^{\bullet} + B_c^{\bullet} \xrightarrow{k_t} P \qquad \text{(xiv)}$$

$$B_c^{\bullet} + A_c^{\bullet} \xrightarrow{\alpha k_t} P \qquad \text{(xv)}$$

$$A_c^{\bullet} + A_c^{\bullet} \xrightarrow{\alpha^2 k_t} P \qquad \text{(xvi)}$$

where α is a constant as before.

Assuming a stationary state:

$$\frac{d[Z^{\bullet}]}{dt} = I - k_i(1+\beta)[Z^{\bullet}][M] = 0 \qquad (4\text{-}22)$$

$$\frac{d[A^{\bullet}]}{dt} = k_i[Z^{\bullet}][M] + k_3[A_c^{\bullet}][M] + k_6[B_c^{\bullet}][M] + k_9[B^{\bullet}][M] - k_1[A^{\bullet}] - k_8[A^{\bullet}][M] = 0 \qquad (4\text{-}23)$$

$$\frac{d[B^{\bullet}]}{dt} = \beta k_i[Z^{\bullet}][M] + k_4[A_c^{\bullet}][M] + k_6[B_c^{\bullet}][M] + k_8[A^{\bullet}][M] - k_2[B^{\bullet}] - k_9[B^{\bullet}][M] = 0 \qquad (4\text{-}24)$$

$$\frac{d[A_c^{\bullet}]}{dt} = k_2[B^{\bullet}] - (k_3 + k_4)[A_c^{\bullet}][M] - \alpha^2 k_t[A_c^{\bullet}]^2 - \alpha k_t[A_c^{\bullet}][B_c^{\bullet}] = 0 \qquad (4\text{-}25)$$

$$\frac{d[B_c^\bullet]}{dt} = k_1[A^\bullet] - (k_5 + k_6)[B_c^\bullet][M] - k_t[B_c^\bullet]^2$$

$$- \alpha k_t[A_c^\bullet][B_c^\bullet] = 0 \qquad (4\text{-}26)$$

Adding equations (4-22) to (4-26) and taking roots:

$$[B_c^\bullet] + \alpha[A_c^\bullet] = (I/k_t)^{\frac{1}{2}} \qquad (4\text{-}27)$$

Using the long kinetic chain assumption it may be found[98] from equations (4-25) and (4-26):

$$[A_c^\bullet] = \frac{k_2[B^\bullet]}{(k_3 + k_4)[M]} \qquad (4\text{-}28)$$

$$[B_c^\bullet] = \frac{k_1[A^\bullet]}{(k_5 + k_6)[M]} \qquad (4\text{-}29)$$

Substituting for $[A_c^\bullet]$ and $[B_c^\bullet]$ in equation (4-27) and rearranging:

$$[A^\bullet] = \frac{(k_5 + k_6)(I/k_t)^{\frac{1}{2}}[M]}{k_1} - \frac{\alpha k_2(k_5 + k_6)[B^\bullet]}{k_1(k_3 + k_4)} \qquad (4\text{-}30)$$

If $[A^\bullet]$, $[A_c^\bullet]$, and $[B_c^\bullet]$ are substituted into equation (4-24), and it is assumed the cyclization constants (k_1 and k_2) are much larger than the propagation constants[71], then the following simplification may be obtained:

$$[B^\bullet] \simeq \frac{k_6(k_3 + k_4)(I/k_t)^{\frac{1}{2}}[M]}{k_2(k_3 + \alpha k_6)} \qquad (4\text{-}31)$$

The rate of polymerization is given by:

$$R_p = (k_3 + k_4)[A^\bullet_C][M] + (k_5 + k_6)[B^\bullet_C][M] + (k_7 + k_8)[A^\bullet][M] + (k_9 + k_{10})[B^\bullet][M] \quad (4\text{-}32)$$

Substituting for $[A^\bullet_C]$, $[B^\bullet_C]$, $[A^\bullet]$, and $[B^\bullet]$:

$$R_p = \left\{k_1 + (k_7 + k_8)[M]\right\} \times \frac{k_3(k_5 + k_6)(I/k_t)^{\frac{1}{2}}[M]}{k_1(k_3 + \alpha k_8)} + \left\{k_2 + (k_9 + k_{10})[M]\right\} \times \frac{k_6(k_3 + k_4)(I/k_t)^{\frac{1}{2}}[M]}{k_2(k_3 + \alpha k_8)} \quad (4\text{-}33)$$

The above equation is analogous to equation (4-7) and reduces to an expression essentially the same as it, as in the simple cyclopolymerization of a symmetrical diene:

$$k_1 = k_2 = k_c \quad (4\text{-}34)$$

$$k_3 = k_4 = k_5 = k_6 = k_2 \quad (4\text{-}35)$$

$$k_7 = k_8 = k_9 = k_{10} = k_1 \quad (4\text{-}36)$$

In a similar manner, rate expressions may be obtained for cases when the biradical termination reactions are solely between noncyclized radicals, by cross-termination, by all three of these modes occurring simultaneously, or by some complex combination of them. Except for the last case, these derivations will have the same relationship to the equivalent expressions for simple cyclopolymerization as equation (4-33) has to equation (4-7).

From equation (4-33) the slope to intercept ratio is:

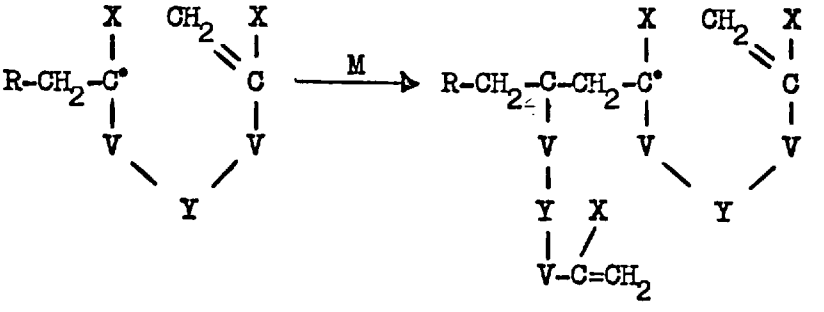
$$R = \frac{(k_3/k_1)(k_5 + k_6)(k_7 + k_8) + (k_6/k_2)(k_3 + k_4)(k_9 + k_{10})}{k_3(k_5 + k_6) + k_6(k_3 + k_4)} \quad (4\text{-}37)$$

The previous expression may be simplified to:

$$R \sim \frac{k_7 + k_8 + k_9 + k_{10}}{k_1 + k_2} = \frac{k_p}{k_c} \quad (4\text{-}38)$$

E. RESIDUAL UNSATURATION IN CYCLOPOLYMERIZATION

Residual unsaturation in cyclopolymers is caused by the addition of monomer to the noncyclized radicals formed in the intermolecular reaction:



(4-39)

II

If f_c and f_L represent the molar fractions of cyclized and noncyclized units respectively then:

$$f_c + f_L = 1.0 \quad (4\text{-}40)$$

and

$$f_c = \frac{R_c}{R_c + R_v} \quad (4\text{-}41)$$

Here R_c and R_v are rates of production of cyclized and noncyclized units respectively. From equation (4-41):

$$\frac{1}{f_c} = 1 + \frac{R_v}{R_c} \qquad (4\text{-}42)$$

For the cyclopolymerization of a symmetrical diene[99]:

$$R_c = k_c[R_i^\bullet] \qquad (4\text{-}43)$$

$$R_v = k_1[R_i^\bullet][M] \qquad (4\text{-}44)$$

Thus

$$\frac{1}{f_c} = 1 + \frac{k_1}{k_c}[M] \qquad (4\text{-}45)$$

For the cyclopolymerization of an unsymmetrical diene[97]:

$$R_c = k_1[A^\bullet] + k_2[B^\bullet] \qquad (4\text{-}46)$$

$$R_v = (k_7 + k_8)[A^\bullet][M] + (k_9 + k_{10})[B^\bullet][M] \qquad (4\text{-}47)$$

Using equations (4-30) and (4-31) it may be shown that R_v/R_c has the same value as the slope to intercept ratio given in equation (4-37).

Therefore

$$(R_v/R_c) \sim (k_p/k_c) \qquad (4\text{-}48)$$

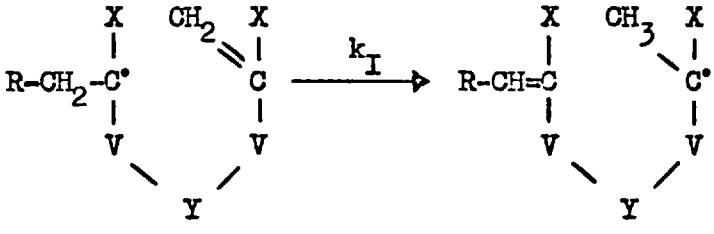
$$\frac{1}{f_c} = 1 + \frac{k_p}{k_c}[M] \qquad (4\text{-}49)$$

For both symmetrical and unsymmetrical dienes, the slope of the linear plot of the reciprocal of the molar fraction of cyclized units in the polymer vs. the monomer concentration will be a measure of the relative importance of intermolecular propagation and intramolecular cyclization. This experimental parameter will also be useful in determining the probable termination mechanism.

As may be seen from either equation (4-45) or (4-49), a linear plot of $1/f_c$ vs. [M] should have an intercept of 1.0 at zero monomer concentration. In many cases, however, the value of the intercept may be greater than unity. This may be due to the following reasons[100]:

(a) If the bromometric method is used to determine f_c, there may be errors due to substitution.

(b) An intramolecular isomerization may occur.



(4-50)

In this case for a symmetrical diene, the rate of production of noncyclized units is given by:

$$R_v = k_1[R_1^\bullet][M] + k_I[R_1^\bullet] \qquad (4\text{-}51)$$

Solving as before:

$$\frac{1}{f_c} = 1 + \frac{k_I}{k_c} + \frac{k_1}{k_c}[M] \qquad (4\text{-}52)$$

Reactions such as that shown in equation (3-15) would have a similar effect.

(c) Chain transfer with the monomer may also lead to an intercept with a value greater than unity. In such a case, for a symmetrical diene, the rate of production of noncyclized units is given by:

$$R_v = (k_1[R_1^\bullet] + k_{tr,1}[R_1^\bullet] + k_{tr,2}[R_2^\bullet])[M] \qquad (4\text{-}53)$$

where $k_{tr,1}$ and $k_{tr,2}$ are the velocity coefficients for chain transfer with noncyclized and cyclized polymer radicals respectively. If such transfer reactions were the dominant mode of termination, then:

$$[R_2^\bullet] = \frac{k_c[R_1^\bullet]}{(k_2 + k_{tr,1})[M]} \qquad (4\text{-}54)$$

and:

$$\frac{1}{f_c} = 1 + \frac{k_{tr,2}}{(k_2 + k_{tr,2})} + \frac{(k_1 + k_{tr,1})}{k_c}[M] \qquad (4\text{-}55)$$

While all of these effects will increase the value of the intercept above unity in a $1/f_c$ vs. $[M]$ plot, they should not affect the value of k_1/k_c. In case (c) above this is true only if $k_1 >> k_{tr,1}$.

F. TEMPERATURE EFFECTS

In cyclopolymerization the effect of temperature on rate polymerization is obtained by the differentiation of the logarithmic rate expression with respect to $1/RT$.

In general, the rate expressions are too complicated to give useful relationships for the overall activation energy. It is possible,

however, to obtain approximate relations, valid within a few kcal./mole, for simple cyclopolymerization by the use of certain simplications.

For example, for the simple cyclopolymerization of a symmetrical diene with $R_2^\bullet + R_2^\bullet$ biradical termination (see equation 4-7) if it is assumed that $E_c \sim E_1$ then:

$$E_T = \tfrac{1}{2}E_d + E_{1(c)} + E_2 - E_c - \tfrac{1}{2}E_t \qquad (4\text{-}56)$$

where the subscripts 1(c), 2, and c refer to the activation energies for the propagation of a noncyclized radical and of a cyclized radical, and for cyclization respectively.

In a similar manner expressions for the overall activation energy can be derived for the rate expressions given in Tables 4-2 and 4-4. These are given in the following table[93].

TABLE 4-5

Overall Activation Energy Expressions for Simple Cyclopolymerization	
Termination Reaction	E_T
monovinyl	$\tfrac{1}{2}E_d + E_p - \tfrac{1}{2}E_t$
$R_2^\bullet + R_2^\bullet$	$\tfrac{1}{2}E_d + E_{1(c)} + E_2 - E_c - \tfrac{1}{2}E_t$
Equation (4-15)	$\tfrac{1}{2}E_d + E_2 - \tfrac{1}{2}E_t$
$R_1^\bullet + R_2^\bullet$	$\tfrac{1}{2}E_d + E_{1(c)} + \tfrac{1}{2}E_2 - \tfrac{1}{2}E_c - \tfrac{1}{2}E_t$
$R_1^\bullet + R_1^\bullet$	$\tfrac{1}{2}E_d + E_{1(c)} - \tfrac{1}{2}E_t$
$R_1^\bullet + M$	$E_d + E_{1(c)} - E_{t1}$
$R_2^\bullet + M$	$E_d + E_{1(c)} + E_2 - E_c - E_{t2}$
$R_1^\bullet$ (intramolecular)	$E_d + E_{1(c)} - E_D$
Equation (4-21)	$E_d + E_c - E_D$

An expression for the difference between E_1 and E_c may be obtained from equation (4-45) and the Arhennius equation:

$$\frac{1}{f_c} = 1 + \frac{k_1[M]}{k_c} \qquad (4\text{-}45)$$

thus:

$$\frac{1}{f_L} - 1 = \frac{k_c}{k_1[M]} = \frac{A_c \exp(-E_c/RT)}{A_1 \exp(-E_1/RT)[M]} \qquad (4\text{-}57)$$

Taking logarithms:

$$\ln(1/f_L - 1) = \ln(A_c/A_1[M]) + (E_1 - E_c)/RT \qquad (4\text{-}58)$$

Thus an experimental value for $(E_1 - E_c)$ may be obtained from the slope of the linear plot of the experimental values of $\ln(1/f_L - 1)$ vs. $1/T$. For unsymmetrical dienes the value of the slope will be designated $(E_p - E_c)$.

SECTION V

THE EFFECT OF PRESSURE ON LIQUID PHASE POLYMERIZATION

A. CHEMICAL REACTIONS AT HIGH PRESSURES

(i) INTRODUCTION

Pressure is an experimentally variable parameter whose increase has an accelerating effect on the rates of many gaseous and liquid phase reactions. In gaseous reactions this acceleration is generally explicable as the result of a Mass Action effect, but in relatively incompressible liquid systems it cannot be explained solely on the basis of changes in the concentration of the reactants.

The effect of pressure on liquid phase reactions may be interpreted by reference to either of two theories: the Collision Theory, and the Transition State Theory.

(ii) The Collision Theory

According to this theory the variation of the rate constant with the absolute temperature may be given by a form of the Arrhenius equation:

$$k = PZe^{-E/RT} \qquad (5\text{-}1)$$

Here P is a factor which represents the probability that molecules may need a particular orientation before they can react. It usually has a value of less than one. Z is the frequency of collision of the reacting molecules in a unit volume at unit concentration.

The Collision Theory assumes that variations in pressure alter the values of both PZ and E, which in turn affect the value of the rate constant. Weale[101] has tabulated the effects of pressure on the values of PZ(A) and E for several liquid phase reactions.

(iii) The Transition State Theory

The effect of pressure on liquid phase reactions is best explained by the Transition State Theory. It assumes the formation of a transition state or activated complex during the course of a reaction.

$$A + B \rightleftharpoons X^{*} \longrightarrow \text{products} \qquad (5\text{-}2)$$

For a bimolecular reaction A and B are the reactants which are in equilibrium with the transition state X^{*}.

On the basis of this theory the variation of the rate constant is most conveniently expressed by the following simplified equation, first developed by Evans and Polanyi[102].

$$\left(\frac{\partial \ln k}{\partial P}\right)_{T} = \frac{-\Delta V^{*}}{RT} \qquad (5\text{-}3)$$

where ΔV^{*} is called the 'volume of activation' and indicates the change in volume per mole in going from the initial reactants to the transition state. A full development of this equation is given elsewhere[101].

Slight errors may be introduced into the value of ΔV^{*} if concentrations are expressed in molar units, as the above equation does not consider the compressibility of the reaction system. In ionic systems the solvation of the ions may account for a large part of ΔV^{*}, but this effect is unimportant for non-polar reactions.

The effect of pressure on a rate constant will depend on the sign and magnitude of the volume of activation. A negative value for ΔV^{*} will indicate that k increases with increasing pressure.

B. THE EFFECT OF PRESSURE ON RADICAL ADDITION POLYMERIZATION

(i) Overall Volume of Activation

In free radical addition polymerization the overall effect of pressure will depend on the contributions to the overall volume of activation (ΔV_T^*) by the initiation, propagation, cyclization and termination reactions. For normal monovinyl polymerization:

$$R_p = k_p(I/k_t)^{\frac{1}{2}}[M] \qquad (1\text{-}15)$$

Using equation (5-3) and ignoring the effect of pressure on initiator and monomer concentrations it may be shown that:

$$\Delta V_T^* = \tfrac{1}{2}\Delta V_d^* + \Delta V_p^* - \tfrac{1}{2}\Delta V_t^* \qquad (5\text{-}4)$$

For simple cyclopolymerization with $R_2^\bullet + R_2^\bullet$ termination it may be shown from equation (4-7) that:

$$\Delta V_T^* = \tfrac{1}{2}\Delta V_d^* + \Delta V_{1(c)}^* + \Delta V_2^* \div \Delta V_c^* - \tfrac{1}{2}\Delta V_t^* \qquad (5\text{-}5)$$

where the subscripts are as defined in section IV-F.

Similarly, in other cases of simple cyclopolymerization, expressions for the overall volume of activation may be obtained and these will be analogous to those derived for the overall activation energy (see Table 4-5).

(ii) Polymerization at High Pressures

The formation of polymer molecules usually involves a decrease in molar volume and thus polymerization is thermodynamically favoured by pressure. The effect of pressure on liquid phase polymerization was first studied by Bridgeman and Conant[103]. For the polymerization of

several compounds at high pressures, they observed a marked increase in the rate of polymerization with an accompanying increase in the molecular weight. Subsequent investigations by Starkweather[104] and others[105,106] who examined the polymerizations of many substances in the pressure range 3000-12,000 atm. showed that many monomers which do not polymerize, or polymerize only to limited amounts, at atmospheric pressure give substantial yields of polymer at high pressures. A recent text by Weale[107] reviews the current status of the field.

(iii) The Effect of Pressure on Initiation

The effect of pressure on the decomposition of initiators is complex and seems to depend a great deal on the nature of the reaction medium. Nicholson and Morrish[108] studied the decomposition of Bz_2O_2 in CCl_4 up to 3000 kg./cm.^{2} and found a slight decrease in k_d with pressure. The rate of induced decomposition was accelerated by pressure but this effect was greatly reduced in the presence of polymerizable monomers[108,109]. However, Walling and Pellon[110] concluded that chain decomposition of the initiator was responsible for results in which the rate of initiation first decreased, then increased in the decomposition of Bz_2O_2 in allyl acetate and acetophenone at high pressures. The decomposition of AIBN in toluene at pressures of up to 10,000 atm. was studied by Ewald[111] and k_d was found to decrease with pressure, while the rate of radical wastage reactions increased.

Walling and Metzer[112] examined the decomposition of di-tert butyl peroxide at 120°C in four solvents at pressures up to 7000 atm.. They found a decrease in the rate of initiation in all cases, but this decrease was greatest in the solvents benzene and CCl_4. The value of ΔV_d^* obtained with these solvents was approximately double that obtained

with the solvents toluene and cyclohexene. They attempted to explain both their own results and those of Ewald on the basis of the 'cage theory'[113] but it is felt that induced decomposition is responsible. As noted previously, certain solvents are susceptible to initiator-radical attack, and such rapid chain decomposition reactions (see equations 1-30 and 1-31) are probably greatly accelerated by pressure. From these and other[101] results the approximate value for ΔV_d^* in polymerization reactions is seen to be + 4 to + 6 cc/mole.

The value of the catalyst exponent in the rate equation generally falls slightly as the pressure is increased. For the polymerization of styrene it was observed[114,115] to fall from 0.5 at atmospheric pressure to about 0.4 by 3000 - 4000 atm.. In the bulk polymerization of allyl acetate[110] at 80°C the value of the exponent fell from 1.0 at atmospheric pressure to 0.5 at 5500 kg./cm.^{2}.

(iv) The Effect of Pressure on Propagation and Termination

Nicholson and Norrish[108] studied the Bz_2O_2-catalysed polymerization of styrene at 30°C and found that the overall rate of polymerization increased 12-fold by 5000 kg./cm.^{2}. The value of k_p was found to increase exponentially with pressure and that of k_t to decrease rapidly up to 1000 kg./cm.^{2} and slowly thereafter. ΔV_p^* was found to be - 13.4 cc/mole. This agrees approximately with results found for the thermal polymerization of styrene[116]. In the emulsion polymerization of styrene at 40°C Walling and Pellon[117] found that the curve of $(k_p)_{press.}/(k_p)_{1\ atm.}$ vs. pressure rises steeply at first, becoming linear between 1000 and 3800 kg./cm.^{2}. The value of ΔV_p^* in this region was - 11.5 cc/mole. Similar results were found for the polymerization of styrene in CCl_4 solution at 60°C.

Measurements of k_t do not permit an accurate evaluation of ΔV_t^* but it has been estimated at values as high[101] as + 12 cc/mole and as low[117] as + 4 cc/mole. This lower value compares well with the value of + 3.1 cc/mole which may be calculated from the near-linear portion of the k_t vs. P curve given by Nicholson and Norrish[108]. The decrease in k_t is felt[108,118] to be due to the decreased rate of diffusion of the polymer radicals at high pressures. The rate of diffusion is less affected when the polymerization is carried out in solution. At high conversions at high pressures autoacceleration occurred. The effect of pressure is thus similar to the gel effect in some ways.

(v) The Effect of Pressure on Transfer Reactions

Although the rate of propagation is increased and the rate of biradical termination is decreased by pressure in the polymerization of styrene, the molecular weight has been found[108] to increase only two- to three-fold and then tend to a constant value. Similar effects occur with other monomers and it is considered that this is the result of a strong acceleration by pressure of chain transfer reactions[117].

From equations (1-19) and (5-3):

$$\left(\frac{\partial \ln C}{\partial P}\right)_T = -(\Delta V_{tr}^* - \Delta V_p^*)/RT \qquad (5\text{-}6)$$

Walling and Pellon[117] found for the polymerization of styrene in CCl_4 solution at 60°C that C_s was relatively insensitive to pressure and decreases only 15% in 4000 kg./cm^2. Therefore, $k_{tr,s}$ must be strongly increased by pressure and $\Delta V_{tr,s}^*$ was calculated to be - 11.0 cc/mole. Similarly, C_I and C_M were also to be slightly decreased by pressure.

As mentioned previously, Walling and Pellon[110] found that for the polymerization of allyl acetate under pressure the value of the catalyst exponent in the rate equation fell from 1.0 at atmospheric pressure to 0.5 at 5500 kg./cm.^{2}. This result was interpreted as being due to the predominance of biradical termination when the DCT reaction (see Section I-C)

$$R^{\bullet} + M \xrightarrow{k_D} RH + M^{*}$$

no longer constituted an effective termination reaction. At high pressure the resonance-stabilized allyl radicals apparently become active enough to re-initiate chain growth

$$M^{*} + M \xrightarrow{k'_p} R^{\bullet}$$

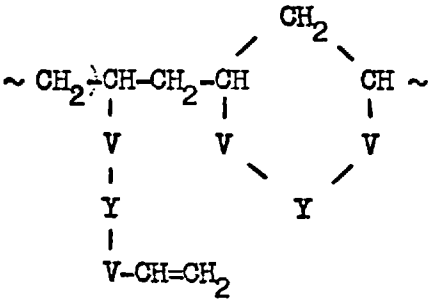
The DCT termination thus tends to become an ordinary transfer reaction at high pressures and, as noted before, such reactions do not usually affect the overall rate of polymerization. The molecular weight of allyl acetate was only slightly increased by pressure and it was found that $\Delta V^{*}_{C_M} \sim +4.7$ cc/mole.. The reduction in resonance stabilization led to a sharp increase in k_p relative to k_D, and R_p was found to increase 50-fold by 8500 kg./cm.^{2}. In the range 5500 to 8500 kg./cm.^{2} (where termination is biradical), ΔV^{*}_{T} was found to be -13.4 cc/mole.

C. CYCLOPOLYMERIZATION AT HIGH PRESSURES

Little information is available about the volume changes associated with the formation or scission of cyclic structures in the transition state. It is known[119] that ring-opening reactions which do not involve the formation of a new covalent bond are favoured by

pressure and numerous ring-opening polymerization[120] are accelerated or made possible under pressure. In contrast, cyclization reactions involving the formation of a new covalent bond are usually strongly favoured by pressure. Fawcett and Gibson[121] studied the equilibrium between 5-methyl-4-heptanoic acid and its δ-lactone at 160°C from 1 to 3000 atm. and found that pressure shifted the equilibrium substantially towards the lactone.

No results have yet been published on the effect of pressure on cyclopolymerization, but as may be seen from the following structure, a cyclic repeating unit in a cyclopolymer chain contains one more covalent bond than the alternative repeating unit with a pendant functional group.



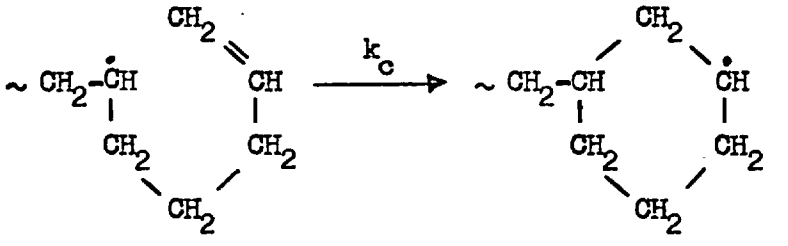
Thus, it might be expected that cyclization would be favoured by pressure.

The relative effect of pressure on cyclization and intermolecular propagation in simple cyclopolymerization may be obtained using equations (4-57) and (5-3):

$$\left(\frac{\partial \ln(1/f_L - 1)}{\partial P}\right)_T = (\Delta V_1^* - \Delta V_c^*)/RT \qquad (5\text{-}7)$$

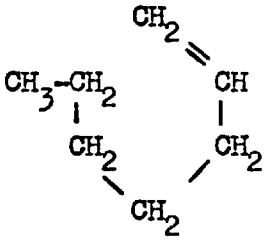
The difference between the volumes of activation for the intermolecular propagation reaction and the cyclization reaction may be obtained from the slope of a linear plot of $\ln(1/f_L - 1)$ vs. pressure at constant temperature. A positive value of $(\Delta V_1^* - \Delta V_c^*)$ would indicate that cyclization was favoured by pressure.

An estimate of the volume of activation for the cyclization reaction in simple cyclopolymerization may be obtained from the difference in actual molar volumes for ring and open-chain groups. For example, the cyclization reaction in the cyclopolymerization of 1,6 heptadiene is:

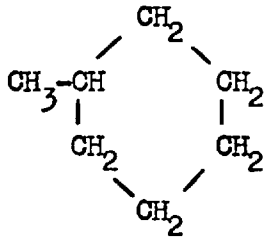


(5-8)

The decrease in volume accompanying this reaction may be approximately represented by the difference between the molar volumes of n-heptene and methylcyclohexane.



n-heptene
V = 140.9 cc/mole

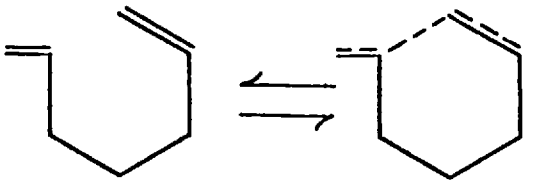


methylcyclohexane
V = 127.5 cc/mole

ΔV is - 13.4 cc/mole and this gives a rough estimate of ΔV_c^*.

Butler[122,123] has recently suggested an activated state-ground state interactions theory based on an across space homoconjunction interaction between the double bonds of a monomer to form a pseudocyclic

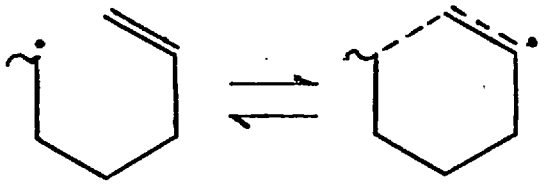
structure. For 1,6 heptadiene this effect may be depicted:



(5-8)

I II

Butler[122] and Marvel and Stille[124] have also suggested a somewhat similar interaction between the pendant double bond and the radical end of a noncyclized ($R_1^\bullet$) radical.



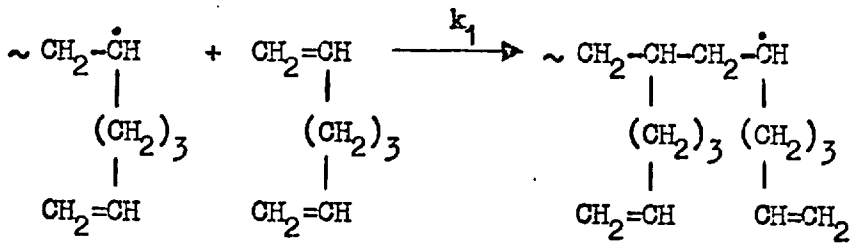
(5-9)

III IV

Recent ultraviolet absorption evidence[125,126] seems to support the existance of the first of these activated state complexes.

If monomer and $R_1^\bullet$ radicals can be represented by structures II and IV above, then the cyclization reaction would be a lower activation energy process than intermolecular propagation and hence, a favoured pathway for reaction, especially at high pressures. A reasonable estimate of the volume of activation for the intramolecular cyclization reaction in cyclopolymerization would probably be $\left|\Delta V_c^*\right| > 15$ cc/mole.

In the polymerization of 1,6 heptadiene, the intermolecular propagation reaction is:



(5-10)

It might be expected that the volume of activation for the reaction shown in equation (5-10) could be estimated in a manner similar to that used to estimate ΔV_c^*. This would be erroneous. The following hypothetical reaction is considered to be a model for the intermolecular propagation reaction (or, for that matter, for any addition polymerization):

$$CH_3-\underset{R}{CH_2} + CH_2=\underset{R}{CH} \longrightarrow CH_3-\underset{R}{CH}-CH_2-CH_2-R \qquad (5\text{-}11)$$

Using various groups (i.e. ethyl, propyl, etc.) in place of R, ΔV is found to be - 25 to - 30 cc/mole. These results give a very poor estimate of the volume of activation in polymerization as it has already been noted that ΔV_p^* is less than half this value in the polymerization of styrene (i.e. R above is a phenyl group). If it is assumed that the volume of activation for the intermolecular propagation of a noncyclized radical in cyclopolymerization has about the same value as that for a normal monovinyl polymerization, then ΔV_1^* may be estimated to be about - 10 cc/mole. ΔV_2^* will probably also be in the same range. Thus it is seen that the values of ΔV_c^* and ΔV_1^* are close to each other, but it seems likely that $|\Delta V_c^*| > |\Delta V_1^*|$ and, despite the fact that the intermolecular propagation reaction is bimolecular, it should probably not be favoured as much by pressure as the intramolecular cyclization reaction.

SECTION VI

EQUIPMENT, MATERIALS AND PROCEDURES

A. HIGH PRESSURE EQUIPMENT

(i) The design and construction of high pressure equipment has been described by many authors[127-129]. The equipment used in the present study has previously been fully described[130-132] so only a brief outline is given here.

The vessels used were capable of containing pressures of 4000 atm. (Vessel No. 4) and 15,000 atm. (Vessel No. 6) respectively. The pressure transmitting medium was liquid paraffin B.P.

A schematic of the system used with Vessel No. 6 is given in Figure 1. The pressure transmitting oil is contained in a reservoir in the top of the hand-operated pump (P) and enters the system through a valve (not shown) in the base of the pump. This valve is non-return when closed and may be opened at the end of an experiment to release the pressure by allowing the oil to expand back into the reservoir. The pressure delivered by the pump is increased to high pressure in the pressure vessel (C) by means of a pressure intensifier (I). Low pressure is applied to a large diameter piston of area 'A' which in turn drives a smaller diameter piston of area 'a'. Thus, if friction is neglected, the low pressure is intensified by a factor of A/a. For vessel No. 6 this ratio is approximately 15. There is a by-pass line (S) around the intensifier, through valve V_s so that the reaction chamber can be primed to a pressure of between 500 and 1000 atm. directly from the pump (when valve V_1 is closed to seal off the line to the intensifier).

In this way the maximum pressure may be attained (because of the limited travel of the intensifier pistons). The connecting lines are

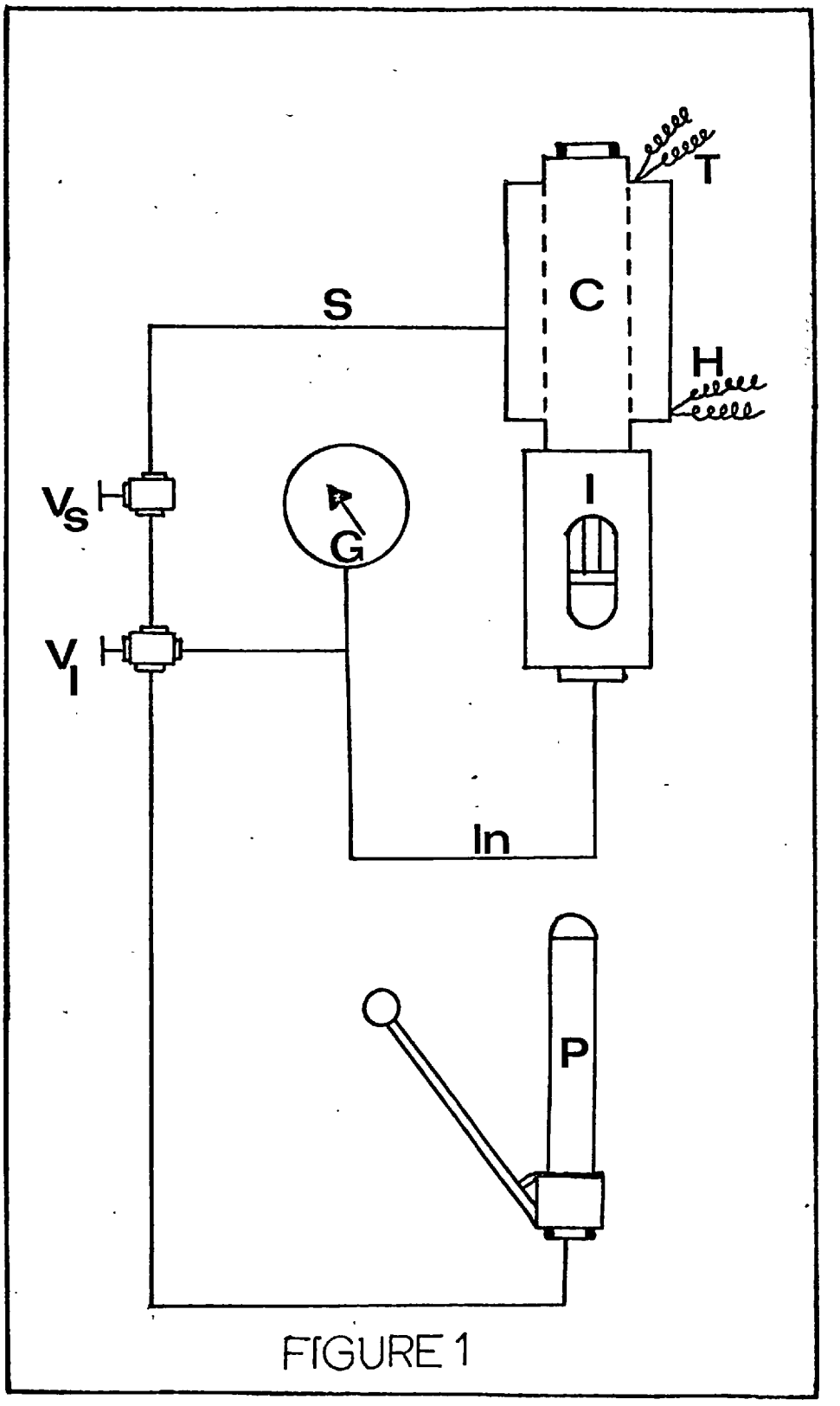


FIGURE 1

3/8" dia., 1/8" bore stainless steel tubing. The pressure vessel is surrounded by an electric heating jacket (H). A Sunvic switch relay operating through a contact therometer inserted between the vessel and the heating jacket provides on-off temperature control within $\pm$ 0.1°C.

Vessel No. 6 is sketched in Figure 2. The upper portion is the pressure vessel proper. It consists of an autofrettaged cylindrical monoblock of "Vibrac V45" steel, six inches in diameter. The reaction chamber (r) is centrally located and has a diameter of 0.6 inches. The steel plug (Pl) is screwed down on a steel mushroom head (m) which holds a Poulter packing (b) against the high pressure in the reaction chamber. The intensifier by-pass line (S) connects into the reaction chamber through a tapered hole (1/30" dia. in the wall of the reaction chamber) and allows the reaction chamber to be filled with oil and primed to the initial pressure from the pump. Below the level of the side entry is another Poulter packing which automatically seals the side entry when it moves past it due to the advancement of the pistons. This 'bung' sits on top of the high pressure piston (hp) which has a clearance of 0.001 inches in the reaction chamber.

The lower part of the sketch is the intensifier. Oil is pumped through the low pressure inlet (In) against the $2\frac{1}{2}$" dia. low pressure piston (lp). The low pressure cylinder is sealed by an unsupported area Bridgman seal (bs) near the top of the piston. A thrust block (t) with a seat of soft metal ensures that the high pressure piston is always aligned with the low pressure piston and the reaction chamber. The pressure vessel and the intensifier are joined with a steel sleeve. The volume of the reaction chamber permits the accommodation of 3 to 5 ml. samples.

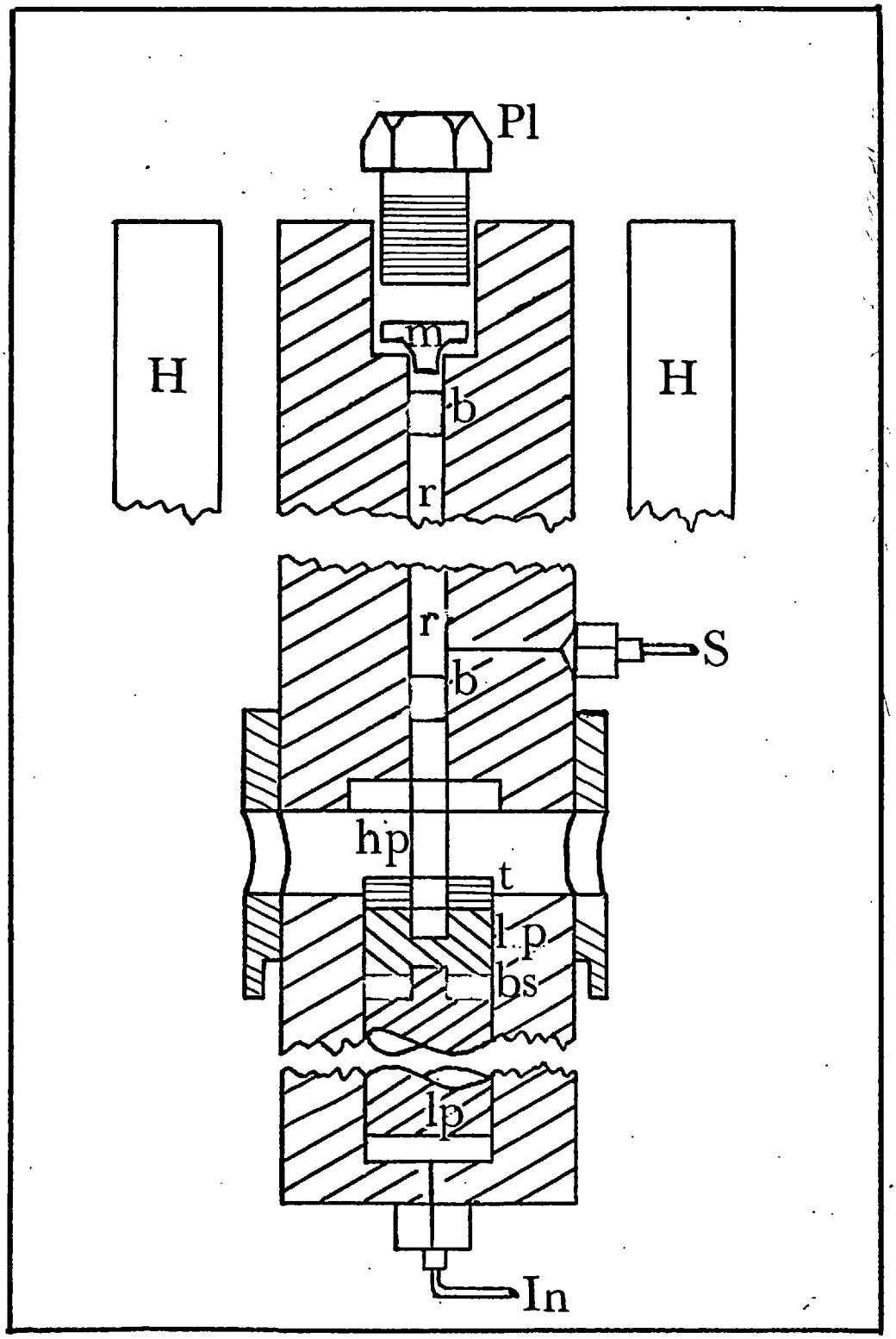


Figure 2

A schematic of the system used with Vessel No. 4 is given in Figure 3. This system is essentially similar to that for Vessel No. 6 except in that the intensifier (I) and the pressure vessel (C) are separated and in that there is no intensifier by-pass line as pre-priming of the reaction chamber is unnecessary at Vessel No. 4's lower operating pressures. The high pressure piston, topped by a Poulter packing advances into a 0.6" dia. tube (clearance 0.001 inches) in a "Vibrac W45" cylinder above the intensifier (which is similar to that of Vessel No. 6). Pressure is transmitted from this cylinder to the pressure vessel by a $\frac{1}{2}$" dia., $\frac{1}{8}$" bore stainless steel tube.

The pressure vessel consists of two cylinders of "Vibrac W45" steel shrunk together and is sealed with a Poulter packing held in place by a threaded steel plug. No steel mushroom head is necessary at Vessel No. 4's operating pressures. The reaction chamber is about 0.75" in dia. and is capable of taking samples of up to 10 mls. in volume. The pressure vessel is immersed in a stirred thermostated oil bath (O) which is heated by a 1 KW electric immersion heater (H). The temperature of the oil bath is controlled within $\pm$ 0.1°C by a Sunvic on-off switch relay operating a contact thermometer (T). The piston area ratio (A/a) for Vessel No. 4 is about 5.

Each pressure vessel has a Bourdon tube pressure gauge (G) to measure pressure on the low-pressure side of the intensifier. The low and high pressures were found[133] to be related by the following expressions:

Vessel No. 4 $\quad H.P. = 5.0(L.P.) + 25$

Vessel No. 6 $\quad H.P. = 14.8(L.P.) + 38$

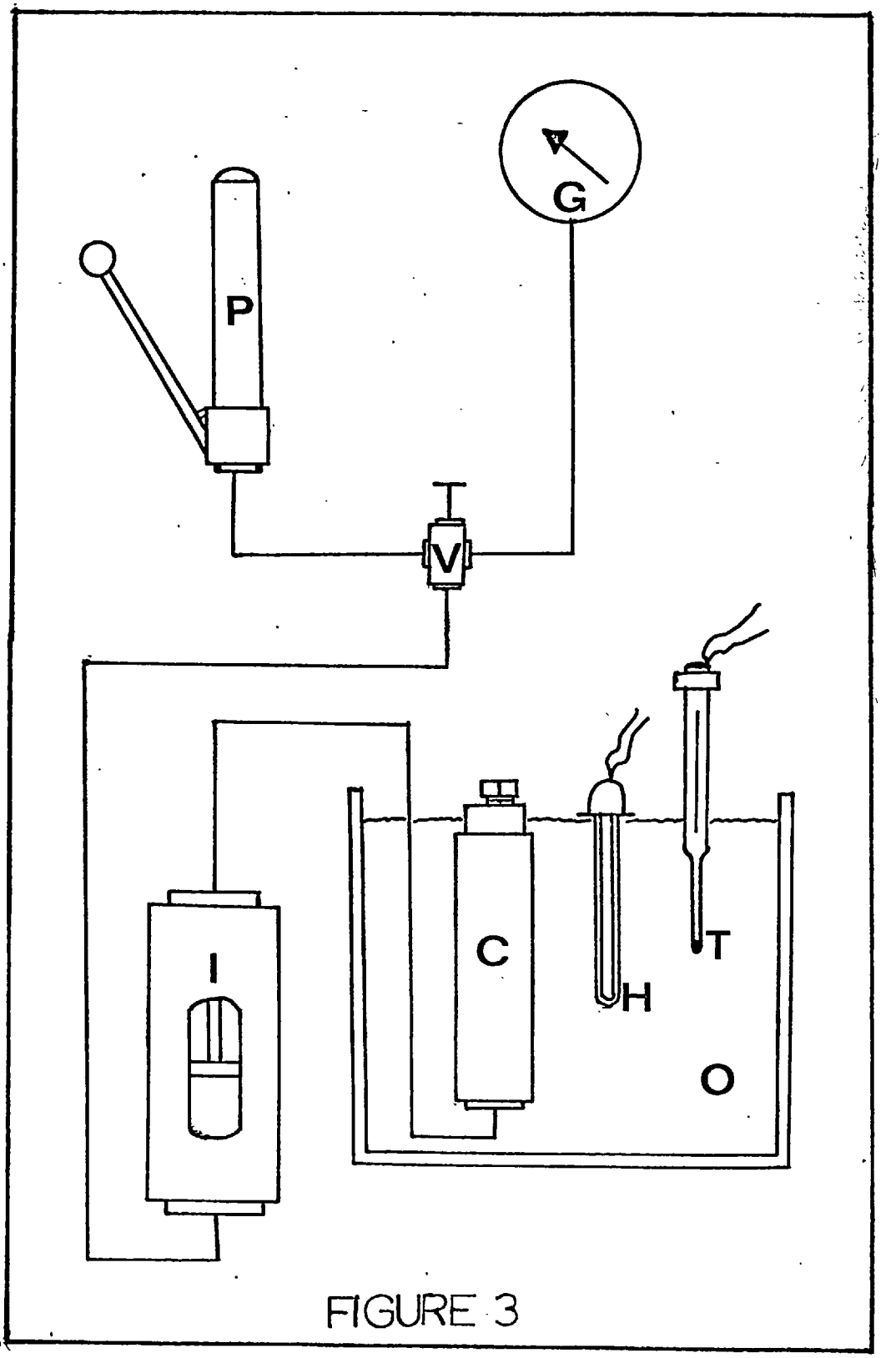


FIGURE 3

(ii) Reaction Tubes and Holders

Experiments under pressure were carried out in P.T.F.E. (Teflon) tubes about 10 cm. long, 8.5 mm. o.d. and 6 mm. i.d.. These tubes were closed at both ends with stoppers machined from Teflon rod and had copper rings at the ends to prevent any extrusion of the tube. After filling, the seal was further ensured by wrapping the ends with P.T.F.E. tape. The tube was then placed in a steel container with a threaded brass plug at one end. This brass plug could be tightened against the end of the P.T.F.E. tube to hold the stoppers in place. Slits in the side of the steel container permitted the pressure transmitting oil to act on the P.T.F.E. tube. The brass plug was fitted with a hook to facilitate removal of the container from the reaction chamber. A bowed steel spring was soldered to the side of the container to hold it in any desired position in the reaction chamber[134].

B. MATERIALS

(i) Monomers

(a) Acrylic Anhydride

The acrylic anhydride supplied (Phase Separations) contained quinol as an inhibitor. This was removed by double-distilling small batches of the monomer under vacuum. In the first distillation the final 10% was discarded and in the second both the first and last 10% were rejected. The distillate was flushed with dry O_2-free nitrogen before being stored at $-10^{\circ}C$. Distilled monomer was always used within 2 days and was distilled a third time immediately before use ($55^{\circ}C/5$ mm. Hg). A typical sample had a density, $d^{20} = 1.071$ gms./ml. and a refractive index, $n_D^{20} = 1.4490$.

(b) Allyl Methacrylate

The allyl methacrylate supplied (Koch Light, B.D.H.) contained quinol as an inhibitor. This was extracted using inhibitor remover (H_2O/NaCl/NaOH = 100 gms./10 gms./ 2 gms.). The monomer was then dried over anhydrous $CaCl_2$ for at least 24 hours and distilled under vaccum (33 - 35°C/30 mm. Hg). The first and last 20% were discarded and the remaining distillate was flushed with nitrogen and stored at 0°C. Purified allyl methacrylate which was exposed to air for a few days turned from water-clear to yellowish in colour, presumably through the absorption of oxygen, and samples of it gave relatively low yields if used in polymerizations. Purified allyl methacrylate was used within 3 days. d^{20} = 0.937 gms./ml.; n_D^{20} = 1.4370.

(c) Diallylamine Hydrochloride

The diallylamine hydrochloride supplied (Eastman Organic Chemicals) was the only non-liquid monomer used. This crystalline solid was purified by recrystallization from a saturated water solution using benzene. The monomer was then dried overnight under vacuum and stored in a dessicator containing anhydrous calcium chloride. m.p. = 168°C.

(d) Diallyl Cyanamide

The diallyl cyanamide supplied (Fluka A.G.) contained quinol as an inhibitor. This was removed by distilling small batches of the monomer under vacuum (65 - 67°C/5 mm. Hg). The first and last 20% were rejected and the distillate was flushed with nitrogen before being stored at 0°C. Crude monomer was a deep violet colour and purified monomer which was exposed to air turned from water-clear to slightly brownish in colour after a few days. Distilled diallyl cyanamide was usually used

immediately and always within 3 days, and was distilled a second time and flushed with N_2 immediately before use. d^{20} = 0.903 gms./ml.; n_D^{20} = 1.4570.

(e) Diallyl Ether

The diallyl ether supplied (Fluka A.G.) contained quinol as an inhibitor. The monomer was purified by vacuum distillation (38°C/58 mm. Hg). The first and last 20% were rejected and the distillate was flushed with dry nitrogen before being stored at 0°C. Diallyl ether, which was also used as a solvent, was distilled a second time before use. d^{20} = 0.802 gms./ml.

(f) Indene

The indene monomer supplied (Ralph Emmanuel Ltd.) was distilled at atmospheric pressure after adding quinol, and the fraction boiling at 180 - 182°C was collected. The product was flushed with dry nitrogen and stored at 0°C. Before use indene was redistilled under vacuum (74 - 75°C/58 mm. Hg), the first and last 20% being rejected, and the distillate flushed with N_2. d^{20} = 0.992 gms./ml.; n_D^{20} = 1.5701.

(g) Styrene

The styrene supplied (Koch Light) was purified by the same method as allyl methacrylate. b.p. = 33°C/10 mm. Hg; d^{20} = 0.903 gms./ml..

(h) Vinyl Methacrylate

Vinyl methacrylate was prepared by the method given in the literature[90,135]. In a typical preparation 86 mls. (1 mole) of methacrylic acid, 460 mls. (5 moles) of vinyl acetate, 2.2 gms. of

mercuric acetate, 0.6 gms. of sulfuric acid, and 1.0 gm. of quinol were mixed in a flask and stirred for 3 days at room temperature. At the end of this period 10 gms. of sodium acetate were stirred in and the reaction mixture was washed several times with water. The organic upper layer was separated, dried for 24 hours over anhydrous magnesium sulfate, and distilled under vacuum. The second fraction (the first is recovered vinyl acetate) collected was the monomer. b.p. = 40°C/38 mm. Hg, 50% yield. Monomer was dried for 48 hours over anhydrous magnesium sulfate and then distilled, the initial and final 10% being rejected. The distillate was flushed with dry nitrogen and stored at - 10°C.
$d^{20} = 0.933$; $n_D^{20} = 1.4090$.

(j) Vinyl Sulfone

The vinyl sulfone supplied (Ralph Emmanuel Ltd.) was purified by vacuum distillation (123°C/7 mm. Hg). The first and last 20% were rejected and the distillate was flushed with dry nitrogen. Distilled vinyl sulfone was stored at 0°C and used within 3 days. d^{20} = 1.168 gms./ml.

(ii) Initiators

(a) Benzoyl Peroxide (Bz_2O_2)

The benzoyl peroxide supplied (B.D.H.) was purified by recrystallization. A saturated solution in chloroform was prepared and the benzoyl peroxide was precipitated as a crystalline solid in cold methanol. The purified material was filtered off, dried under vacuum and stored at 0°C in a sealed container. Fresh material was prepared at regular intervals.

(b) Azo-bis-isobutronitrile (AIBN)

The AIBN supplied (Koch Light) was purified in the same manner as was Bz_2O_2 except that the saturated solution was prepared in dry ethyl ether rather than chloroform.

(c) Tert-butyl hydroperoxide (TBHP)

The liquid TBHP was used as supplied (Koch Light).

(d) Tert-butyl perbenzoate (TBPB)

The liquid TBPB was used as supplied (B.D.H.).

(iii) Solvents

High purity reagents were used whenever possible. Those reagents used for molecular weight determination or as solvents in polymerization experiments were distilled before use, the first and last 20% being discarded. The phenol used (B.D.H.) was chromatographically pure. NN-dimethylformamide (Koch Light) was first dried for one hour over phosphorous pentoxide to remove traces of acid and water and then distilled from P_2O_5. Distilled water was boiled to remove CO_2 and then cooled before use.

C. PROCEDURES

(i) Preparation of Samples

Reaction mixtures were prepared by weighing the appropriate amounts of vacuum-degassed and N_2-flushed monomer and solvent (if necessary) into a flask containing the appropriate amount of initiator. A weighed amount of the solution was then transferred by pipette to a reaction tube which had just been flushed with O_2-free nitrogen. In

experiments carried out under high pressure, the P.T.F.E. tubes described above were used. In experiments carried out at atmospheric pressure, 5 and 10 ml. glass ampoules, which were flushed with N_2 and sealed after filling, were used. Polymerizations at one atmosphere were carried out in a constant temperature oil bath.

Although the nature of experiments carried out under pressure makes extreme purification procedures unfeasible, for comparison, a few of the atmospheric pressure experiments were prepared using the vacuum filling technique.

The operation of the high pressure equipment has been described before[130]. The length of the reaction time was usually chosen so as to give an estimated 5 - 10% conversion. With experience, the time required at given concentrations and pressure could be predicted with reasonable accuracy.

(ii) Collection of Polymer

At the end of an experiment the reaction tube was removed from the pressure vessel (or oil bath if the experiment was carried out at atmospheric pressure), cleaned and opened. The polymer was precipitated by pouring the solution into cold methanol (for experiments using acrylic anhydride and diallyl cyanamide, dry ethyl ether was used in place of methanol).

The polymer was collected by filtration in a weighed sintered-glass crucible and dried in vacuo at 30°C to a constant weight. In cases where gelation had occurred the monomer and solvent were leached out of the gel by allowing it to remain in the precipitant for 2 days before filtration.

(iii) Experimental Parameters

The percentage conversion of monomer to polymer was calculated from the following formula:

$$\% \text{ Conv.} = \frac{w}{m} \times 100 \qquad (6\text{-}1)$$

where w represents the weight of polymer obtained in an experiment, and m represents the weight of monomer initially present in that experiment. The weight of solvent incorporated into the polymer is neglected. This is a reasonable assumption for all normal solvents.

The rate of polymerization in moles/litre/second is calculated from:

$$R_p = \frac{\% \text{ Conv.} \times [M]}{t \times 100} \qquad (6\text{-}2)$$

where t is the duration of the experiment, expressed in seconds.

Concentrations are expressed as the number of moles of a compound in a reaction mixture over the total volume of that reaction mixture at 20°C. Expansion on heating, volume contraction on mixing, and compressibility effects are neglected in calculating the volume. Initiator concentrations are either expressed in moles/l. or as a molar percentage of the experimental monomer concentration.

The solvent concentration [S] may be related to the monomer concentration, assuming the additive property of specific volumes on mixing, by the following equation:

$$[S] = (1/10^3 V_s) - (V_m/V_s)[M] \qquad (6\text{-}3)$$

where V_m and V_s are the specific volumes of monomer and solvent, respectively.

The value of the gas constant (R) is 1.98 ca./mole^{o}K in the calculation of activation energies, and 82.06 cc-atm./mole^{o}K in the calculation of volumes of activation.

D. DETERMINATION OF MOLECULAR WEIGHT

The molecular weights of the various polymers were determined using different methods.

(i) Osmometry

The molecular weights of poly(allyl methacrylate) samples were determined by osmometry. Using this technique the number average molecular weight is given by:

$$\bar{M}_n = \frac{RT}{(\pi/c)_o} \qquad (6\text{-}4)$$

where R is the gas constant (97.8 psi-dl./mole^{o}K).

T is the absolute temperature (^{o}K).

π is the difference in osmotic pressure between the polymer solution and the pure solvent (psi).

c is the polymer concentration (gms./decalitre).

$(\pi/c)_o$ is the value of π/c obtained when the straight line obtained by plotting values of π/c vs. c is extrapolated to zero concentration (psi-dl./gm.).

Osmometric pressures were calculated in toluene solution at 25^{o}C. A Mechrolab Model 502 Membrane Osmometer was used with a cellulose derivative type 0-8 membrane (supplied by Schleicher & Schnell Ltd.).

(ii) Viscometry

The molecular weights of poly(acrylic acid) samples obtained by the hydrolysis of poly(acrylic anhydride) samples were found by viscometry. In this technique the correlation between the viscosity average molecular weight, $(\overline{M}_v)$, and the intrinsic viscosity, $[\eta]$ is given by the Mark-Houwink-Sakurada equation:

$$[\eta] = K(\overline{M}_v)^{\alpha} \qquad (6\text{-}5)$$

where K and α are constants for a given polymer-solvent system at a given temperature. The intrinsic viscosity may be obtained from values of the specific viscosity η_{sp} where:

$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} \qquad (6\text{-}6)$$

η is the viscosity of the polymer solution and η_o is the viscosity of the pure solvent. The intrinsic viscosity $[\eta]$ is the value of η_{sp}/c obtained when the straight line obtained by plotting values of η_{sp}/c vs. c is extrapolated to zero concentration.

For poly(acrylic anhydride) the Mark-Houwink-Sakurda equation used is a form of that used to determine molecular weights for poly(acrylic acid)[68]:

$$[\eta] = 4.27 \times 10^{-3}(\overline{DP})^{0.69} \qquad (6\text{-}7)$$

Here viscosities are determined in 2N NaOH solution at 30°C. It is assumed that, in a strong NaOH solution, poly(acrylic anhydride) is completely hydrolized to poly(acrylic acid). Viscosities were obtained using an Ubbelode viscometer suspended in a constant temperature water bath.

(iii) Cryoscopy

The relatively low (< 2000) molecular weight of poly(diallyl cyanamide) samples were determined by cryoscopy. Using this technique the molecular weight is given by:

$$\overline{M}_n = \frac{1000K_f w}{\Delta T_f W} \qquad (6\text{-}8)$$

where w is the weight of polymer (gms.).

W is the weight of solvent (gms.).

K_f is the molal freezing point depression constant.

The freezing point depression ΔT_f is given by:

$$\Delta T_f = T_s - T_f \qquad (6\text{-}9)$$

where T_s is the freezing point of the pure solvent, and T_f is the freezing point of the polymer-solvent solution.

The values of the molecular weight for poly(diallyl cyanamide) were obtained using liquid phenol as a solvent. For phenol, the value[136] of K_f is 7.4. Water at 35 - 40°C was used in the outer bath of the cryoscopic equipment and ΔT_f was determined using a Beckmann thermometer.

(iv) Melting Point

The molecular weights of polyindene samples were obtained using a curve determined by Whitby and Katz[137] which relates the molecular weight of polyindene to its melting point. Melting points were obtained by sealing a small sample of the polymer in a glass tube and observing the approximate temperature of melting using a Gallenkamp Melting Point Determination apparatus.

The determinations of molecular weight by osmometry, viscometry and cryoscopy are standard techniques and the equipment used, derivation of equations and limits of applicability of these methods are discussed elsewhere[138,139].

E. INFRA-RED SPECTROSCOPY

Infra-red absorption spectra were obtained for monomers and polymers using a Hilgar H-800 spectrometer with sodium chloride prisms. Monomer spectra were obtained using a sample of purified monomer placed in a liquid cell. Polymer spectra were obtained either from a polymer film deposited on a NaCl prism or from a Nujol mull.

F. BROMOMETRY

The mole fraction of residual double bonds was usually determined by bromometry in a method similar to that outlined by Siggia[140]. A 0.1N bromide-bromate solution was used as a brominating agent with freshly prepared 0.2N $HgSO_4$ solution added to increase the rate of bromine addition to double bonds. In a typical experiment 20 mls. of bromide-bromate solution (50% excess), 5 mls. of 20% H_2SO_4 solution, 20 mls. of freshly prepared $HgSO_4$ solution, 60 mg. of polymer, 40 mls. of CCl_4 and 25 mls. of glacial acetic acid were placed in a flask which was then evacuated, covered and stirred in darkness. For water soluble polymers the acetic acid is omitted.

After 30 minutes the seal was broken and 15 mls. of 2N NaCl solution and 15 mls. of 20% KI solution were added. The resulting iodine was then titrated with standardized 0.1N $Na_2S_2O_3$, using starch indicator.

The reactions are as follows:

1) Bromine Production

$$K_2BrO_3 + 5KBr + 3H_2SO_4 \longrightarrow 3K_2SO_4 + 3H_2O + 3Br_2$$

2) Bromination of Residual Double Bonds

$$Br_2 + (CH_2{=}CH)\sim \longrightarrow (CH_2Br\text{-}CHBr)\sim$$

3) Iodine Titration

$$Br_2 + 2NaI \longrightarrow 2NaBr + I_2$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$$

A 'blank' determination was first conducted to obtain the volume (V_b) of sodium thiosulfate solution (of normality N_t) required to titrate the iodine when no polymer was present. When the volume (V_s) of the $Na_2S_2O_3$ required to titrate the iodine in a determination, where w grams of polymer was present, was subtracted from V_b, it gave a measure of the amount of bromine which was taken up in brominating the residual double bonds of the polymer.

The mole fraction of residual double bonds (see section IV-E) may be easily derived as:

$$f_L = \frac{M}{2w}(V_b - V_s)N_t \times 10^{-3} \qquad (6\text{-}10)$$

where M is the repeating unit (monomer) molecular weight.

In a few experiments where a relatively large amount of polymer was available, (i.e. the polymerization of acrylic anhydride in toluene solution to ~ 100% conversion) the amount of bromine used to brominate the residual double bonds of the polymer was determined using the method of Polgar and Jungnickel[141].

PART II

THE SCOPE OF THIS WORK

The effect of pressure on cyclopolymerization has not yet been examined. This thesis examines the free radical cyclopolymerizations of several non-conjugated dienes at atmospheric pressure and at higher pressures. Where experimental results for the polymerization of one of the monomers have been published in the literature, the reported experiments are repeated under similar conditions, if suitable, and expanded on, if necessary. If kinetic results at atmospheric pressure are lacking, then these are determined. If feasible, the results at atmospheric pressure are then compared with the results obtained at higher pressures and the effect of high pressure on the cyclopolymerization reaction is determined.

The monomers examined are the symmetrical 1,6 dienes diallyl ether, acrylic anhydride, diallylamine hydrochloride, and diallyl cyanamide; the unsymmetrical 1,6 diene allyl methacrylate, the unsymmetrical 1,5 diene vinyl methacrylate; and the symmetrical 1,4 diene vinyl sulfone. In addition, the effect of pressure on a few styrene polymerizations in solution is obtained and the bulk polymerization of indene is examined at atmospheric pressure and at higher pressures. Indene was chosen because accurate kinetic data on the effect of pressure on this monomer was lacking, and because it serves as a useful example of monovinyl polymerization for comparison with the 'divinyl' polymerization of non-conjugated dienes. Also it produces polymers of low $\overline{DP}$, as do the diallyl monomers.

Particular attention is paid to the effect of pressure on overall rate effects, cyclization, activation energies and volumes of activation. Where possible, the results are compared with the theoretical expressions derived in the previous part.

SECTION VII

RESULTS AND DISCUSSION

A. DIALLYL ETHER

Various attempts were made to homopolymerize dially ether (I) in bulk and in solution by free radical methods at temperatures from 30°C to 100°C and pressures from 1 to 10,000 atmospheres. All were unsuccessful.

$$CH_2=CH-CH_2-O-CH_2-CH=CH_2$$

I

The following table lists a few of the experiments in bulk.

TABLE 7-1

Diallyl Ether

Experiments Attempting Bulk Polymerization by Free Radical Methods

Experiment	Time (hrs)	Pressure (atm.)	T (°C)	Initiator Type	Initiator % Conc.
DE1	44.8	1	80	TBHP	2.0
DE2	50.0	1	60	Bz_2O_2	2.0
DE3	20.4	3000	60	Bz_2O_2	2.0
DE4	48.0	10,000	60	AIBN	2.0
DE5	44.4	10,000	60	Bz_2O_2	1.0
DE6	43.7	10,000	80	TBHP	1.0
DE7	504.0	1	30	AIBN	2.0

It is concluded, therefore, that the free radical homopolymerization of diallyl ether is negligible in the range of experimental conditions studied. This is probably due to the resonance stabilization of the allyl groups.

It was noted, however, that when a few drops of boron trifluoride diethyl etherate were added to the liquid monomer (at room temperature and atmospheric pressure) an extremely vigorous cationic polymerization ensued. The resulting polymer was cross-linked and insoluble in any solvent. It has been reported[142] that diallyl ether (DE) will cyclo-copolymerize with maleic anhydride (MA), another monomer which will not homopolymerize by free radical methods. The resulting polymer was said to be 2:1 (MA:DE). To test this claim 1 gm. of maleic anhydride was dissolved in 8 mls. of pure diallyl ether with 1.0% Bz_2O_2 initiator. This mixture was polymerized at 60°C and 1 atm. pressure for about 20 hours, and a white polymer resulted. A comparison of the elemental analyses for the polymer and the calculated composition for 2:1 and 1:1 copolymers is given in the following table.

TABLE 7-2

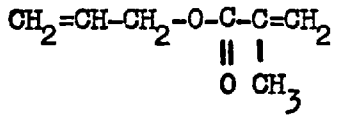
Copolymerization of Diallyl Ether and Maleic Anhydride at 60°C					
	Percentage Composition				
Element	Experimental			Calculated	
	A	B	C	2:1	1:1
Carbon	58.6	58.5	54.5	57.1	60.7
Hydrogen	6.8	7.0	6.3	4.8	6.1
Oxygen	-	34.4	34.8	38.1	33.2
Monomers - Diallyl ether: C = 72.4%, H = 10.6%, O = 17.0% Maleic anhydride: C = 49.0%, H = 2.0%, O = 49.0%					

These results seem to indicate that more diallyl ether is involved in the copolymer than was claimed. Copolymerization of diallyl ether and allyl methacrylate were also attempted (unsuccessfully).

As both cationic polymerization and copolymerization were outside the scope of this work, no attempt was made to follow up these results. Diallyl ether was, however, found suitable for use as a solvent in which certain free radical cyclopolymerizations could be carried out at relatively high monomer concentrations and this is discussed in the results for the cyclopolymerization of allyl methacrylate.

B. ALLYL METHACRYLATE

Kinetic investigations of the free radical cyclopolymerization of the 1,6 diene allyl methacrylate (II) were carried out in solution at 60°C.



II

The experimental pressure range was 1 - 4000 atm. and Bz_2O_2 was used as the initiator. Polymerization was carried out in various solvents and the range of monomer concentrations was 1.1 to 7.4 moles/litre.

Most previous attempts[90,143,144] to obtain a soluble (i.e. linear and not cross-linked) polymer by the free radical polymerization of allyl methacrylate have not been successful although Trossarelli et al[88] obtained soluble cyclopolymers in benzene solution at 60°C for very low monomer concentrations ([M] < 0.6 moles/l.). D'Alelio and Hoffend[144] obtained soluble polymers in the anionic bulk polymerization of allyl methacrylate at low temperatures but ascribed the formation of linear polymers to the insensitivity of allylic groups to anionic initiation rather than to cyclopolymerization.

Allyl methacrylate was polymerized in bulk and in solution in toluene, benzene, acetone, CCl_4, cyclohexanone, iso-propyl ether, epoxy-propane, dioxan, and diallyl ether ([M] ~ 1.1 moles/l., T = 60°C, P = 1 atm., [In] = 1.0% Bz_2O_2, t ~ 3 hours). With the reactions in bulk and in the solvents toluene, benzene, acetone, iso-propyl ether, and epoxy-propane, gelation occurred at very low conversions. The resulting polymers were insoluble in the common organic solvents, in the monomer,

and in dimethyl sulfoxide. In contrast, soluble polymers were formed with the reactions in dioxan, cyclohexanone, CCl_4 and diallyl ether solutions.

The following table gives results for the polymerization of allyl methacrylate at 60°C and atmospheric pressure in the latter four solvents at a fixed monomer concentration.

TABLE 7-3

Polymerization of Allyl Methacrylate at 60°C and 1.1 moles/l.		
Experiment	Reaction Time (hrs)	% Conversion
a) Solvent: dioxan, [In] = 1.1×10^{-3} moles/l.		
AM1	0.5	5.0
AM2	1.0	9.3
AM3	2.0	20.8
AM4	3.2	28.2
AM5	4.0	32.3
b) Solvent: dioxan, [In] = 1.4×10^{-2} moles/l.		
AM6	0.3	6.6
AM7	0.5	13.1
AM8	1.0	22.4
AM9	2.0	38.4
AM10	2.8	46.6
AM11	4.0	58.9
AM12	4.0	58.1 †
AM13	5.0	66.6
c) Solvent: diallyl ether, [In] = 1.1×10^{-2} moles/l.		
AM14	1.5	13.7
AM15	3.3	26.4
AM16	4.5	33.4
AM17	6.3	43.5
AM18	7.0	49.0

Table 7-3 continued

d) Solvent: carbon tetrachloride, [In] = 1.1×10^{-2} moles/l.			
AM19	3.0	3.1	
AM20	4.0	4.8	
AM21	4.3	5.6	†
AM22	5.0	9.8	
AM23	5.1	14.2	†
AM24	5.3	19.2	
AM25	6.0	23.6	
AM26	6.5	26.7	
AM27	7.3	32.7	
AM28	7.8	38.9	
Gelation occurs at ~ 40% conversion			
e) Solvent: cyclohexanone, [In] = 1.1×10^{-2} moles/l.			
AM29	2.0	3.9	
AM30	3.0	6.1	
AM31	4.0	13.6	
Gelation occurs at ~ 15% conversion			

† vacuum-filling technique used

Figure 4 shows the results for the polymerization of allyl methacrylate at 60°C and atmospheric pressure when [M] = 1.1 moles/l. with 1.0% Bz_2O_2 in four solvents.

Cyclohexanone and CCl_4 are seen to be unsuitable solvents for carrying out kinetic investigations in, because of the occurrence of autoacceleration and the relatively low gel points. Normal conversion-time curves (i.e. no autoacceleration) were found for polymerizations in dioxan and diallyl ether solutions, although for polymerization in dioxan solution above a monomer concentration of 2.2 moles/l., gelation began to occur at relatively low conversions. Table 7-4 gives results obtained for the polymerization of allyl methacrylate in dioxan and diallyl ether solutions at high pressure.

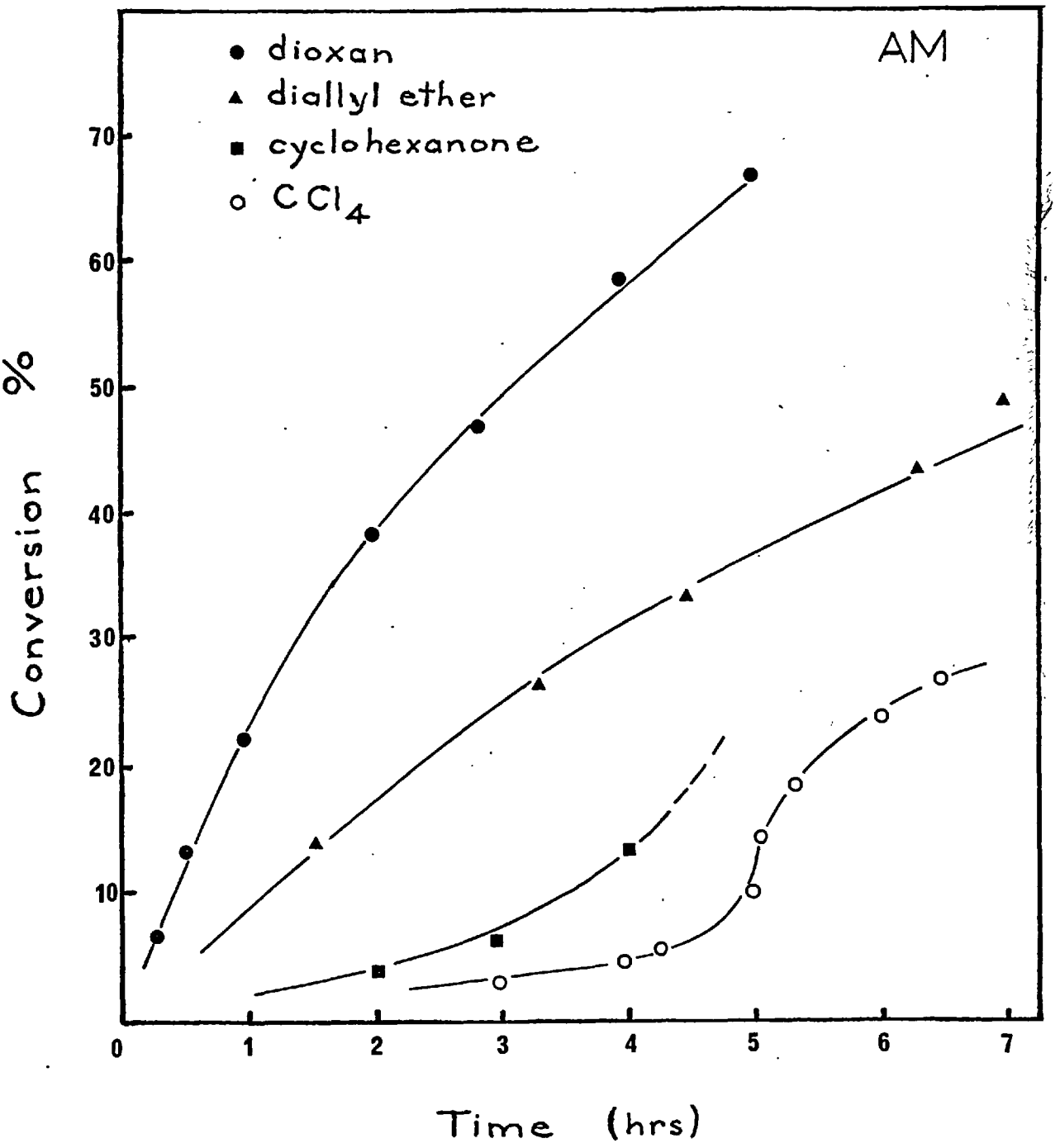


FIG. 4: Polymerization at 60 °C in various solvents

TABLE 7-4

Solution Polymerization of Allyl Methacrylate under Pressure†			
	Experiment	Reaction Time (hrs.)	% Conversion
a)	Solvent: dioxan, [M] = 1.1 moles/l., P = 2000 atm.		
	AM32	0.5	40.8
	AM33	0.6	44.5 gel
	AM34	1.0	66.5 "
b)	Solvent: dioxan, [M] = 1.1 moles/l., P = 2000 atm.		
	AM35	0.5	15.5
	AM36	0.5	19.0
	AM37	0.8	22.0
	AM38	1.0	31.1
	AM39	1.1	35.1 gel
	AM40	1.5	69.2 "
	AM41	2.0	~ 74.0 "
c)	Solvent: diallyl ether, [M] = 2.2 moles/l., P = 3000 atm.		
	AM42	0.5	15.7
	AM43	1.0	46.2
	AM44	1.5	59.0
	AM45	2.0	75.5 gel
	AM46	2.5	~ 97.0 "

† T = 60°C, (a) and (c) are at 1.0% Bz_2O_2, and (b) at 0.1%

From these results it may be seen that autoacceleration occurs with the polymerizations in dioxan at 2000 atm.. In contrast, the conversion-time curve is linear to above 60% conversion at double the monomer concentration, and $1\frac{1}{2}$ times the pressure with the experiments in diallyl ether solution. Of the solvents examined, diallyl ether is by far the best for kinetic investigations of the polymerization of allyl methacrylate.

This is, of course, providing that no copolymerization between diallyl ether and allyl methacrylate occurs. Table 7-5 gives the results for elemental analyses of polymers formed at various conditions in the polymerization of allyl methacrylate in diallyl ether solution.

TABLE 7-5

Allyl Methacrylate

Elemental Analyses of Poly(allyl methacrylate) Samples from Polymerization in Diallyl Ether Solution†

Experiment	[M] (moles/l.)	Pressure (atm.)	Time (hrs.)	% Conv.
AM46	2.2	3000	2.5	97 gel
AM47	3.0	3000	0.8	98 "
AM48	2.2	1	4.9	48
AM49	3.0	1	4.9	55 gel
AM50	3.6	1	4.9	69 "

	% Carbon	% Hydrogen	% Oxygen
AM46	66.6	8.1	25.5
AM47	66.8	8.7	25.8
AM48	66.9	8.0	23.8
AM49	65.3	8.2	25.9
AM50	-	-	25.3
monomer(calc.)	66.5	8.2	25.3

† 1.0% Bz_2O_2, 60°C

These results indicate that under the reaction conditions used, the amount of copolymerization of diallyl ether with the monomer is negligible and that it may be assumed that allyl methacrylate homopolymerizes in this solvent. All of the following polymerization experiments with allyl methacrylate were carried out in diallyl ether solution unless otherwise noted.

The following table lists the conversion-time results for the polymerization of allyl methacrylate at monomer concentrations varying from 2.2 to 6.1 moles/l. (results for [M] = 1.1 moles/l. were given in Table 7-3).

TABLE 7-6

Allyl Methacrylate Polymerization of Allyl Methacrylate at 60°C and 1 atm.†			
Experiment	[M] (moles/l.)	Time (hrs.)	% Conversion
AM51	2.2	0.5	8.6
AM52		1.0	13.8
AM53		2.8	34.5
AM54		3.0	33.8
AM55		4.3	46.8
AM48		4.9	48.2
AM56		5.2	54.4
AM57	3.0	0.8	14.3
AM58		2.0	27.4
AM59		3.0	38.7
AM49		4.9	55.1
AM60	3.6	1.3	22.3
AM61		2.0	29.8
AM50		4.9	68.7 gel
AM62	6.1	0.3	10.3

† 1.0% Bz_2O_2

All of the conversion-time curves are linear below 20% conversion and there is no evidence of autoacceleration.

The polymers in these, and in all of the following cases, were precipitated as white solids (unless gels). Polymer which was dissolved

in toluene was deposited as a transparent film when the solvent was evaporated. Polymer samples which were exposed to air for more than a short time gradually became insoluble. D'Alelio and Hoffend[144] found that a similar situation occurred for poly(allyl methacrylate) formed in the anionic polymerization of this monomer, and attributed the result to the cross-linking of polymer chains via pendant allyl groups.

Molecular weight results show that considerable chain branching occurs at higher conversions, as may be seen from the following table.

TABLE 7-7

Allyl Methacrylate

Variation of Molecular Weight with Conversion

Experiment	% Conv.	$\overline{M}_n$
AM51	8.6	90,000
AM52	13.8	90,700
AM53	34.5	111,930
AM56	54.4	303,390

[M] = 2.2 moles/l., 1.0% Bz_2O_2

The molecular weight of the polymer from experiment AM32 (in dioxan solution at 2000 atm., 40.8% conversion - just below the gel point) was found to be 592,930.

That the polymer formed was indeed a cyclopolymer was shown by examination of the infra-red spectra of monomer and polymer. Typical spectra are given in Figure 5 for the purified monomer (liquid cell) and the polymer (from AM51 - evaporated from toluene solution as a film on the NaCl prism) in the range 1800 to 1100 $cm.^{-1}$.

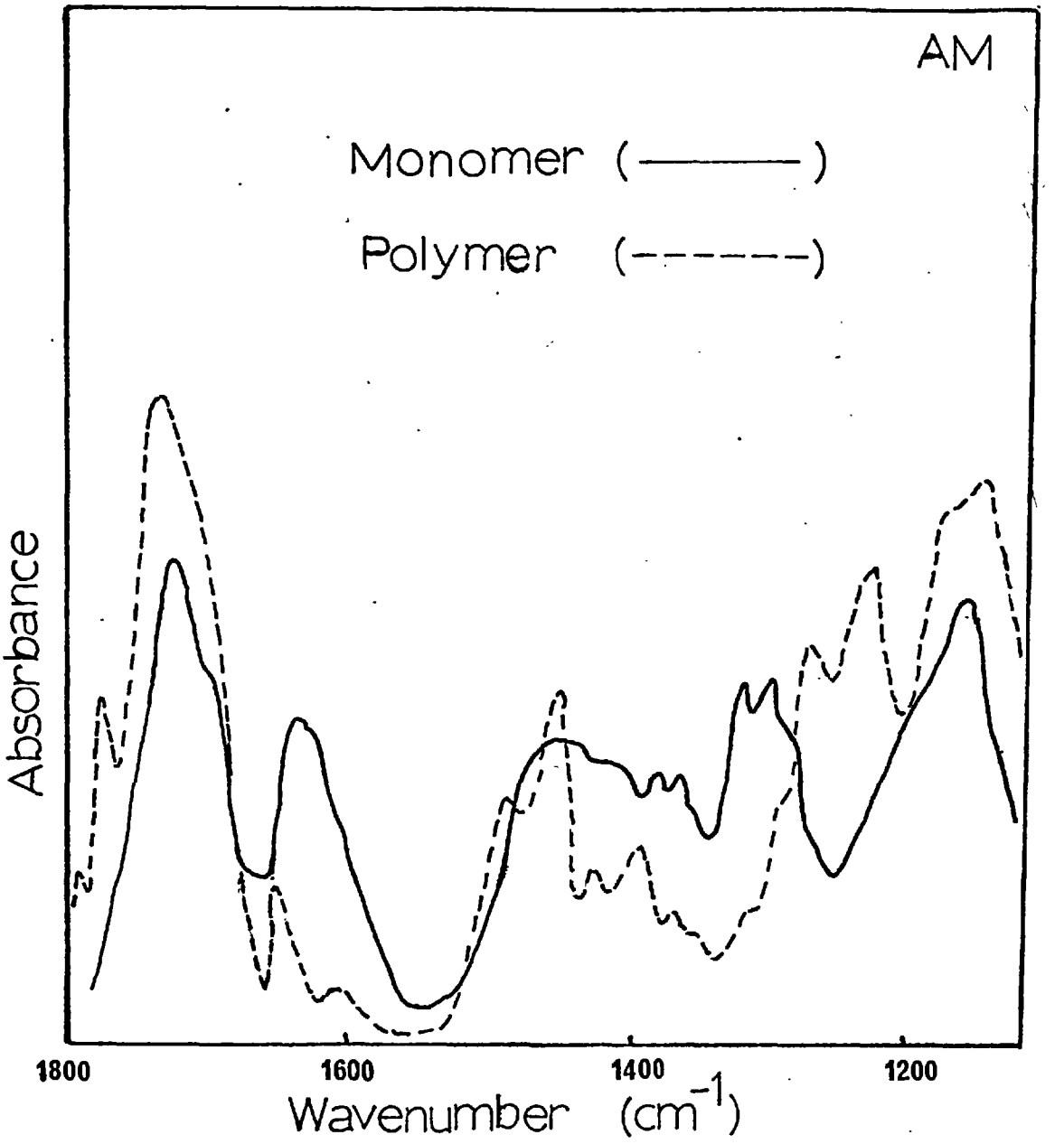
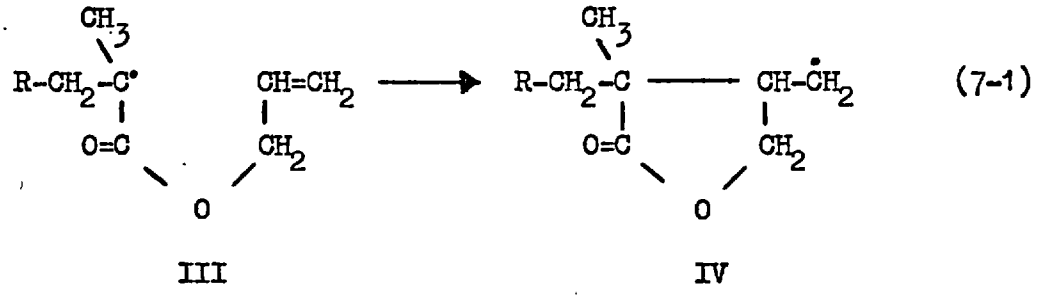


FIG. 5: Infra-red Spectra

In the spectrum of the monomer the carbonyl stretch frequency absorption exhibits a peak at 1725 $cm.^{-1}$ but in the polymer this peak is broadened and shifted towards 1740 $cm.^{-1}$. This indicates[145] the presence of δ-lactone units (six-membered rings) in the polymer.

The spectrum of the polymer also shows a small absorption at 1775 $cm.^{-1}$. This attributed to the presence of a small proportion of γ-lactone units (five-membered rings) which may be formed as follows:



III IV (7-1)

for cyclization via the methacrylyl group.

The presence of two types of lactone ring in the polymer is supported by the absorptions at 1230 and 1275 $cm.^{-1}$. These are probably due to the -CO- stretching frequencies in the δ- and γ-lactone rings. The presence of both hexatomic and pentatomic rings has also been reported for the polymer formed in the cyclopolymerization of acrylic anhydride at 60°C[89].

Using freeze-dried polymer samples which were immediately dissolved in toluene, the intrinsic viscosity-molecular weight relationship was determined by comparing intrinsic viscosity results at 25°C with the osmometrically determined molecular weights for the same samples. These are given in Table 7-8.

TABLE 7-8

Allyl Methacrylate Intrinsic Viscosity-Molecular Weight Determination for poly(allyl methacrylate)		
Experiment	$[\eta]$	$10^{-4}\bar{M}_n$
AM63	0.365	7.77
AM51	0.402	9.00
AM64	0.520	13.93
AM65	0.760	24.87

The Mark-Houwink-Sakurada equation for poly(allyl methacrylate) in toluene at 25°C was determined to be:

$$[\eta] = 2.4 \times 10^{-4}(\bar{M}_v)^{0.65} \qquad (7\text{-}2)$$

from the above results.

The following table gives the variation in the rate of polymerization with monomer concentration for the polymerization of allyl methacrylate in diallyl ether solution at atmospheric pressure.

TABLE 7-9

Allyl Methacrylate Variation of Rate with Monomer Concentration at 1 atm.†			
Experiment	[M] (moles/l.)	$10^5 R_p$ (moles/l./sec.)	$10^5 R_p/[M]$ ($sec.^{-1}$)
AM14	1.1	2.77	2.53
AM66	1.8	5.76	3.22
AM51	2.2	8.49	3.82
AM67	3.3	17.27	5.29
AM60	3.6	17.69	4.95
AM68	4.4	28.22	6.48
AM62	6.1	58.01	9.46

† 60°C, 1.0% Bz_2O_2

The logarithmic plot of R_p vs. [M] is given in Figure 6 and the slope of this linear plot is 1.64. Plots of R_p vs. [M] (A) and $R_p/[M]$ vs. [M] (B) are given in Figure 7. The former is a curve while the latter is a straight line. A plot of $R_p/[M]^{\frac{1}{2}}$ vs. [M] (not shown) is also not a straight line. The slope and intercept of the linear $R_p/[M]$ vs. [M] plot are 1.23×10^{-5} and 1.15×10^{-5}, respectively. Thus, the slope to intercept ratio is 1.07 and with the unsaturation results (to follow) this strongly suggests that termination is solely between cyclized radicals.

The variation of rate of polymerization with initiator concentration at 1 atm. and constant monomer concentration is given in the following table.

TABLE 7-10

Allyl Methacrylate

Variation of Rate with Initiator Concentration at 1 atm.†

Experiment	10^3[In] (moles/l.)	$10^5 R_p$ (moles/l./sec.)
AM69	1.03	1.10
AM63	2.23	1.77
AM70	5.80	3.04
AM71	16.80	5.16
AM51	27.20	8.49
AM72	45.20	12.40

† Solvent: diallyl ether, 60°C, [M] = 2.2 moles/l.

The logarithmic plot of R_p vs. [In] is given in Figure 8. The slope of this plot is 0.69.

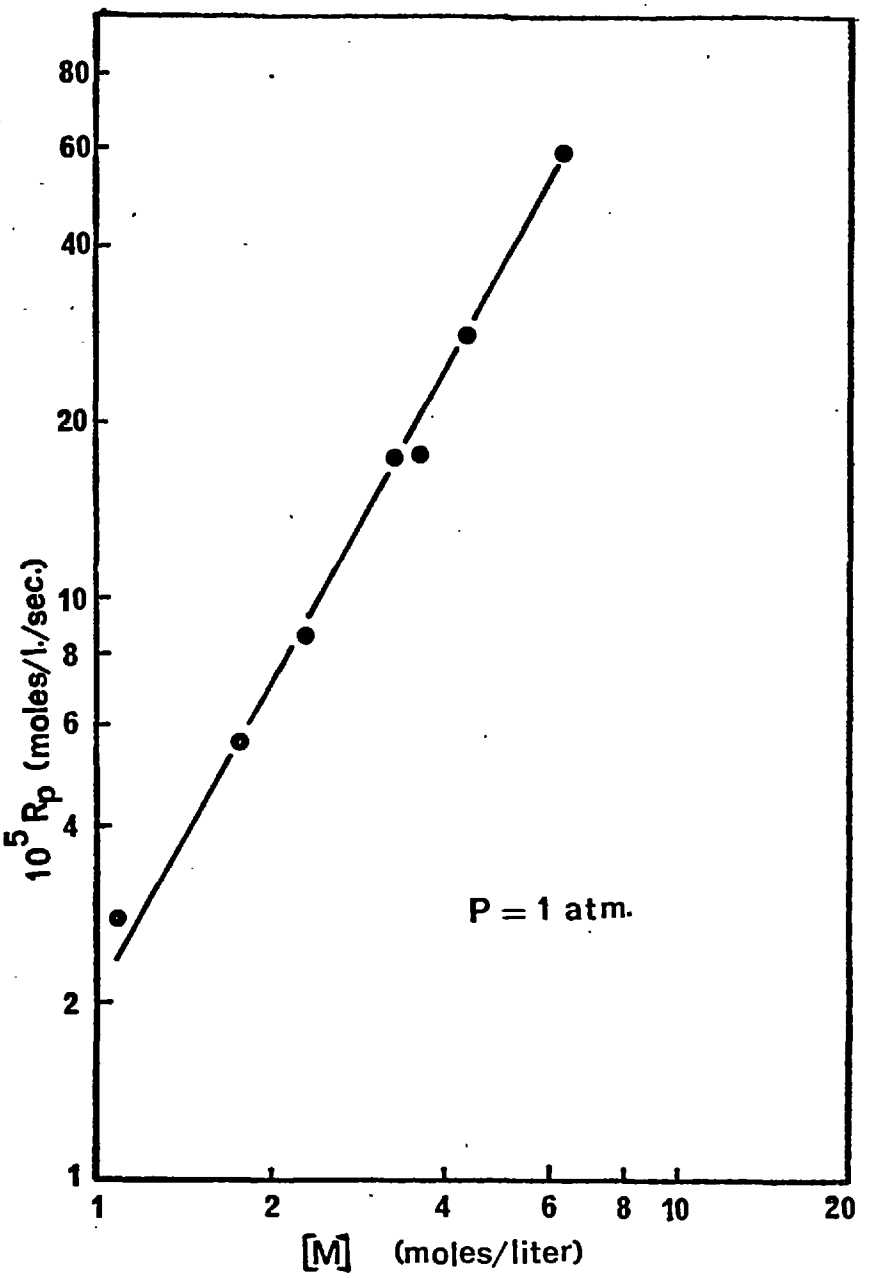


Figure 6 : Polym. of Allyl Methacrylate
Rate vs Monomer Concentration

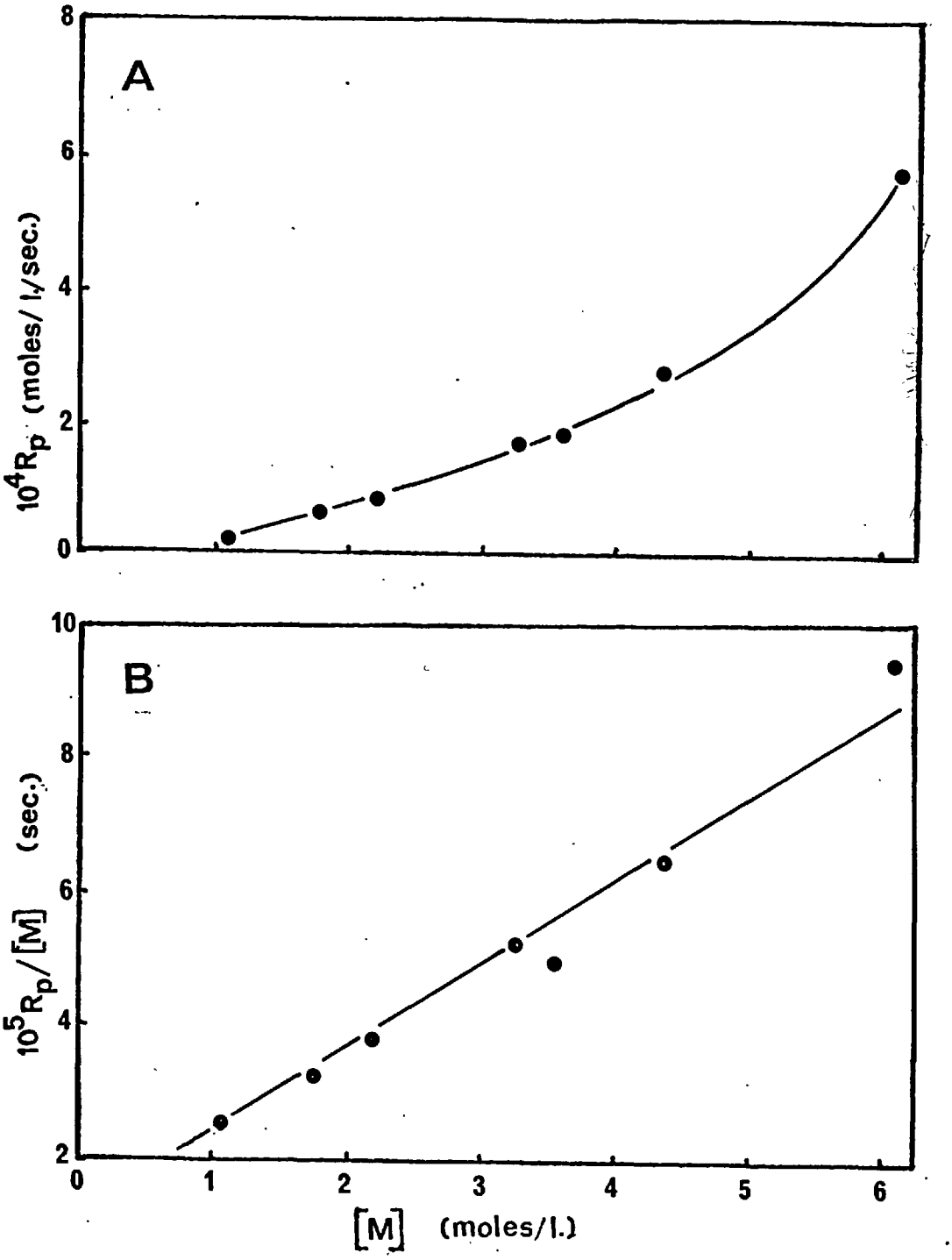


Figure 7: Polym. of Allyl Methacrylate
Rate vs monomer concentration

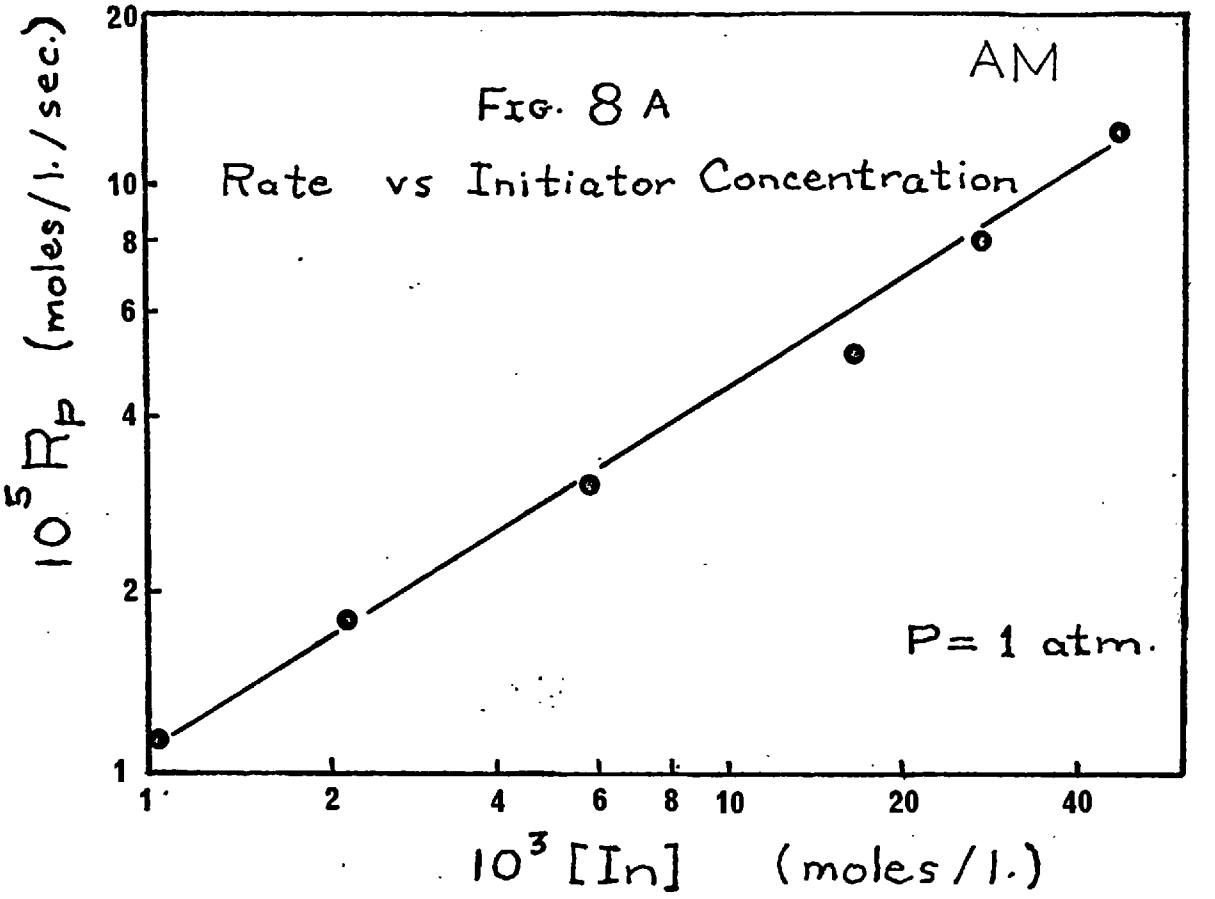


FIG. 8 A

Rate vs Initiator Concentration

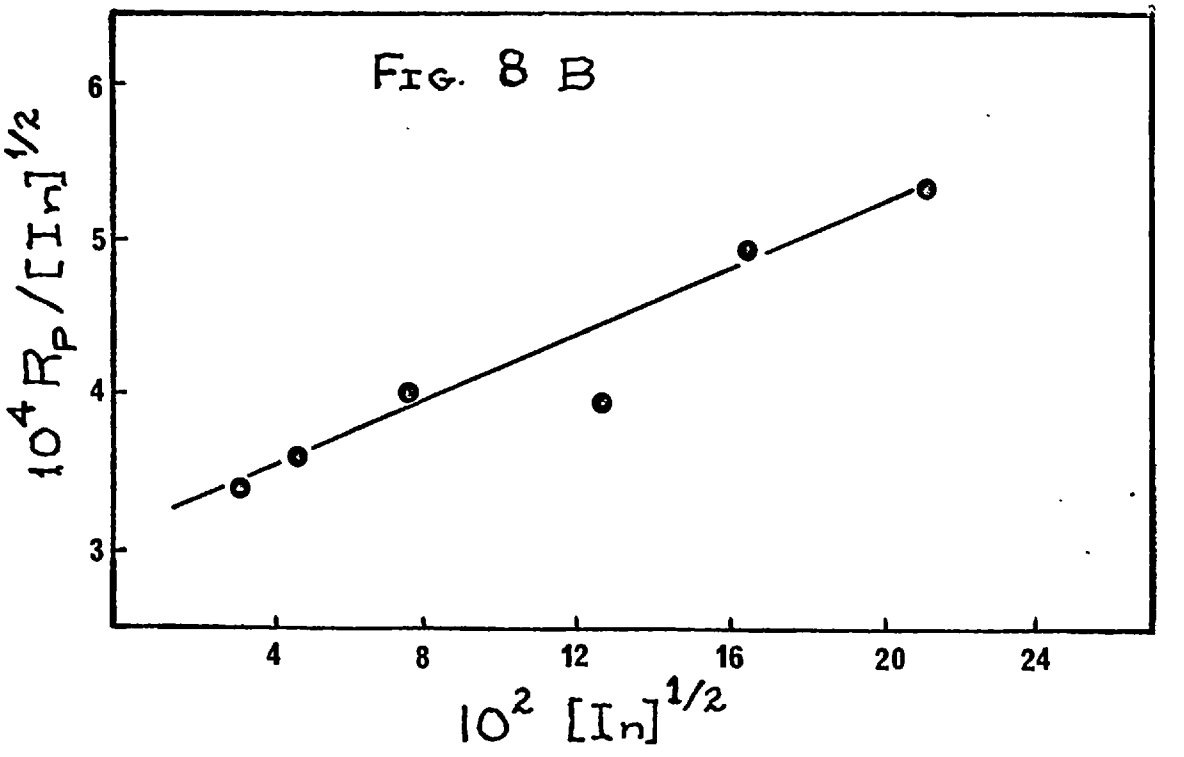


FIG. 8 B

Therefore, the overall rate of polymerization in diallyl ether solution at atmospheric pressure may be represented:

$$R_p = K_1[In]^{0.69}[M]^{1.64} \qquad (7\text{-}3)$$

For comparison, the variation of rate with initiator concentration in dioxan solution is given in the following table.

TABLE 7-11

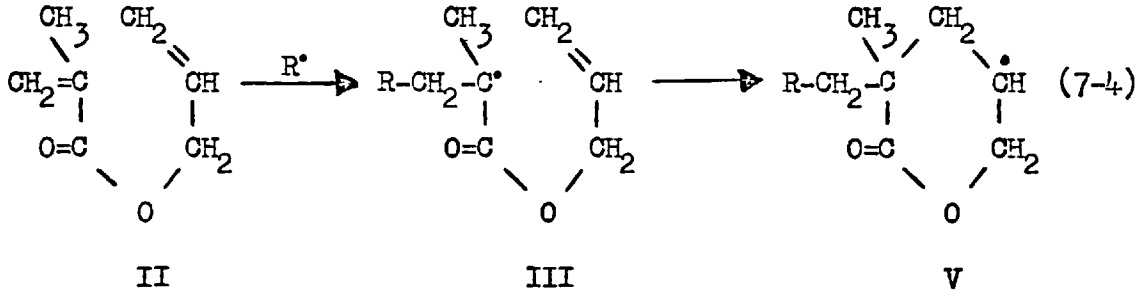
Allyl Methacrylate Variation of Rate with Initiator Concentration at 1 atm.†		
Experiment	$10^3[In]$ (moles/l.)	$10^5 R_p$ (moles/l./sec.)
AM1	1.15	1.51
AM73	5.65	4.19
AM74	8.78	5.01
AM6	11.10	6.02

† Solvent : dioxan, [M] = 1.1 moles/l., 60°C

In this case a logarithmic plot of R_p vs. [In] is also linear and has a slope of 0.65.

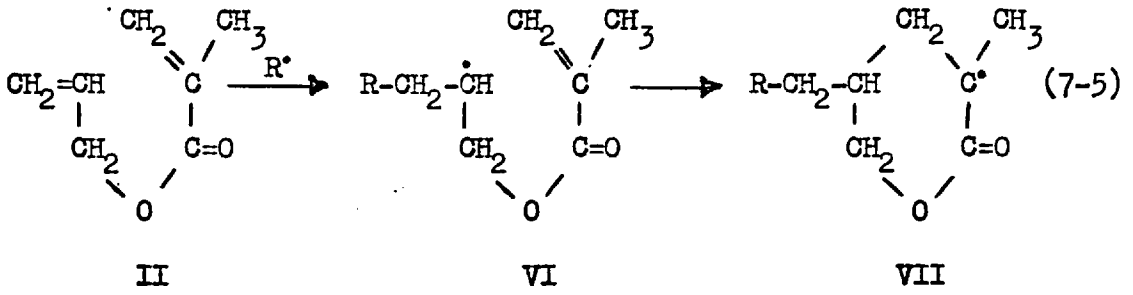
The two possible modes of cyclopolymerization to hexatomic rings for the unsymmetrical diene, allyl methacrylate, are as follows:

(a) Via the Methacrylyl Group



(7-4)

(b) Via the Allyl Group



II VI VII

Residual unsaturated groups may be left pendant on the polymer chains by the addition of monomer to either of the noncyclized radicals (structures III and VI).

Since the methacrylyl groups are known[16,88,90,143] to be much more reactive than allyl groups, it is probable that cyclopolymerization reactions via the allyl groups (equation 7-5) are relatively uncommon and that the polymerization of this monomer proceeds primarily via the methacrylyl groups (equations 7-1 and 7-4). The less reactive allyl groups may become involved in the cyclization reaction via the methacrylyl groups or they may persist as unsaturated groups pendant from polymer chains, but otherwise they should play no important role in the cyclopolymerization process.

Cohen et al[143] have shown that, for the pre-polymer formed in the light-induced bulk polymerization of allyl methacrylate, the pendant groups are, within the limits of experimental error, all allyl groups. D'Alelio and Hoffend[144] have reported that, for the anionic polymerizations of allyl acrylate and allyl methacrylate, polymerization took place substantially through the (meth)acrylyl groups. A similar result was found by Solomon et al[146] for the bulk polymerizations of the acrylic and methacrylic esters of 2-allyl-phenol at 60 - 80°C using

AIBN and Bz_2O_2 initiators. Thus, the unsymmetrical diene, allyl methacrylate, may be regarded as 'pseudo-symmetric' and the kinetics of polymerization should be given by the theoretical expressions derived for simple cyclopolymerization.

The pendant allyl groups may remain unreacted, be initiated and propagate to give chain branches, or engage in DCT reactions. Pendant allyl groups would be expected to cause the eventual cross-linking of the polymer, especially in the solid state, but this effect would be kinetically unimportant in solution at low conversions. If pendant allyl groups engaged in DCT reactions, then cross-linking and gelation might occur relatively early, due to the bimolecular combination of pendant resonance-stabilized allyl radicals on adjacent chains. Since only a minute degree of cross-linking (about one cross-link for four polymer molecules) is required to cause gelation[147] and since the $\overline{DP}$ is large (> 1000), the pendant allyl groups can affect the nature of the polymer even though they are much less reactive than the methacrylyl groups. Such an effect, coupled with the fact that the monomer and most solvents are relatively poor swelling agents for the polymer probably explains the relatively early gel points found for the polymerization of allyl methacrylate in bulk and in most solvents.

The formation of soluble polymers in diallyl ether, dioxan, cyclohexanone and CCl_4 solutions suggests that in these solvents, the resonance-stabilized allyl radicals are preferentially terminated by a process which does not lead to cross-linking. Carbon tetrachloride is an active chain transfer agent in some polymerizations[148,149] and it has been noted[19] that dioxan and ethers can promote the rapid induced decomposition of Bz_2O_2. The allyl groups in the solvent diallyl ether

can also take part in DCT reactions. Radical-solvent and radical-initiator reactions will produce small, rapidly diffusing radicals which would be expected to react with pendant resonance-stabilized allyl radicals much more rapidly than the latter can combine mutually. In this manner, it is possible to obtain soluble cyclopolymers from allyl methacrylate at monomer concentrations and conversions not previously achieved.

The variation in the rate of polymerization with pressure is given in the following table for experiments at constant initiator and monomer concentrations.

TABLE 7-12

Allyl Methacrylate

Variation of Rate with Pressure†

Experiment	Pressure (atm.)	$10^5 R_p$ (moles/l./sec.)	R_p/R_1	$\bar{M}_n$
AM63	1	1.77	1.00	77,700
AM64	1000	3.25	1.84	139,320
AM75	1500	3.67	2.07	-
AM76	2000	5.50	3.11	295,450
AM65	3000	9.42	5.31	248,710
AM77	4000	16.84	9.50	-

† [M] = 2.2 moles/l., 1.0% Bz_2O_2, 60°C

Thus, the rate of polymerization increases over five-fold by 3000 atm. while the molecular weight increases four-fold. A plot of $\log R_p$ vs. P is linear with a slope of 2.52×10^{-4} $atm.^{-1}$. Therefore;

$$\Delta V_T^* = -2.52 \times 10^{-4} atm.^{-1} \times 82.06 \text{ cc-atm./}^\circ K \text{ mole} \times 333^\circ K \times 2.3$$

$$= -15.9 \text{ cc/mole.}$$

The plot of $\log(R_p/R_{1\ atm.})$ vs. P is given in Figure 9.

For comparison, styrene was polymerized in benzene solution at varying pressures and the results are given in the following table.

TABLE 7-13

Styrene Variation of Rate with Pressure†		
Experiment	Pressure (atm.)	$10^5 R_p$ (moles/l./sec.)
S1	1	1.26
S2	1000	2.26
S3	2000	4.43
S4	3500	10.03

† Solvent : benzene, [M] = 3.45 moles/l., 0.05% AIBN, 60°C

A plot of log R_p vs. pressure is linear and from its slope it is found that $\Delta V_T^* = -17.8$ cc/mole. For monovinyl monomers, the overall volume of activation is given by equation (5-4):

$$\Delta V_T^* = \tfrac{1}{2}\Delta V_d^* + \Delta V_p^* - \tfrac{1}{2}\Delta V_t^* \qquad (5\text{-}4)$$

Substituting for ΔV_T^* in the above equation and using a value of + 5 cc/mole for ΔV_d^* and a value of - 11 cc/mole for ΔV_p^*, it is seen that the larger value of ΔV_t^* suggested in Section V-B-4 ($\sim$ + 12 cc/mole) seems more appropriate. Therefore, this value shall be used in the estimations of the individual volumes of activation for cyclopolymerization.

The variation of the rate of polymerization with initiator concentration for the solution polymerization of allyl methacrylate at 3000 atm. is given in Table 7-14.

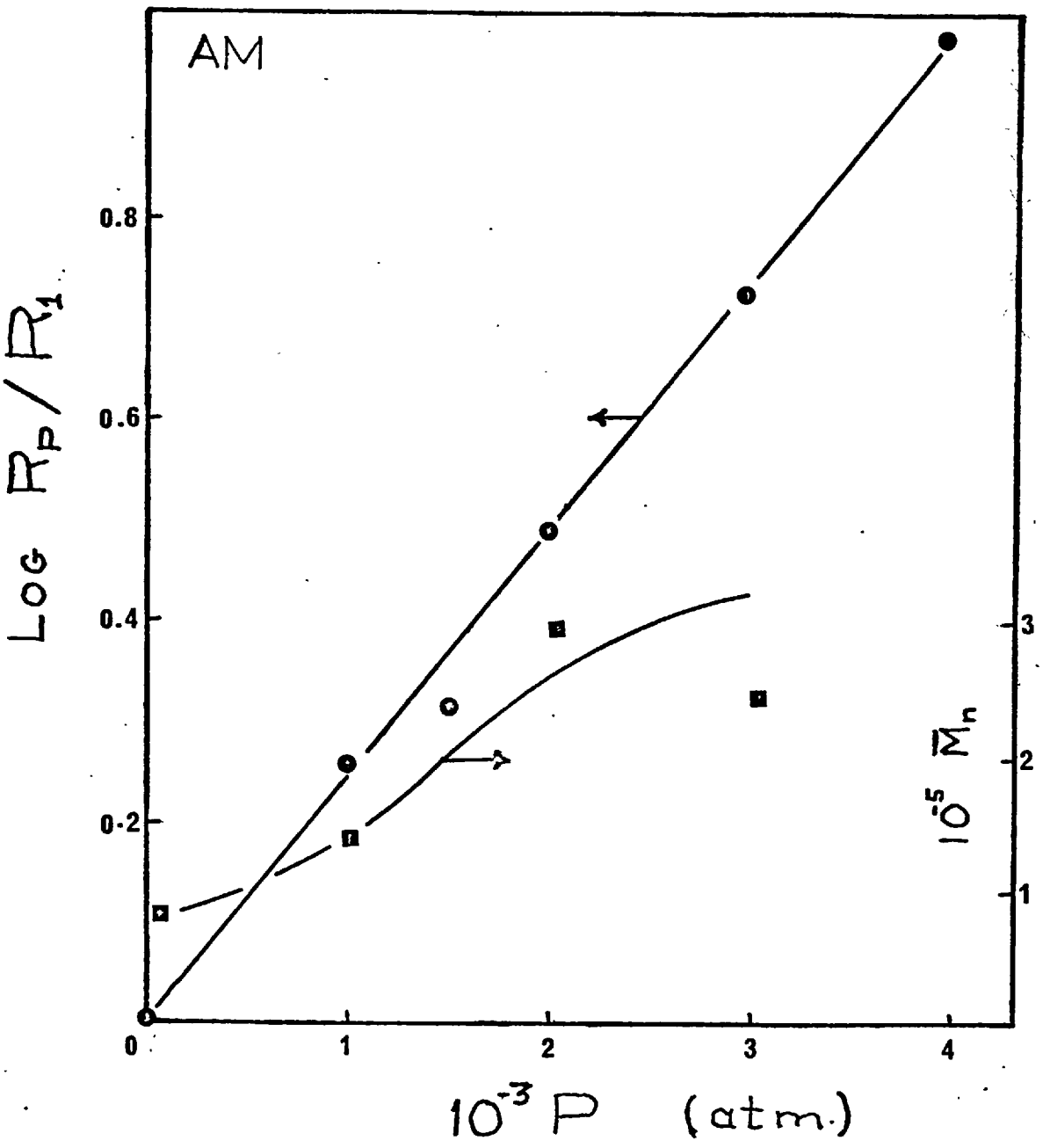


FIG 9: Variation of relative rate with pressure

TABLE 7-14

Allyl Methacrylate Variation of Rate with Initiator Concentration at 3000 atm.†		
Experiment	10^3[In] (moles/l.)	$10^5 R_p$ (moles/l./sec.)
AM78	1.10	6.49
AM65	2.26	9.42
AM79	6.95	20.35
AM80	12.25	28.80
AM81	16.90	33.30

† [M] = 2.2 moles/l., 60°C

The logarithmic plot of R_p vs. [In] is given in Figure 10. The plot is linear with a slope of 0.62. The variation of the rate of polymerization with monomer concentration of the polymerization of allyl methacrylate at 3000 atm. is given in the following table.

TABLE 7-15

Allyl Methacrylate Variation of Rate with Monomer Concentration at 3000 atm.†			
Experiment	[M] (moles/l.)	$10^5 R_p$ (moles/l./sec.)	$10^5 R_p/[M]$ ($sec.^{-1}$)
AM82	1.1	2.41	2.58 *
AM84	1.2	3.59	2.92
AM85	1.4	5.85	3.01 *
AM65	2.2	9.42	3.80 *
AM86	3.0	13.50	4.47
AM87	6.2	41.60	6.75

† 0.1% Bz_2O_2, 60°C, * Corrected from log-log graph

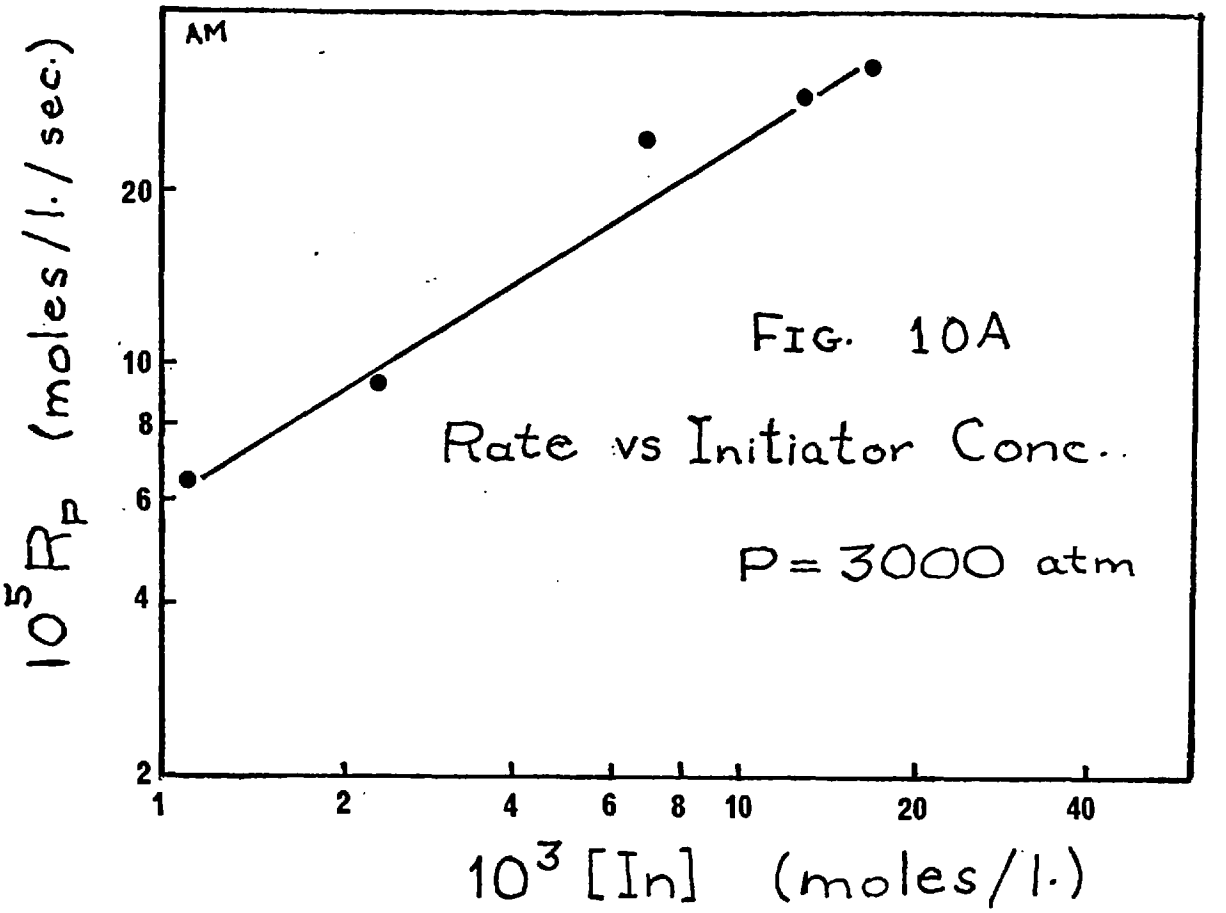


FIG. 10A

Rate vs Initiator Conc..

P = 3000 atm

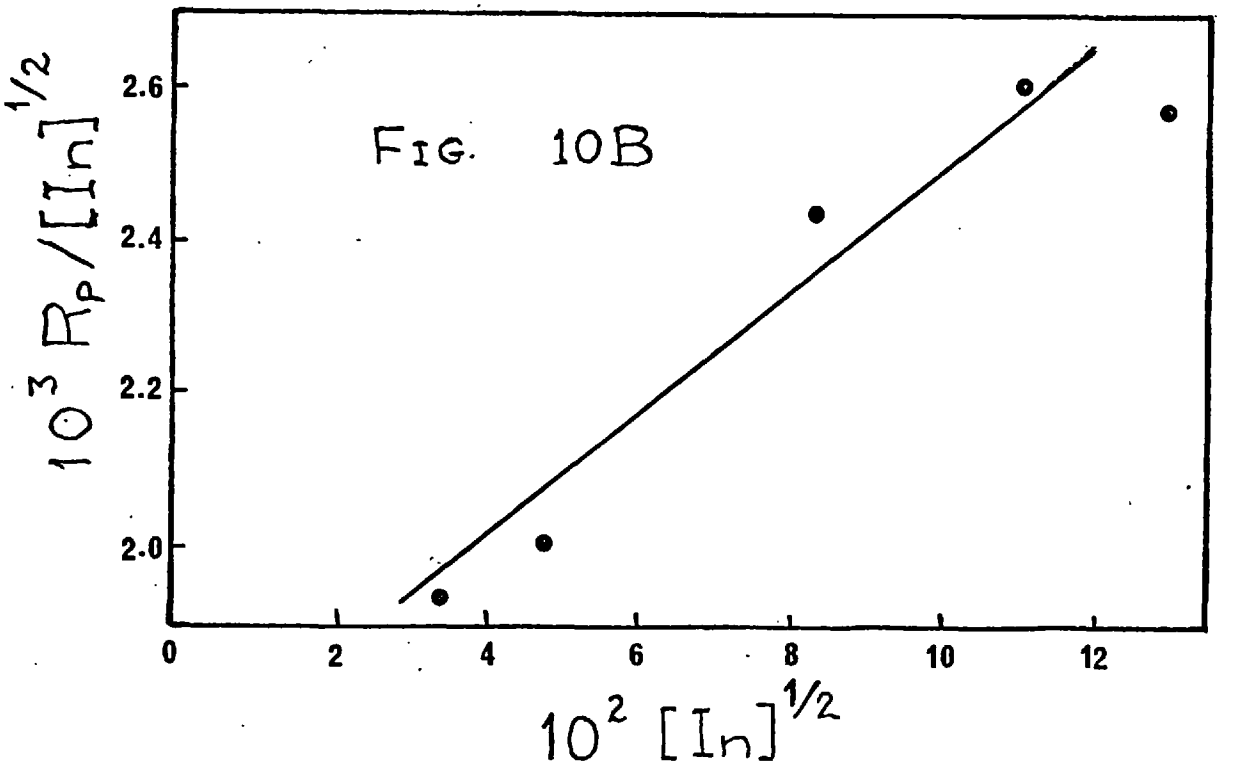


FIG. 10B

A logarithmic plot of R_p vs. [M] is given in Figure 11. It is linear with a slope of 1.53. Thus, the overall rate of polymerization of allyl methacrylate at 60°C and 3000 atm. pressure may be represented by:

$$R_p = K_{3000}[In]^{0.62}[M]^{1.53} \qquad (7\text{-}6)$$

A plot of R_p vs. [M] at 3000 atm. is not a straight line but plots of $R_p/[M]$ vs. [M] and $R_p/[M]^{\frac{1}{2}}$ vs. [M] (not shown; $\mathcal{R} = -33$ l./mole) are both straight lines. Plots of $R_p/[M]$ vs. [M] at both 1 atm. and 3000 atm. are given in Figure 12. The plot at 3000 atm. pressure has a slope to intercept ratio of 0.44.

The bromometrically-determined residual unsaturation results for pressures of 1 to 3000 atm. are listed in the following table.

TABLE 7-16

Allyl Methacrylate
Residual Unsaturation Results at Varying Pressures†

Experiment	Pressure (atm.)	[M] (moles/l.)	f_c	$1/f_c$
AM88	1	1.1	0.45	2.22
AM89		1.5	0.44	2.28
AM90		2.2	0.33	3.03
AM91		3.0	0.30	3.33
AM92		3.8	0.27	3.76
AM93		4.5	0.24	4.22
AM94	1000	1.1	0.53	1.91
AM95		1.5	0.51	1.96
AM96		2.2	0.45	2.22
AM97		3.3	0.40	2.50

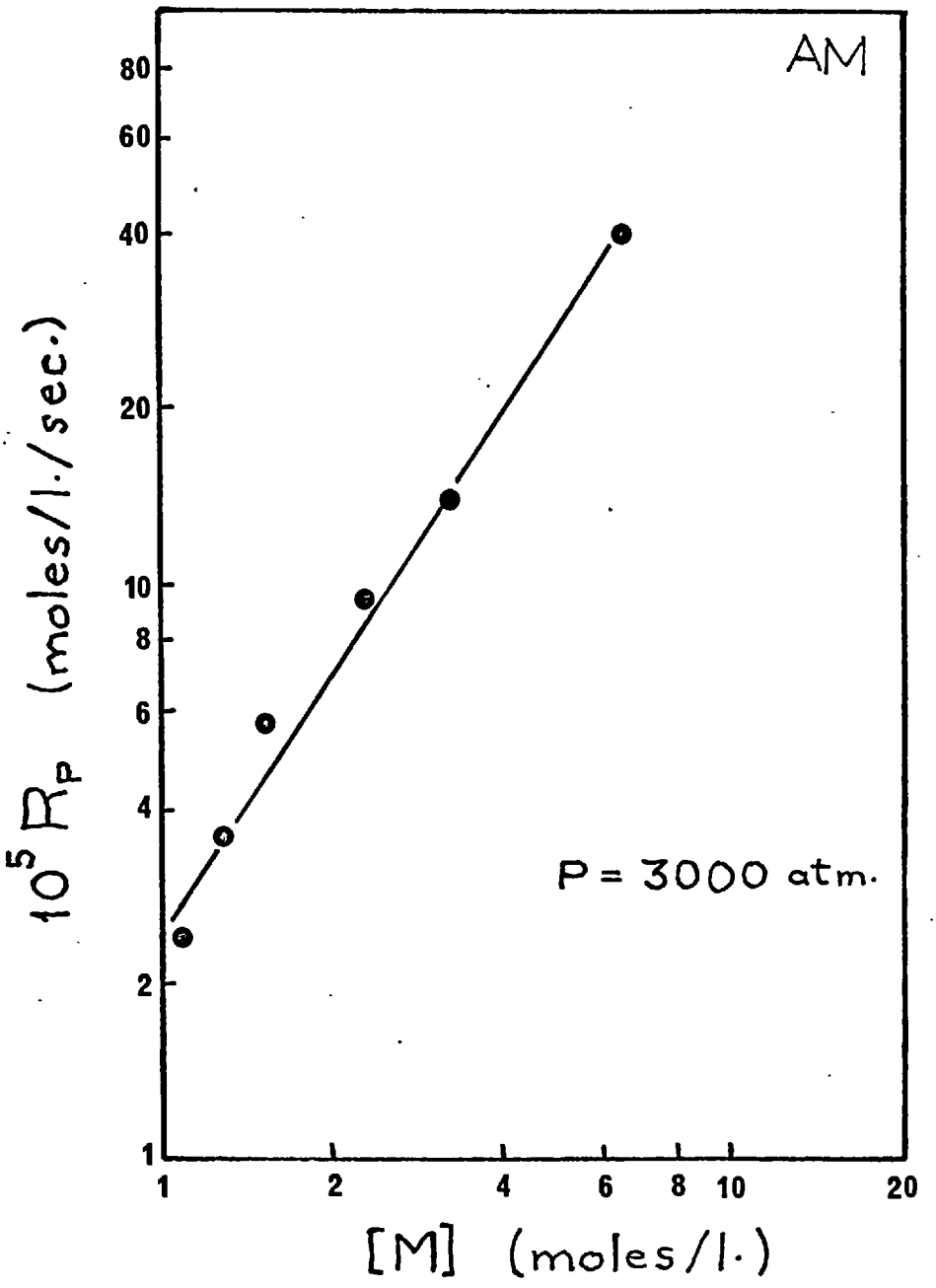


FIG.11: Rate vs Monomer Concentration

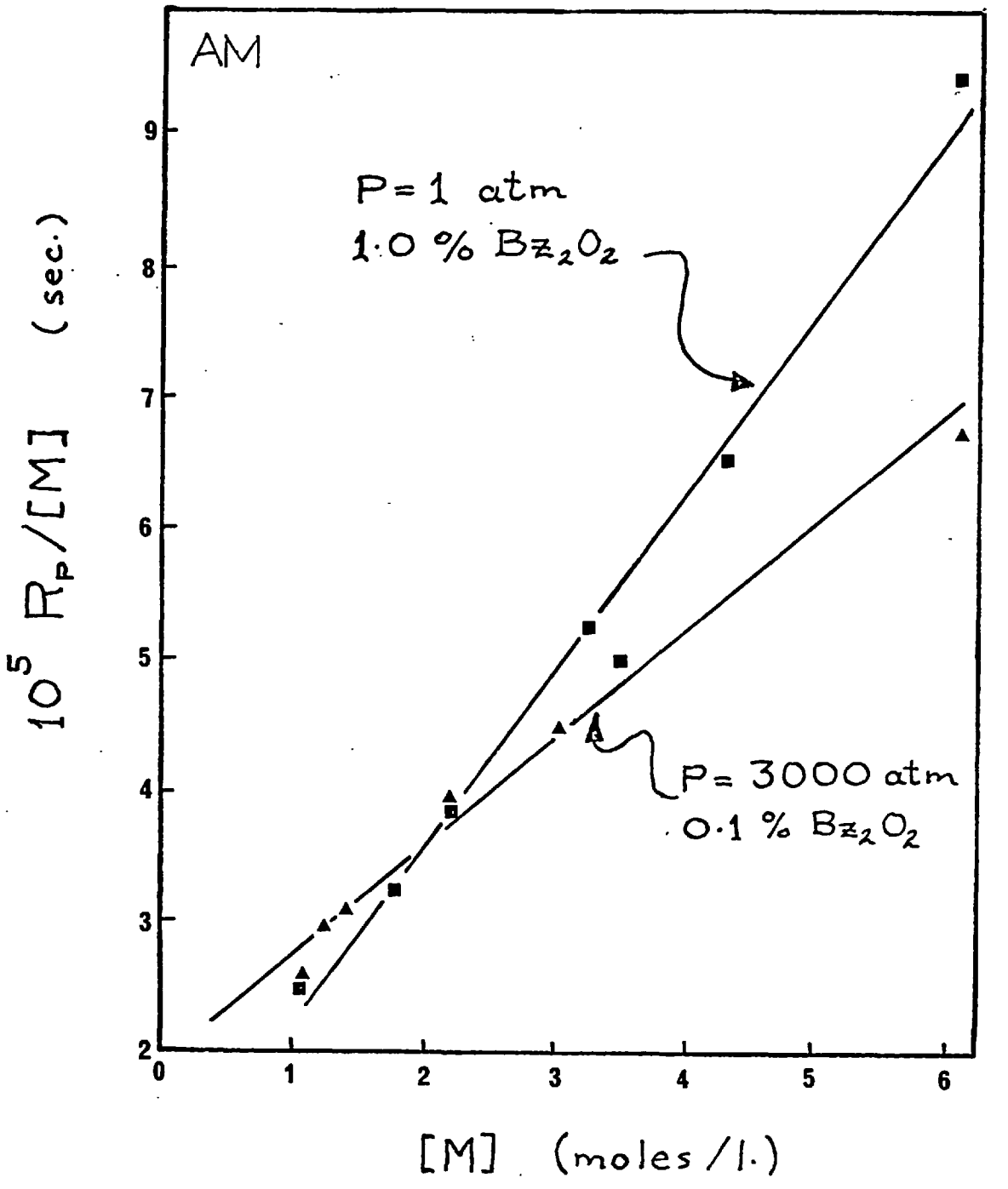


FIG. 12: $R_p/[M]$ vs [M]

Table 7-16 continued:

Experiment	Pressure	[M]	f_c	$1/f_c$
AM98	2000	1.1	0.55	1.83
AM99		1.5	0.52	1.92
AM100		2.2	0.54	1.90
AM101		3.0	0.49	2.02
AM102	3000	1.1	0.63	1.60
AM103		1.5	0.62	1.61
AM104		2.2	0.61	1.64
AM105		3.3	0.58	1.74

† Polymers produced in diallyl ether solution at 60°C, 0.1% Bz_2O_2

The plots of $1/f_c$ vs. [M] are shown in Figure 13. These plots are linear and their zero intercepts are greater than 1.0, probably due to substitution or isomerization (see Section IV-E). A plot of f_c vs. pressure (at [M] = 2.2 moles/l.) is given in Figure 14A and it is seen that the molar fraction of cyclized units in the polymers increases almost linearly with pressure.

From the slopes of the $1/f_c$ vs. [M] graphs at each pressure, the values of k_1/k_c may be obtained and these results are listed in Table 7-17.

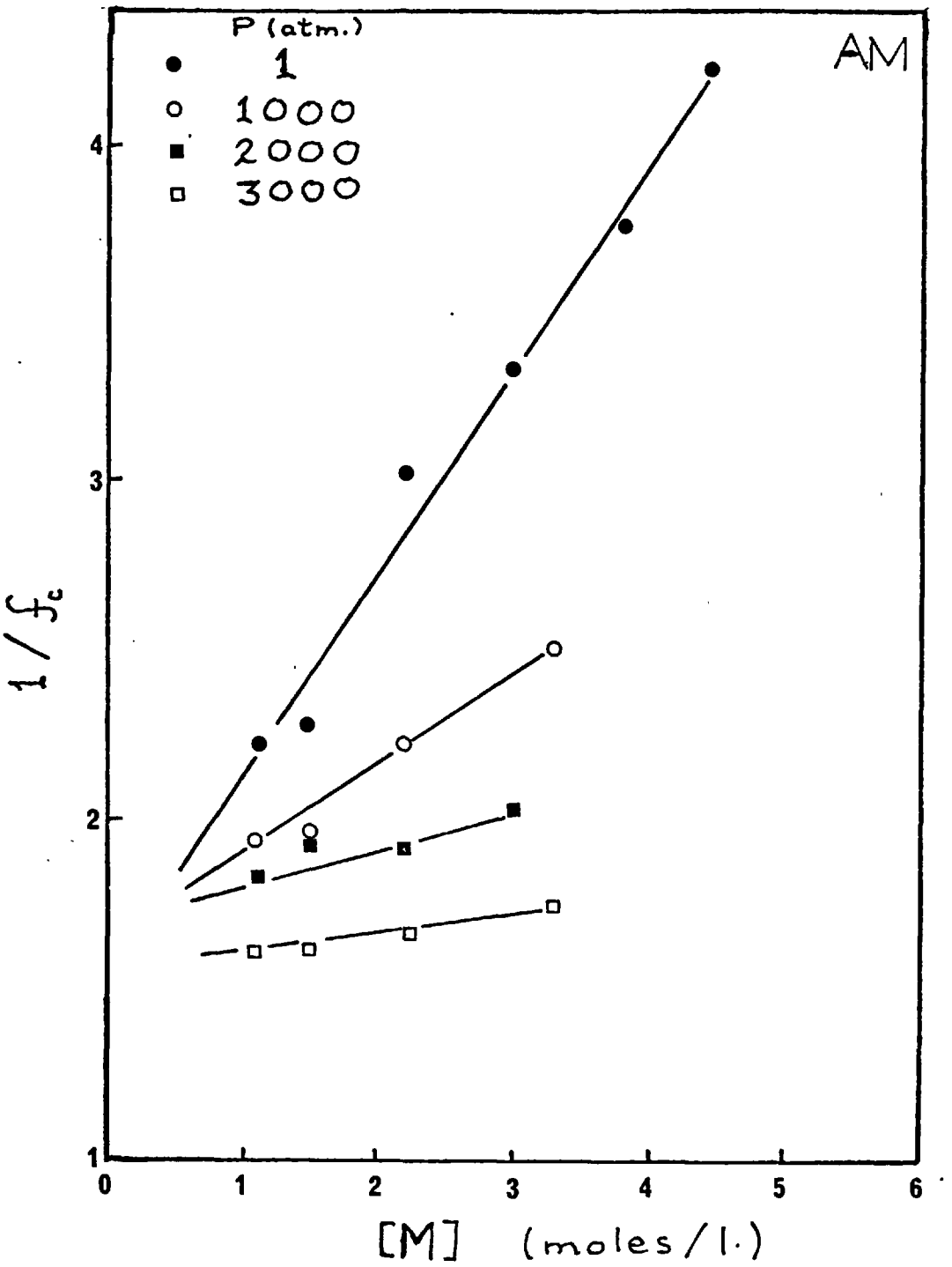


FIG. 13: Variation of cyclization with monomer concentration

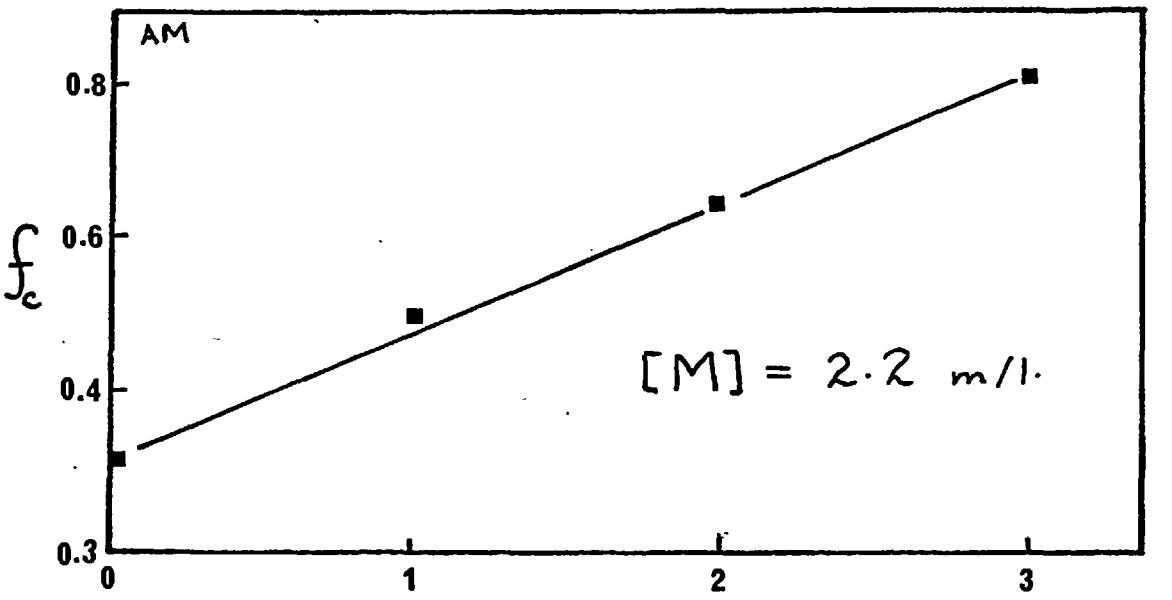


FIG. 14A: Variation cyclization with pressure

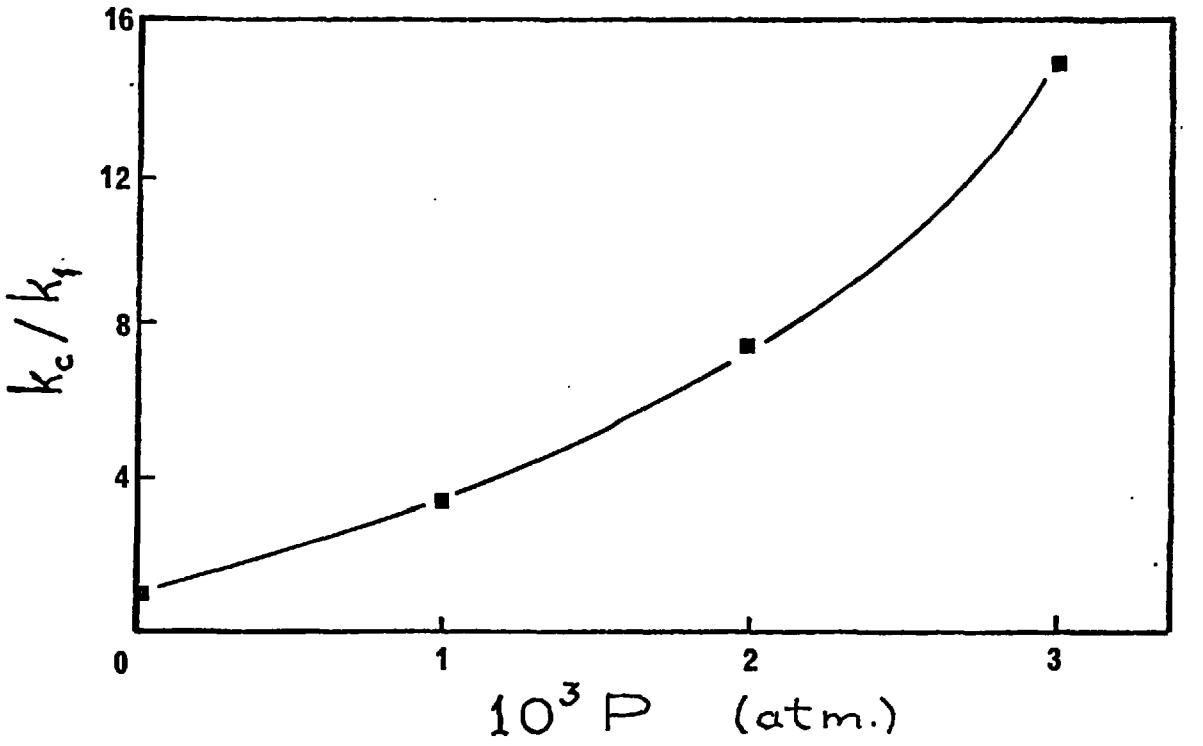


FIG. 14B k_c/k_1 vs Pressure

TABLE 7-17

Allyl Methacrylate Values of k_1/k_c at Different Pressures	
Pressure (atm.)	k_1/k_c (l./mole)
1	1.10
1000	0.29
2000	0.14
3000	0.07

A graph of k_c/k_1 vs. pressure is given in Figure 14B.

The value of k_1/k_c obtained at one atmosphere pressure (1.10 l./mole) is in excellent agreement with the slope to intercept ratio ($\mathcal{R}$ = 1.07 l./mole) found for the $R_p/[M]$ vs. $[M]$ plot at this pressure (see Figure 7B). Therefore, since the R_p vs. $[M]$ and $R_p/[M]^{\frac{1}{2}}$ vs. $[M]$ plots are not linear, it is seen from the relations proposed in Section IV, that in the cyclopolymerization of allyl methacrylate (at 1 atm. and 60°C in DE solution), the biradical termination reaction occurs solely between cyclized radicals.

The value of k_1/k_c at 3000 atm. pressure (0.07 l./mole) is in poor agreement with the experimental slope to intercept ratios ($\mathcal{R}$ = 0.44 from $R_p/[M]$ vs. $[M]$ and $\mathcal{R}$ = - 33 from $R_p/[M]^{\frac{1}{2}}$ vs. $[M]$). This suggests that at the higher pressure the steric hindrance to noncyclized radicals taking part in biradical termination reactions is not as severe as it is at atmospheric pressure, and $R_1^{\bullet} + R_2^{\bullet}$ terminations are probably also occurring.

From the result given in Table 7-16, values of $1/f_L - 1$ may be derived and these are tabulated for $[M] = 2.2$ moles/l. in the following table.

TABLE 7-18

Allyl Methacrylate Variation of Structure with Pressure			
Experiment	Pressure	f_L	$(1/f_L - 1)$
AM90	1	0.65	0.54
AM96	1000	0.55	0.82
AM100	2000	0.48	1.08
AM104	3000	0.40	1.52

The plot of $\log(1/f_L - 1)$ vs. pressure is shown in Figure 15. It is linear with a slope of 1.49×10^{-4} atm.$^{-1}$. From this value $\Delta V_1^* - \Delta V_c^*$ may be determined to be + 7.1 cc/mole (see equation 5-7). This value indicates that cyclization is favoured very strongly by pressure over intermolecular propagation.

The overall activation energy may be calculated from the rate of polymerization at varying temperatures. Values of E_T for the polymerization of allyl methacrylate at atmospheric pressure and at 3000 atm. may be obtained from the results listed in Table 7-19.

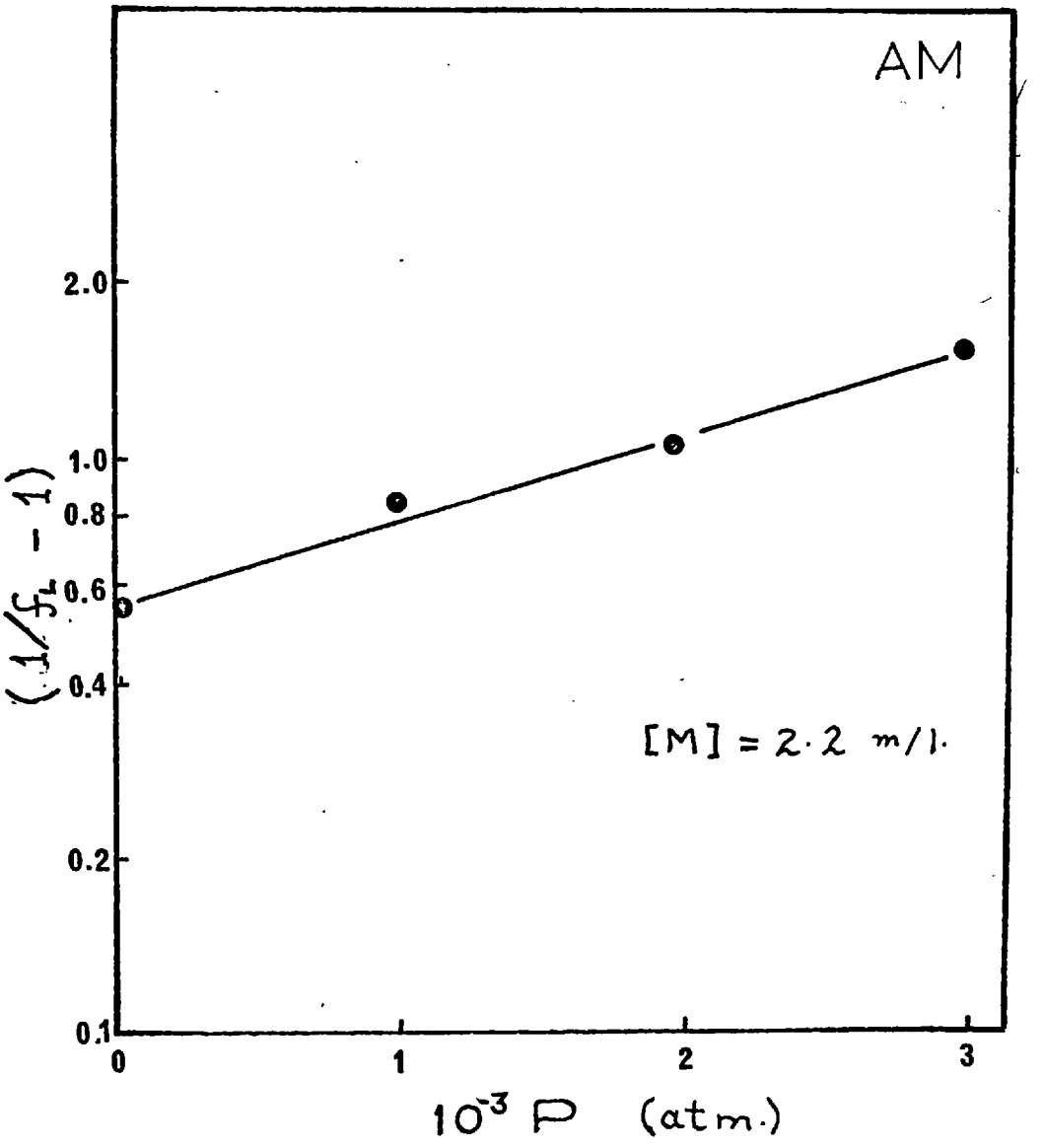


FIG. 15: Variation of Structure with Pressure

TABLE 7-19

Allyl Methacrylate

Effect of Temperature on Rate of Polymerization†

Experiment	Pressure (atm.)	Temperature (°C)	$10^6 R_p$ (moles/l./sec.)
AM106	1	40	1.92
AM107		50	5.42
AM63		60	17.70
AM108		65	39.20
AM109		70	50.64
AM110		75	19.25
AM111	3000	40	19.88
AM112		50	73.40
AM65		60	94.20
AM113		65	182.40
AM114		70	311.80

† [M] = 2.2 moles/l., 0.1% Bz_2O_2

Experiment AM110 may be at a temperature above the ceiling temperature[150]. Plots of log R_p vs. $10^3/T$ are shown in Figure 16. At both atmospheric pressure and 3000 atm. the plots are linear, and from their slopes the values of E_T are found to be 24.4 and 22.4 kcal./mole at 1 atm. and at 3000 atm., respectively.

The effect of temperature on unsaturation for polymers produced at atmospheric pressure and 3000 atm. may be determined from the results given in Table 7-20.

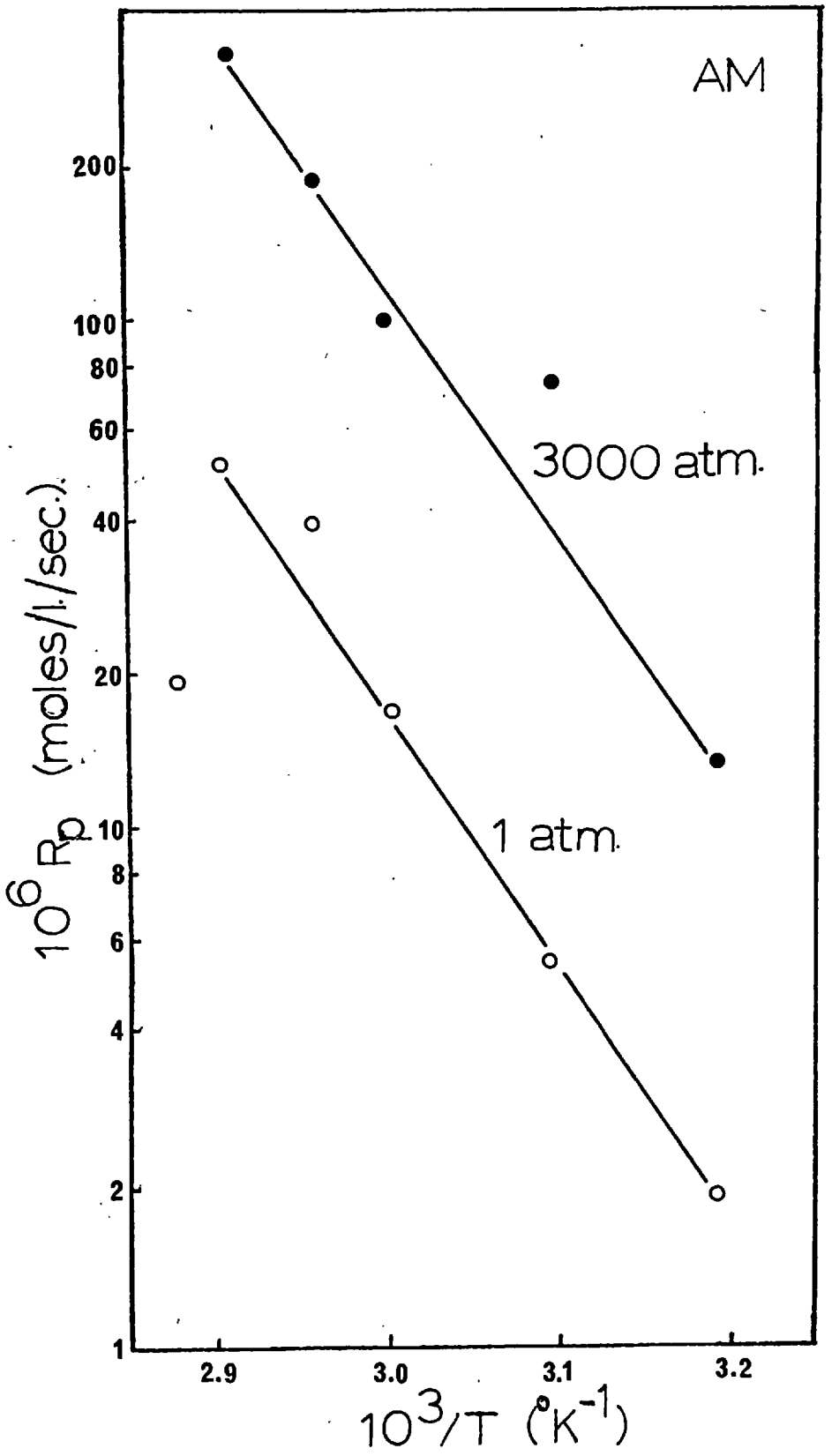


FIG. 16: Activation Energy

TABLE 7-20

Allyl Methacrylate

The Effect of Temperature on Polymer Structure†

Experiment	Pressure (atm.)	Temperature (°C)	f_c	$(1/f_L - 1)$
AM115	1	40	0.55	1.20
AM116		50	0.46	0.84
AM90		60	0.33	0.49
AM117		65	0.31	0.45
AM118		70	0.26	0.35
AM119	3000	40	0.77	3.35
AM120		50	0.70	2.33
AM104		60	0.61	1.59
AM121		65	0.58	1.36
AM122		70	0.51	1.05

† From polymers produced at [M] = 2.2 moles/l., 0.1% Bz_2O_2

The graph of $\log(1/f_L - 1)$ vs. $10^3/T$ is given in Figure 17. The plots are linear at both pressures and from their slopes the values of $(E_1 - E_c)$ are found to be 6.7 and 8.0 kcal./mole at atmospheric and at 3000 atm. pressure, respectively. (See equation 4-58). These results indicate that cyclization is slightly more favoured (by ~ 1.3 kcal./mole) at the higher pressure.

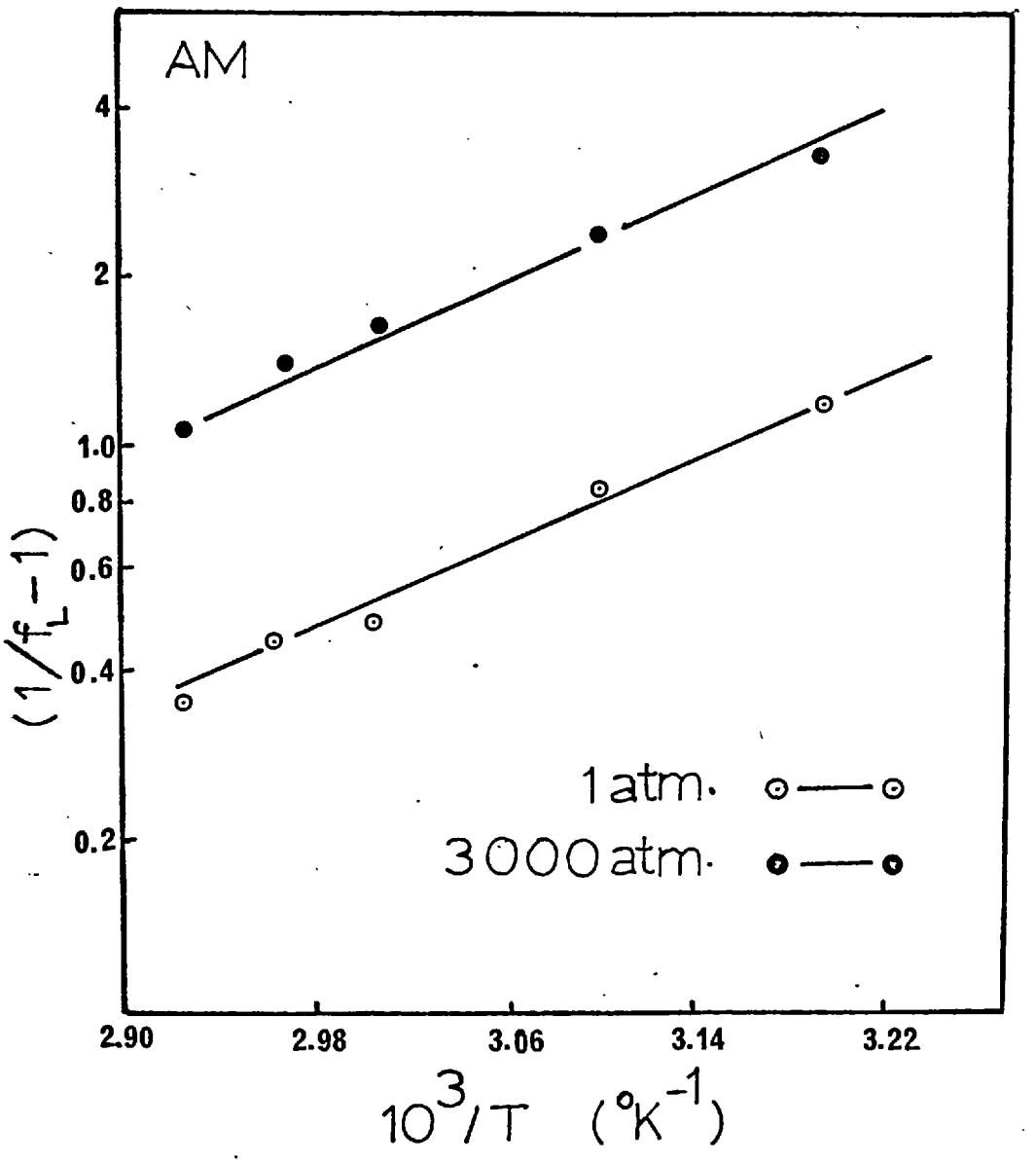
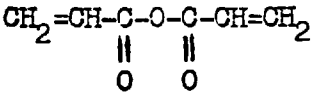


FIG. 17: Effect of Temperature

C. ACRYLIC ANHYDRIDE

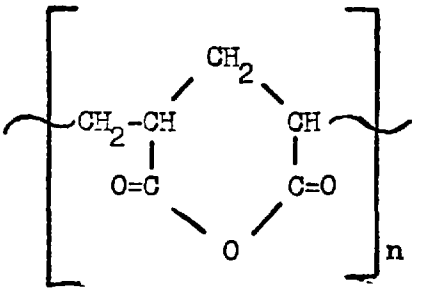
Investigations of the free radical cyclopolymerization of the symmetrical 1,6 diene, acrylic anhydride (VIII), were carried out in solution at 50 and 60°C.



VIII

The experimental pressure range was 1 - 4000 atm. and AIBN and Bz_2O_2 were used as initiators. Polymerization experiments were attempted in three solvents: dioxan, toluene, and dimethylformamide (DMF). The range of monomer concentrations was 0.5 to 5.0 moles/litre.

The cyclopolymerizations of acrylic anhydride and its α-CH_3 substituted homolog, methacrylic anhydride, have been well studied at atmospheric pressure. Crawshaw and Butler[68] and Jones[69] suggested that the polymerization of acrylic anhydride proceeds through alternate propagation and cyclization steps only. Consequently, the cyclopolymer could be considered to be much the same as the polymer of α-methylene-glutaric anhydride.



The cyclopolymer was soluble in DMF and dimethyl sulfoxide and when hydrolized gave poly(acrylic acid) samples with a high degree of stereoregularity. Subsequent investigations[99,100,151] have examined the cyclopolymerization of acrylic anhydride and the structure of its polymer

under various conditions and have shown that the polymer always has some residual unsaturation due to acrylyl groups pendant on the polymer chains.

In view of these results and because only a relatively small amount of the monomer was available, only a few comparative results were attempted at atmospheric pressure. That the polymers obtained were indeed cyclopolymers was confirmed from infra-red spectra (Nujol mull) of several of them (AA30, AA34, AA39, and AA41 - see below). In each case the spectra showed absorptions at ~1760 and 1810 cm.$^{-1}$. Mercier and Smets[89] have made an extensive study of the polymers of acrylic anhydride and ascribe such absorptions to hexatomic glutaric anhydride units in the polymer chain. Attempts to obtain the infra-red spectrum of the monomer were unsuccessful as the monomer polymerized on contact with the NaCl prisms.

Acrylic anhydride was polymerized at 60°C in dioxan and in toluene solutions at a monomer concentration of 1.2 moles/l. with 0.5% Bz_2O_2 initiator. In both solvents the polymerization was heterogeneous but in dioxan solution the rate of polymerization was so large that experiments in this solvent were discontinued as unfeasible. In an experiment in which purified monomer was sealed in a glass ampoule with no special precautions to exclude atmospheric oxygen, the bulk polymerization (at 60°C and 0.1% AIBN) ended with an explosion after 10 minutes. This was presumably due to the accumulation of peroxidic material during an induction period. Solution polymerization samples which were exposed to air before sealing gave relatively low results but samples which were vacuum degassed and flushed with nitrogen gave results which compared well with the experiments listed in the literature

(which were reported to have been prepared by the vacuum-filling technique). Experiments carried out in DMF solution at 50°C were ostensibly homogeneous to high conversions and had normal conversion-time curves.

Conversion-time results for the polymerization of acrylic anhydride in toluene and DMF solutions are listed in the following table.

TABLE 7-21

Acrylic Anhydride

Conversion-time Results in Solution Polymerization

Experiment	Time (hrs.)	% Conversion
(a) Solvent: DMF, [M] = 1.7 moles/l., 0.1% AIBN, 50°C, 1 atm.		
AA1	1.2	3.1
AA2	2.7	10.2
AA3	2.9	10.5
AA4	3.8	13.6
AA5	7.1	21.0
AA6	18.5	55.2
(b) Solvent: Toluene, [M] = 1.2 moles/l., 0.5% Bz_2O_2, 60°C, 1 atm.		
AA7	1.0	0.9
AA8	1.1	1.0
AA9	2.0	1.2
AA10	3.1	2.3
AA11	3.6	3.6 †
AA12	5.0	13.9 †
AA13	6.0	18.8 †
AA14	8.0	39.4 †
AA15	21.4	~ 94.0 †
(c) Solvent: Toluene, [M] = 1.2 moles/l., 0.5% Bz_2O_2, 60°C, 3000 atm.		
AA16	1.0	2.6
AA17	1.7	13.1 †
AA18	2.0	18.1 †

† Polymer precipitates

The conversion-time curves at atmospheric pressure are illustrated in Figure 18. The polymerization in DMF was normal and the reaction medium took on a slightly reddish tinge after 2 - 3 hours. When precipitated in ether the polymer was highly swollen and a typical sample (AA3) had a molecular weight of 210,000. Polymerizations in toluene solution exhibited autoacceleration and the reaction medium became milky after a few percent conversion due to suspended polymer particles. At higher conversions the polymer precipitated as a granular white solid. A typical sample (AA15) had a molecular weight of 54,200.

In view of the relatively low molecular weights of samples polymerized in toluene it was decided that calculations of the molar fraction of cyclized units could be obtained under somewhat similar conditions, despite the autoacceleration, if samples polymerized almost to 100% conversion were used. The following table illustrates the effect of monomer concentration on the structure of poly(acrylic anhydride) samples obtained from polymerizations to high conversions in toluene solution at 60°C.

TABLE 7-22

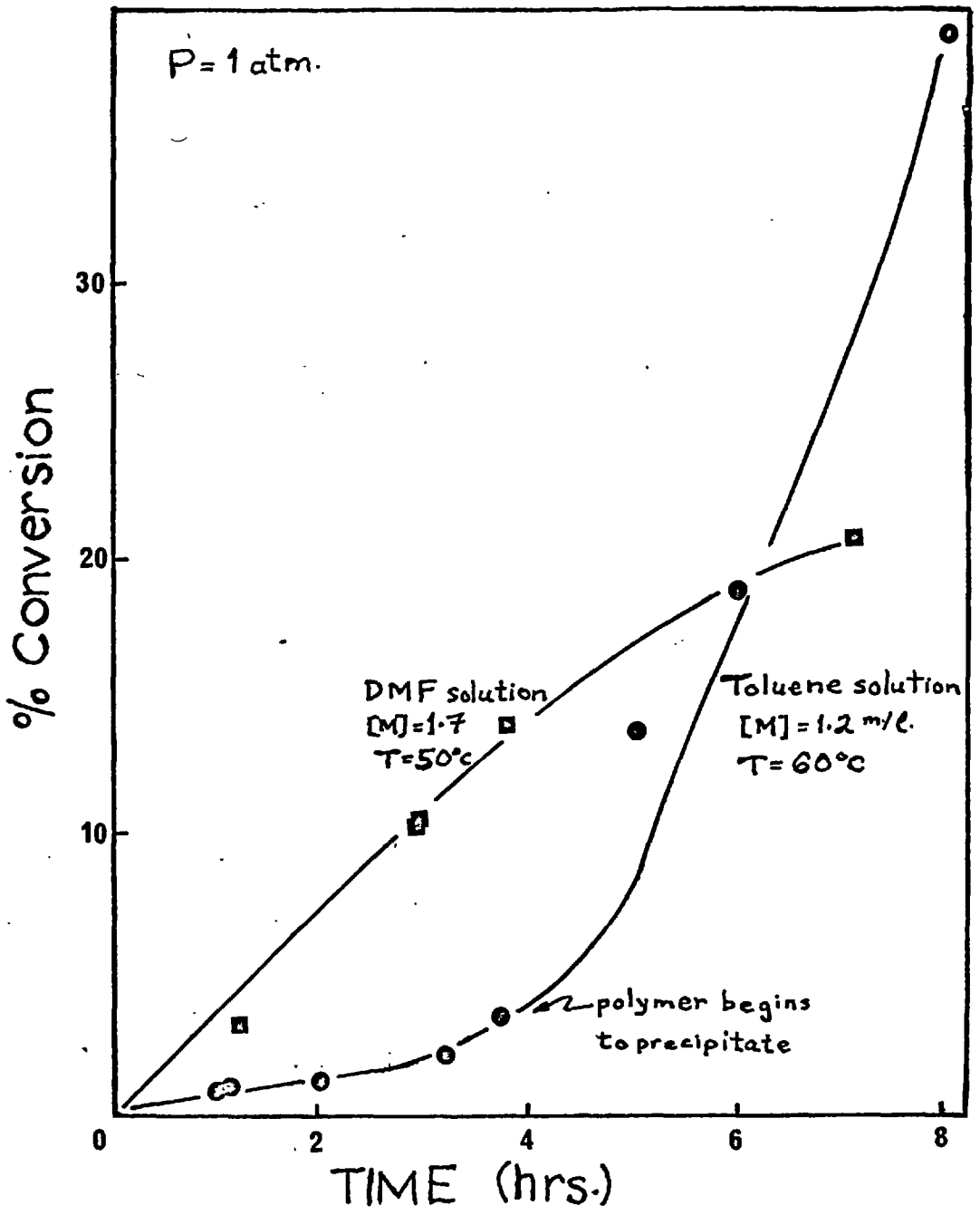
Acrylic Anhydride

Variation of Cyclization with Monomer Concentration*

Experiment	[M] (moles/l.)	f_c †	[η] (dl./gm.)	$10^{-3}\overline{M}_v$
AA19	0.6	0.97	-	-
AA20	0.8	0.95	0.33	68.9
AA15	1.2	0.92	0.28	54.2
AA21	1.3	0.82	-	-
AA22	1.6	0.86	0.51	129.0

* Polymerizations carried to 90-100% conversion, 1 atm., 0.5% Bz_2O_2

† Calculated by method of Polgar and Jungnickel (ref. 141)



FIG·18: Polymerization of Acrylic Anhydride

From a plot of $1/f_c$ vs. [M] the value of k_1/k_c obtained (see equation 4-45) as 0.13 l./mole. In view of the inaccuracies involved in using high conversion heterogeneous polymer this value compares very well with the result of 0.17 l./mole reported by Smets et al[100] for the homogeneous polymerization of acrylic anhydride in cyclohexanone solution at 35°C.

The following table lists the variations of rate with initiator concentration for the homogeneous polymerization of acrylic anhydride in DMF solution.

TABLE 7-23

Acrylic Anhydride Variation of Rate with Initiator Concentration†		
Experiment	10^3[In] (moles/l.)	$10^5 R_p$ (moles/l./sec.)
AA3	1.71	1.74
AA23	4.62	4.63
AA24	5.05	5.10
AA25	15.10	16.54

† Initiator: AIBN, [M] = 1.7 moles/l., 50°C, 1 atm.

At higher initiator concentrations gelation occurred. A logarithmic graph of R_p vs. [In] is linear with a slope of 1.0. This value is identical to the result obtained by Mercier and Smets[99] for the polymerization of acrylic anhydride in DMF solution at 34.6°C. These authors also obtained values of 0.75 to 0.83 (depending on monomer concentration) for this monomer in cyclohexanone solution, and 0.67 in bulk for the catalyst exponent in the overall rate equation.

The variation of the rate of polymerization of acrylic anhydride with monomer concentration is given in the following table.

TABLE 7-24

Acrylic Anhydride Variation of Rate with Monomer Concentration†		
Experiment	[M] (moles/l.)	$10^5 R_p$ (moles/l./sec.)
AA26	0.8	0.93
AA27	1.3	1.42
AA3	1.7	1.74
AA28	2.5	11.00 *
AA29	3.3	22.30 *
AA30	4.2	33.20 *
AA31	5.0	43.00 *

† DMF solution, 0.1% AIBN, 50°C, 1 atm.

* polymer precipitates

The results given in the above table are illustrated in Figure 19. After the precipitation threshold (~ 1.8 moles/l. from the graph) the polymer separated as small, hard white beads which conglomerated at the bottom of the reaction tube to form an insoluble mass. The volume of the reaction medium increased as these nodules formed. Such a phenomenon is an extreme form of heterogeneous polymerization usually called 'popcorn' polymerization and it is quite common for many diene monomers[37]. A rapid rate increase such as found with acrylic anhydride, also occurred above the precipitation threshold in the polymerization of acrylonitrile in DMF solution[47]. The results published by Mercier and Smets[99] for the polymerization of acrylic anhydride at 34.6°C in cyclohexanone solution

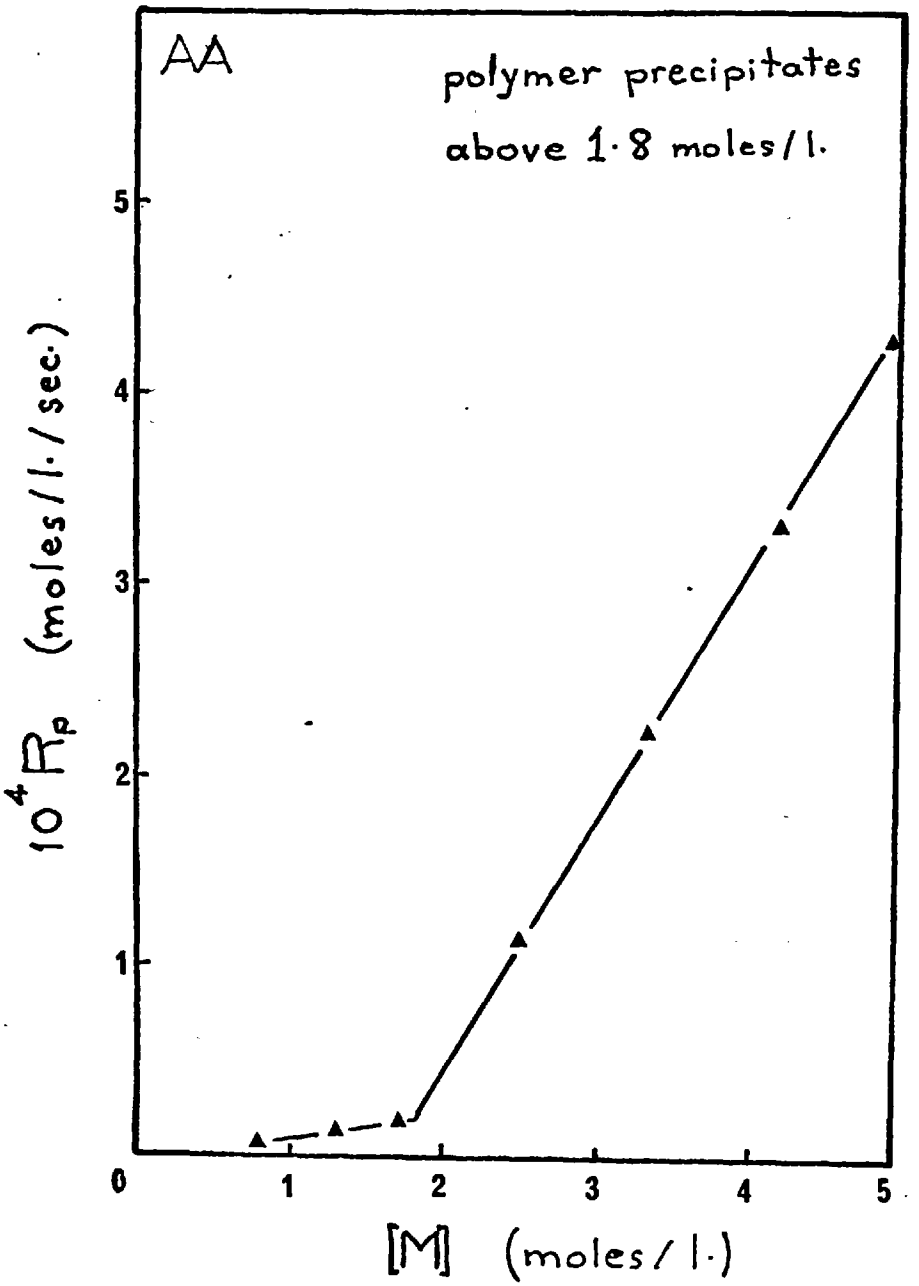


Fig.19: Polymerization at 50°C
Rate vs monomer concentration

yield a curve which is similar in form to that given in Figure 19. However, no precipitation was reported for the region of the rapid rate increase (above~ 4.5 moles/l. in cyclohexanone). These authors also noted that the turbidity of the polymerization medium increased 240 times by 1.6% conversion (at 4 moles/l.) and they concluded that this was due to the presence of microgel particles suspended in the apparently homogeneous solution. ESR measurements indicated a large amount of radical entrapment in the growing microgel particles and the trapped radical concentration increased with both percent conversion and temperature. It seems obvious that a similar but more severe effect occurred in the DMF solution polymerizations listed above, and this occlusion explains the first order rate dependance of the initiator concentration. Thus, it is seen that the 'homogeneous' cyclopolymerization of acrylic anhydride in DMF solution has many features in common with the heterogeneous bulk polymerization of acrylonitrile (see Section II).

The results given in this thesis for the polymerization of acrylic anhydride at atmospheric pressure support the published results[99,100] and considered along with them, lend credence to the supposition advanced in Section II that heterogeneous and gel polymerizations are facets of the same phenomenon. The difference between the two modes of polymerization is due to the relative importance of physical effects in a particular reaction medium-polymer system. Thus, the free radical cyclopolymerization of acrylic anhydride ranges from the ostensibly homogeneous polymerization in cyclohexanone solution[99] and the gel polymerization in DMF solution (at high [In] - this work) to the heterogeneous polymerization in toluene solution (this work) and the popcorn polymerization in DMF solution at high monomer concentration (this work).

Polymer formed in the polymerization of acrylic anhydride is highly branched due to reactions involving highly reactive pendant acrylyl groups which are the results of intermolecular propagation reactions of noncyclized radicals. In polymerization, suspended microgel particles are formed by the coalescence of 'dead' polymer molecules and polymer radicals. In dilute DMF solution at high initiator concentration gelation occurs when adjacent microgel particles throughout the solution come into contact and cross-link. As monomer concentration is increased the microgel particles become more and more swollen, since the monomer is a better swelling agent for the polymer than DMF. This permits the penetration of the microgel particles by an increasingly greater number of monomer molecules and above the precipitation threshold, cross-linked aggregates precipitate as a result of rapid propagation, branching and monomer transfer reactions in the microgel particle. The presence of numbers of pendant acrylyl groups in each microgel particle will enhance such reactions. It is also quite possible that non-isothermal conditions exist in the aggregates formed at higher monomer concentrations. In cyclohexanone solution the microgel particles do not precipitate and the effects are less severe as this solvent is a better swelling agent than DMF. In toluene solution high transfer to solvent reactions probably limit the coalescence and occlusion and the polymer molecules become insoluble in the reaction medium and precipitate at an early stage.

In DMF solution at a monomer concentration of 1.7 moles/l, the microgel particles which form are sufficiently dispersed throughout the dilute solution to preclude either gelation or precipitation. The variation in the rate of the polymerization of acrylic anhydride with pressure at this concentration is given in table 7-25.

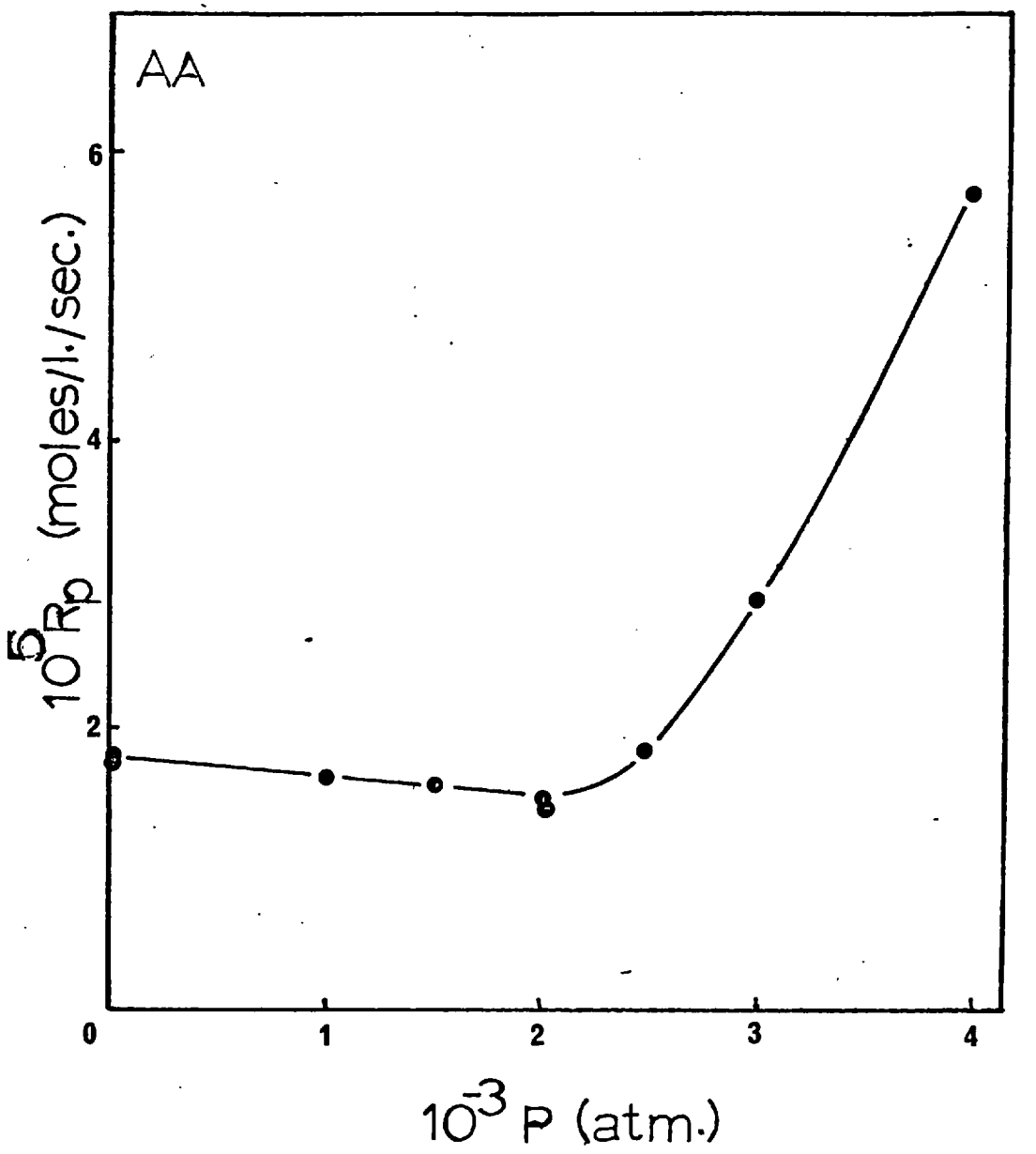
TABLE 7-25

Acrylic Anhydride Variation of Rate with Pressure below the Precipitation Threshold†		
Experiment	Pressure (atm.)	$10^5 R_p$ (moles/l./sec.)
AA2	1	1.74
AA3	1	1.78
AA32	1000	1.66
AA33	1500	1.60
AA34	2000	1.52
AA35	2000	1.47
AA36	2500	1.90
AA37	3000	2.87
AA38	4000	5.75

† DMF solution, [M] = 1.7 moles/l., 0.1% AIBN, 50°C

Figure 20 illustrates these novel results. Up to ~ 2500 atm. the rate of polymerization is almost unaffected by pressure and it actually decreases by 12%. A logarithmic plot of R_p vs. pressure is linear in this range and from its slope ΔV_T^* is found to be + 1.5 cc/mole. Above 2500 atm. the rate increases normally with pressure and ΔV_T^* is found to be - 13.8 cc/mole.

Table 7-26 shows the variation of molecular weight and polymer structure with pressure.



FIG·20: Variation of Rate with Pressure

TABLE 7-26

Acrylic Anhydride Variation of Molecular Weight and Cyclization with Pressure†				
Experiment	Pressure (atm.)	$[\eta]$ (dl./gm.)	$10^{-3}\overline{M}_v$	f_c
AA3	1	0.74	210	0.49
AA32	1000	0.99	327	0.79
AA33	1500	-	-	0.91
AA34	2000	1.24	469	-
AA35	2000	1.34	515	0.90
AA36	2500	-	-	0.93
AA37	3000	1.41	570	0.95
AA38	4000	1.44	605	-

† polymers produced at [M] = 1.7 moles/l., 0.1% AIBN, 50°C

The results given in the above table are illustrated in Figure 21. Experiment AA34 was carried to 8.5% conversion while Experiment AA35 was carried to 15.6% conversion so the increase in molecular weight is probably an indication of a large amount of chain branching.

Zhulin et al[152] have reported a somewhat similar effect in the bulk polymerization of acrylonitrile. The effect of pressure on the rate of polymerization of this monomer was normal for the homogeneous reaction in DMF solution, but the heterogeneous bulk polymerization of acrylonitrile at 50°C (with 0.019% by wt. AIBN) showed a decrease of 60% in R_p by 4000 kg./cm.^{2}. In this same range the molecular weight decreased by 90%. At higher pressures the rate increased with increasing pressures becoming equal to its initial (1 atm.) value again by 5000 kg./cm.^{2}. At 6000 kg./cm.^{2} the rate became explosively rapid.

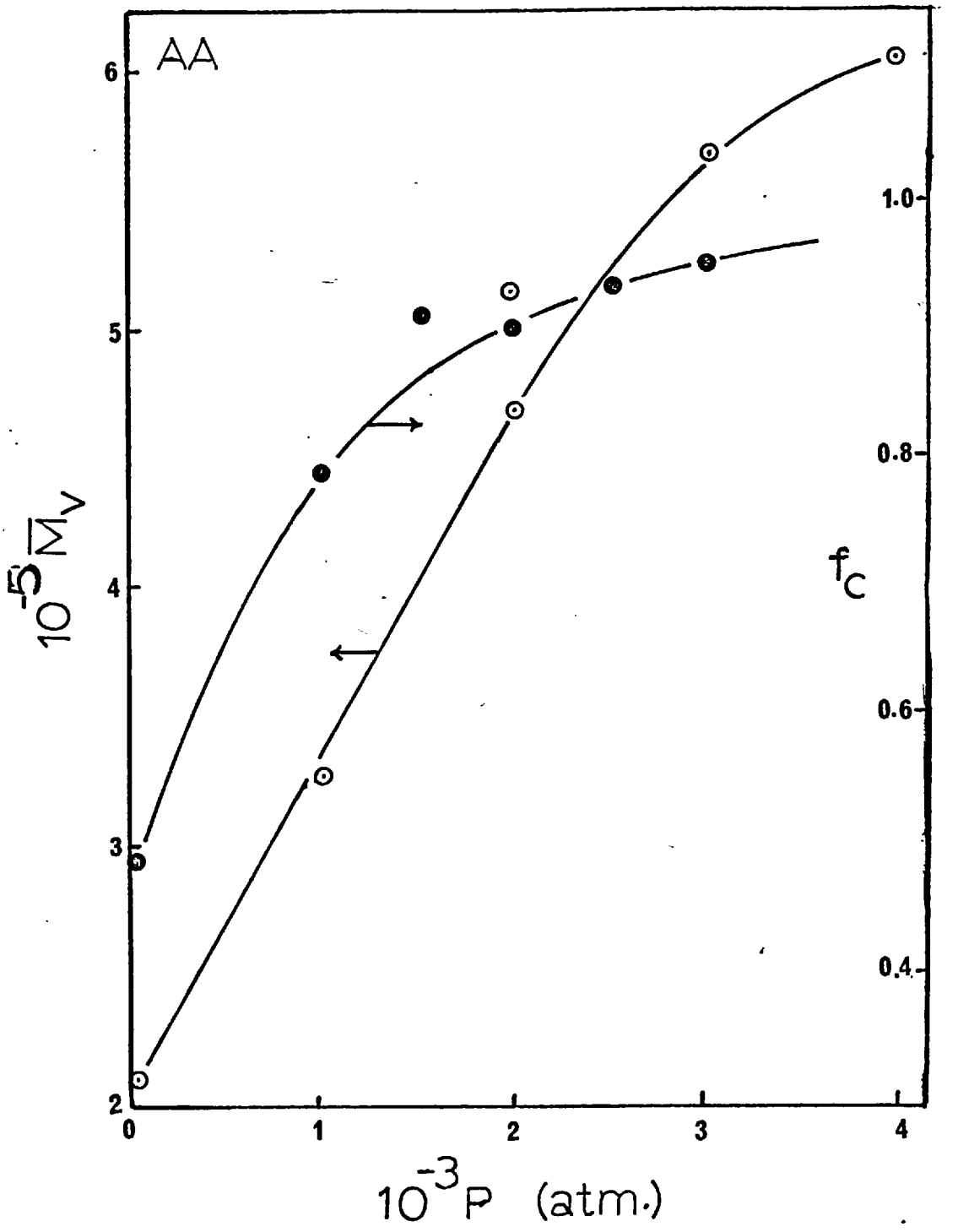


Figure 21

They also reported that the heterogeneous polymerization of methacrolein in MeOH obeyed normal kinetics under pressure. In contrast, the decrease in the rate of the polymerization of acrylic anhydride with pressure is slight, and the molecular weight actually increases steadily with pressure despite the rate decrease. The fraction of cyclized units in the cyclopolymer increases sharply in the region of rate decrease and then levels off.

The following interpretation is suggested as an explanation for this phenomenon. At any fixed initiator concentration, for the cyclopolymerization of a fixed concentration of acrylic anhydride in DMF solution, a certain amount of polymer chains are started by initiator radicals. These growing chains quickly coalesce with each other and with 'dead' polymer molecules. This leads to the formation of a certain (smaller) number of microgel particles. Once these suspended particles have formed, the rate of polymerization is largely governed by the rate of diffusion of monomer molecules in them. Residual unsaturation measurements show that the polymer molecules have highly active acrylyl groups pendant on the chains. It has been shown that a large amount of radical trapping occurs and many pendant acrylyl groups are occluded in the growing microgel particles.

At higher pressures the increased rates of propagation and monomer transfer accelerate those reactions in the microgel particles involving pendant acrylyl groups. This leads to an increase in the amount of cross-linking and chain branching, and this in turn decreases the penetrability of monomer molecules into the microgel particles. The resulting decreased rate of diffusion causes a decrease in the rate of polymerization.

In contrast to the results reported for acrylonitrile, this does not lead to a decrease in the molecular weight, as the poly(acrylic anhydride) microgel particles contain pendant acrylyl groups which can react with the active ends of occluded polymer radicals in the same particle. Such reactions further increase the density of the microgel particles and lead to a steady increase in the molecular weight with pressure.

As the pressure increases the rate of cyclization also increases. This leads to two opposing effects. As the pressure and microgel density increase, the decreasing rate of diffusion of monomer leads to an effective reduction in the monomer concentration at the sites of reaction in the microgel particles. This leads to a sharp increase in the amount of cyclization (f_c is inversely proportional to the monomer concentration). However, as the amount of cyclization increases, the number of pendant acrylyl groups in the microgel particles decrease, and this in turn decreases the number of chain branches and cross-links. This allows more monomer molecules to penetrate the microgel particles and the increased monomer concentration causes the amount of cyclization to level off. When the cyclization has increased to such an extent that the microgel particles are relatively permeable to monomer molecules, the rate of polymerization begins to increase normally with pressure and the increases in the molecular weight and the amount of cyclization are reduced.

For the polymerization of methacrylonitrile at atmospheric pressure, Grassie and Vance[36] suggested that a cyanide initiation reaction:

$$\sim \underset{\underset{C\equiv N}{|}}{C} \sim \xrightarrow{R^{\bullet}} \sim \underset{\underset{R-C=N^{\bullet}}{|}}{C} \sim \longrightarrow \sim \underset{\underset{R-C=N}{|}}{C} \sim \qquad (7\text{-}7)$$

might explain the high degree of chain branching which occurred. Such a reaction might also explain the severe occlusion and high degree of branching which occurs in the bulk polymerization of acrylonitrile (see Section II-C) since branching initiated by chain transfer would lower the molecular weight and tend to prevent occlusion. Since polyacrylonitrile is insoluble in the monomer, the resulting aggregates are probably far denser than the suspended microgel particles found in the 'homogeneous' polymerization of acrylic anhydride. Also, pendant cyanide groups on polymer chains occluded in polymer aggregates would not be expected to be as active as the chain-forming vinyl groups in acrylonitrile. These differences may explain the large decreases in rate and molecular weight reported[152] for the polymerization of acrylonitrile under pressure. It is suggested that an accurate kinetic analysis of the effect of pressure on the polymerization of acrylonitrile and its homologs would be a fruitful subject for research.

The variation of the rate of polymerization of acrylic anhydride with temperature at atmospheric pressure is given in the following table.

TABLE 7-27

Acrylic Anhydride

Variation of Rate with Temperature†

Experiment	Temperature (°C)	$10^6 R_p$ (moles/l./sec.)
AA39	30	1.33
*	34.6	3.34
AA40	40	5.13
AA3	50	17.40
AA41	60	44.80

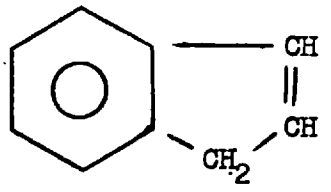
† DMF solution, [M] = 1.7 moles/l., 0.1% AIBN, 1 atm.

* From results given in ref. 99 at [M] = 1.8 moles/l.

A plot of log R_p vs. $10^3/T$ is a straight line and from its slope E_T is found to be 24.5 kcal./mole. The value of $(E_1 - E_c)$ has been reported[89] as 2.4 kcal./mole.

D. INDENE

Investigations of the free radical polymerization of indene (IX) were carried out in bulk at 80°C.



IX

The experimental pressure range was 1 - 10,000 atm. and Bz_2O_2 was used as the initiator.

The polymerization of indene was one of the earliest examples of polymerization to be studied. On the basis of the $SbCl_5$ - and $SnCl_4$ - catalysed and thermal polymerizations of this monomer, Whitby and Katz[137] advanced a 'stepwise' reaction theory for polymerization in opposition to the currently accepted chain reaction theory proposed by Staudinger[4]. The polymerization of indene at atmospheric pressure using free radical, anionic, cationic, and Ziegler catalysts has also been examined[153-155]. Polymers of indene are usually soft yellow solids of low molecular weight (< 3000) although Sigwalt[156] has shown that polymers of much higher molecular weight may be obtained in solution at - 70°C with Friedel-Crafts catalysts.

No systematic investigations of the effect of pressure on the polymerization of indene have previously been reported. Klaasens and Gisolf[157] have reported, however, a rapid and complete thermal polymerization in bulk at 10,000 atm., during which the temperature rose slowly from 100 to 175°C, then sharply to 325°C. The solid yellow polymer obtained was not further characterized. Holmes-Walker and Weale[158]

investigated the polymerization of this monomer at 90°C and pressures of 5100 and 10,100 atm. using Bz_2O_2 initiator. After 23 hours the product, a white powder, was separated into fractions with molecular weights of 450 - 850.

The effect of pressure on the free radical polymerization of indene is examined in this thesis. Besides their intrinsic value the results are a convenient example of the free radical polymerization of a monovinyl compound which may be compared with cyclopolymerization, especially that of diallyl cyanamide.

Indene was polymerized in bulk at 80°C using 0.5% Bz_2O_2 initiator. The variation of percent conversion with time is given in the following table.

TABLE 7-28

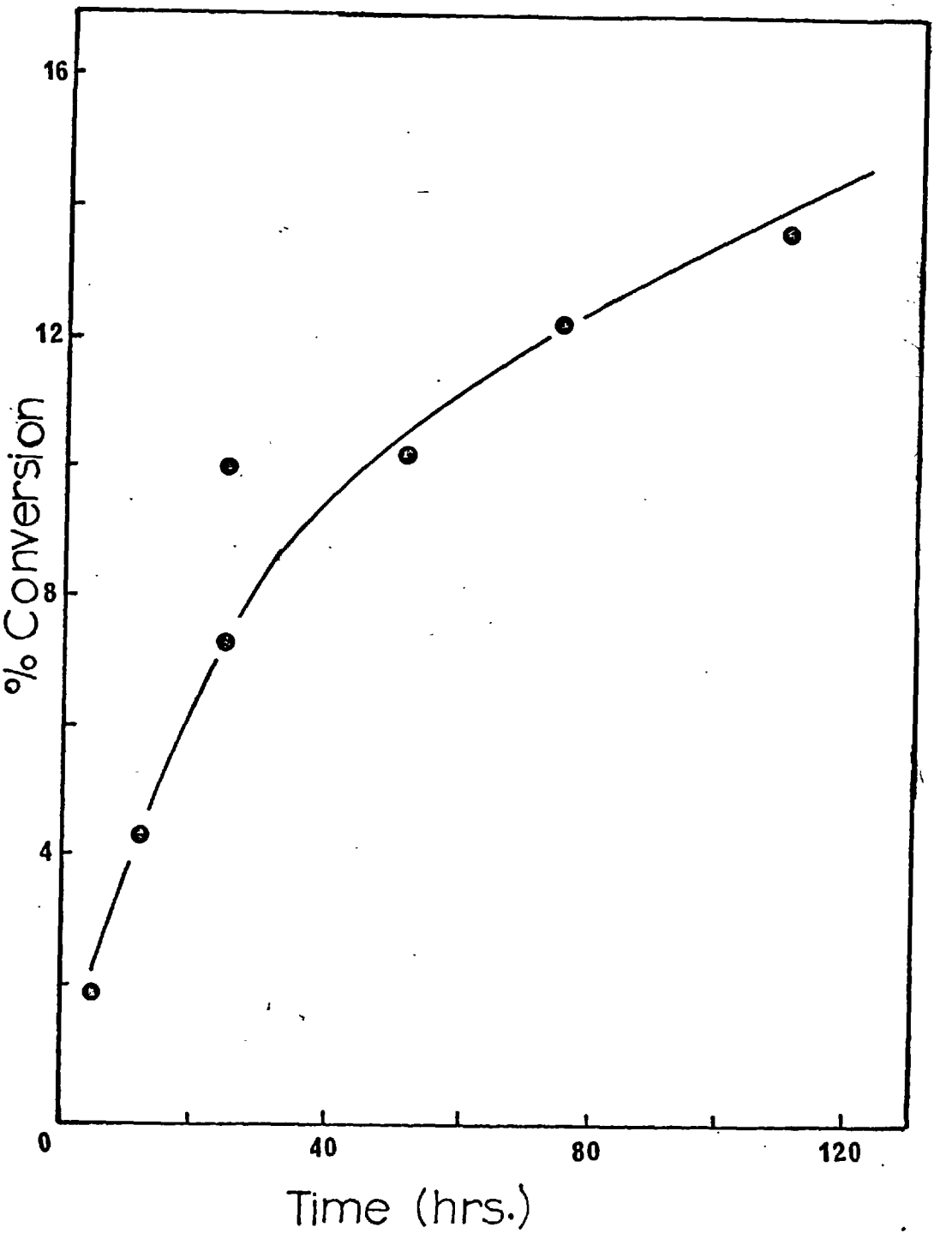
Indene

Conversion-Time Results for Bulk Polymerization†

Experiment	Time (hrs.)	% Conversion
I1	4.2	1.9
I2	11.0	4.3
I3	23.2	7.3
I4	24.1	9.9
I5	52.0	10.1
I6	75.8	12.2
I7	110.0	13.6
I8	142.0	13.8

† 0.5% Bz_2O_2, 80°C, 1 atm.

The above results are illustrated in Figure 22. The conversion-time curve is normal but as the rate falls off after only a few percent



Polymerization of Indene at 80°C

Figure 22

conversion. In view of these results, experiments used for rate determinations were carried to less than 5% conversion.

The recovered polymer was a soft yellow solid that melted at ~ 80°C to form a mobile straw-coloured liquid. This melting point indicates[137] that the polymer is composed mainly of dimers and trimers. It is assumed that, despite the low molecular chain lengths found, the kinetic chain length is large. This view is supported by the relatively high transfer to monomer results found by other authors[155,159]. This in turn is probably due to resonance-stabilization[160] and steric hindrance[153].

The following table shows the effect of pressure on the bulk polymerization of indene at 80°C.

TABLE 7-29

Indene Variation of Rate with Pressure			
Experiment	Pressure (atm.)	$10^6 R_p$ (moles/l./sec.)	Molecular Weight
I1	1	1.08	380
I9	1000	2.30	400
I10	2000	4.48	445
I11	3000	5.96	480
I12	3000	5.55	-
I13	4000	7.10	500
I14	5000	9.89	520
I15	6000	3.44	-
I16	10000	7.08	-

0.5% Bz_2O_2, 80°C

A plot of log R_p vs. pressure is shown in Figure 23. As may be seen from this graph ΔV_T^* is a function of pressure, but from the near-linear portions of the curve in the ranges 1 - 2000 atm. and 2000 - 5000 atm. the approximate values of ΔV_T^* are found to be 21 cc/mole and 8 cc/mole, respectively. The relatively low rate results in Table 7-29 above 5000 atm. pressure probably indicate that the freezing pressure of indene lies between 5000 - 6000 atm.. The relatively small increase in molecular weight is similar to that found in the polymerization of allyl acetate[110] under pressure, and is probably due to $k_{tr,M}$ being accelerated almost as much by pressure as k_p.

The variation in the rate of polymerization of indene with varying initiator concentration is given in the following table for experiments at atmospheric pressure and at 3000 atm..

TABLE 7-30

Indene

Variation of Rate with Initiator Concentration†

Experiment	Pressure (atm.)	10^3[In] (moles/l.)	$10^7 R_p$ (moles/l./sec.)
I17	1	1.36	1.69
I18		8.59	4.23
I19		21.30	9.74
I1		42.70	10.82
I20		85.50	15.10
I21		172.00	23.50
I22	3000	3.18	19.05
I23		8.51	30.30
I11		42.80	59.60
I12		42.40	55.50
I24		84.80	70.80

† 80°C

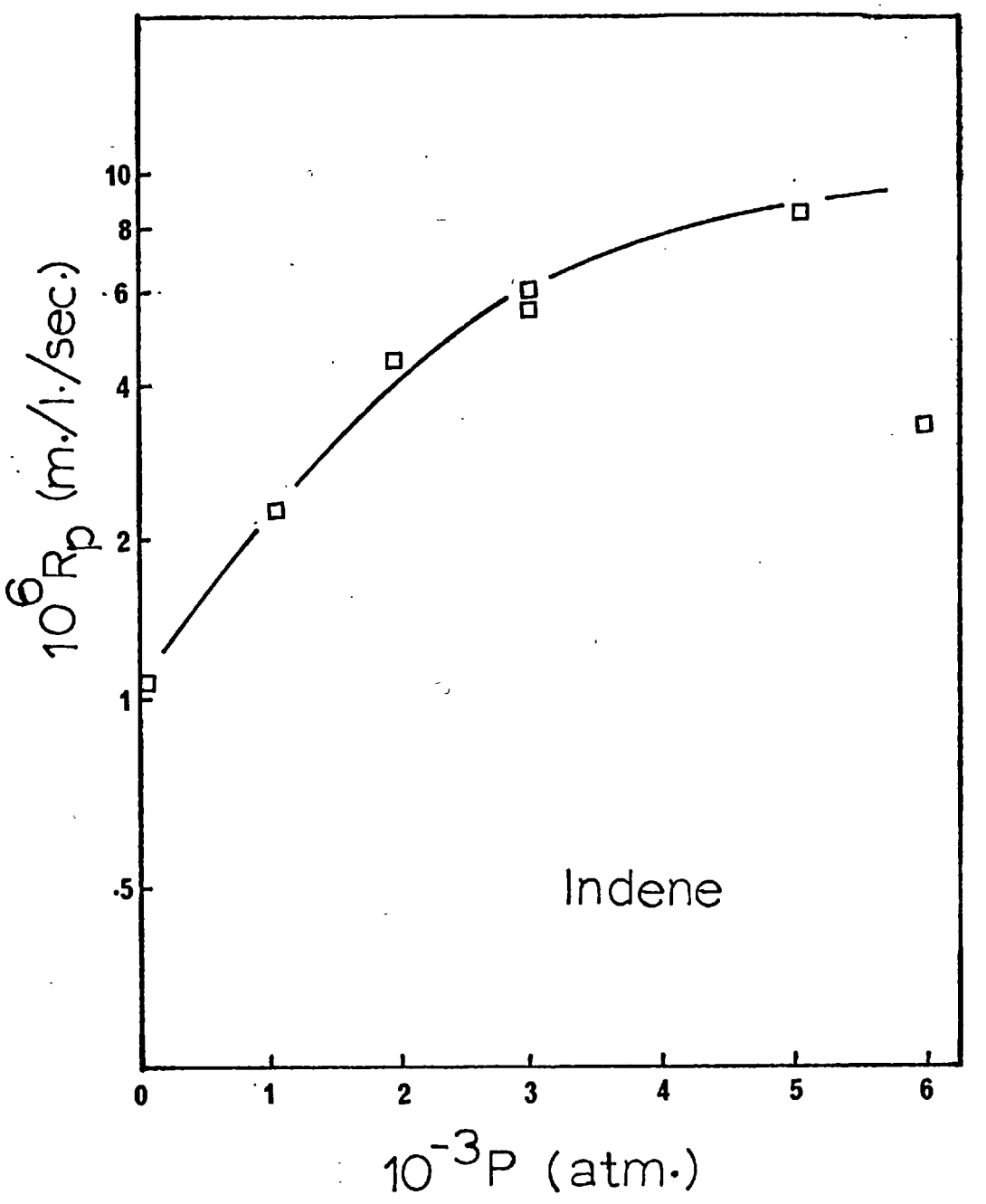


Figure 23

The logarithmic plots of R_p vs. [In] for these results are illustrated in Figure 24. The plots are straight lines at both pressures with slopes at 1 atm. and at 3000 atm. of 0.5 and 0.4 respectively. A similar decrease in the catalyst exponent of the rate equation was noted for the polymerization of styrene under pressure[115].

The following table gives the variation of the rate of polymerization of indene with temperature at atmospheric pressure.

TABLE 7-31

Indene Variation of Rate with Temperature†		
Experiment	Temperature (°C)	$10^7 R_p$ (moles/l./sec.)
I1	80	10.82
I25	70	6.17
I26	60	3.31
I27	50	1.90

† 0.5% Bz_2O_2

A plot of log R_p vs. $10^3/T$ is linear and from its slope E_T is found to be 23.2 kcal./mole.

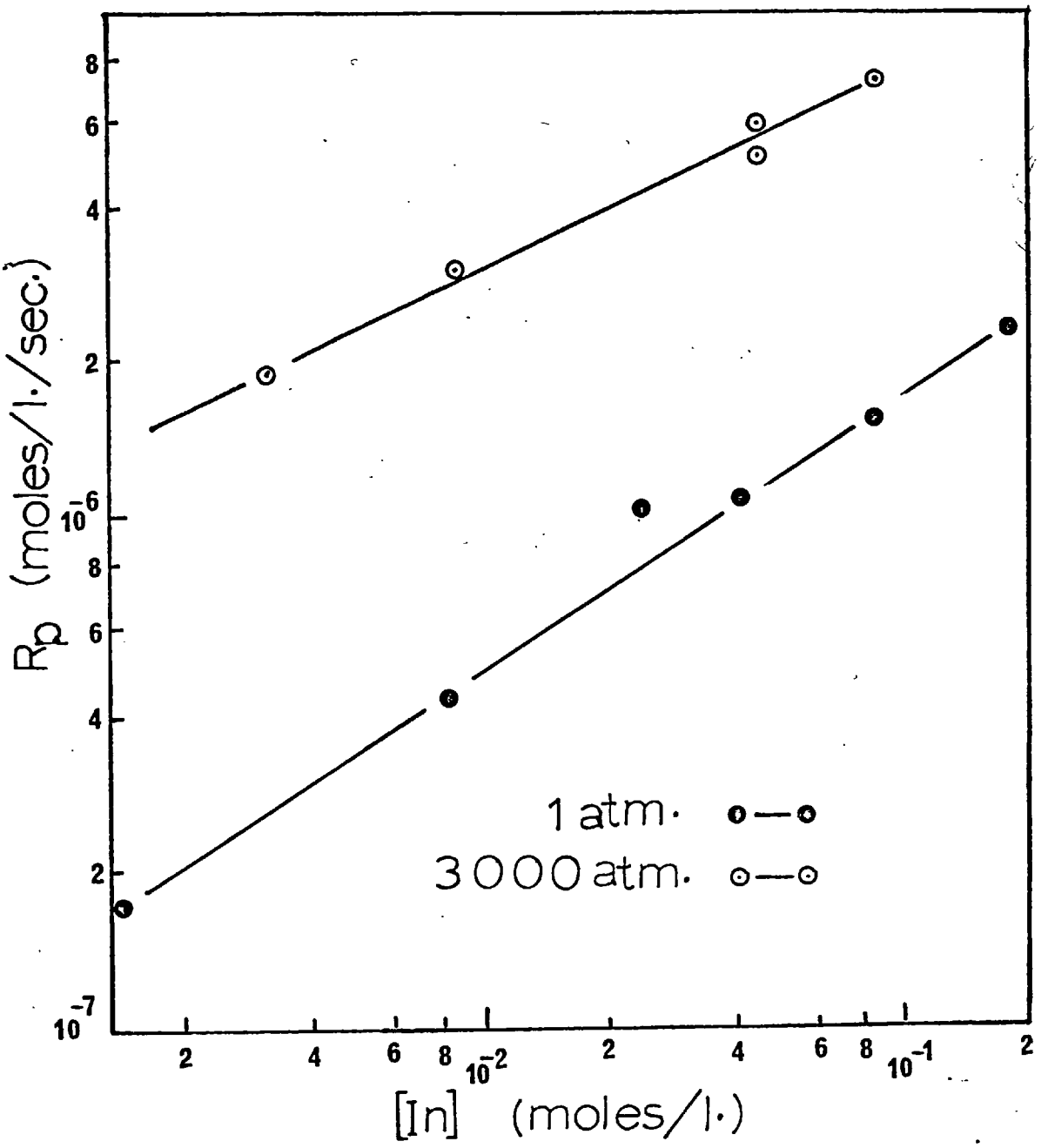

8
6
4
2
10^{-6}
8
6
4
2
10^{-7}
R_p (moles/l./sec.)
1 atm.
3000 atm.
2
4
6
8
10^{-2}
2
4
6
8
10^{-1}
2
[In] (moles/l.)

Figure 24

E. DIALLYLAMINE HYDROCHLORIDE

Investigations of the free radical cyclopolymerization of the symmetrical diene, diallylamine hydrochloride (X) were carried out in aqueous solution at 65°C.

$$CH_2=CH-CH_2-\overset{+}{N}H_2(Cl^-)-CH_2-CH=CH_2$$

X

Experiments were attempted at atmospheric pressure and at 3000 atm. using tert-butyl hydroperoxide (TBHP) as the initiator.

The only previous examination of this monomer was by Butler et al[63] who reported that they dissolved 1.7 grams of diallylammonium chloride in an equal amount of water with 0.05 mls. of 60% TBHP and heated the solution at 65°C for 4 days. The resultant polymer after powdering and vacuum drying was a pale brown hydroscopic solid (1.6 gms.), readily soluble in water. The following table lists a few similar experiments with this monomer.

TABLE 7-32

Diallylamine Hydrochloride
Polymerizations at 65°C and [M] = 3.9 moles/l.†

Experiment	Pressure (atm.)	% TBHP	Time (hrs.)	Result
DA1	1	0	97	yellowish, slightly viscous liquid.
DA2	1	2	97	brownish-yellow very viscous liquid.
DA3	1	4	97	brown solid.
DA4	3000	4	48	" " .

† aqueous solution, 1 gm. DA/gm. H_2O

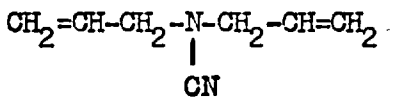
It was assumed that the conversion in each case was approximately 100%. The polymers from the experiments at 4% TBHP (DA3 and DA4) were hydroscopic. Residual unsaturation examinations showed that $f_c = 0.95$ for the polymer from experiment DA2. In the bromination of the solid polymers (DA3 and DA4) it was found that $V_s \sim V_b$ which indicates that the polymers were probably 100% cyclized.

The polymers were soluble in water, dimethyl sulfoxide, DMF, MeOH, $CHCl_3$, dichloroethylene, and epoxy propane. They were insoluble in acetone, CCl_4, benzene, ether, cyclohexanone, toluene, and n-butanol. The monomer was soluble in the same solvents as the polymer and no solvent system could be found which would dissolve the monomer and not the polymer. Consequently, kinetic investigations of the polymerization of this monomer were unfeasible.

The results do, however, confirm the suppositions by Butler et al[63] that the polymers formed in the cyclopolymerization of diallylammonium salts are 100% cyclized.

F. DIALLYL CYANAMIDE

Investigations of the free radical cyclopolymerization of the symmetrical 1,6 diene, diallyl cyanamide (XI) were carried out in solution at 80°C.



XI

The experimental pressure range was 1 - 6000 atm. and tert-butyl perbenzoate was the initiator. Polymerization experiments were carried out in bulk and in toluene solution. The range of monomer concentrations was 0.9 to 7.3 moles/l. and the polymerization was heterogeneous in all of the experiments studied.

The cyclopolymerization of this monomer at atmospheric pressure has been reported by Uno et al[72]. They found the overall rate of polymerization of diallyl cyanamide to be first order with respect to the initiator, and either first or second order with respect to monomer concentration, depending on the solvent used. It was also found that the molecular weight of the polymer was independant of both initiator and monomer concentrations and the major mode of termination was proposed to be intramolecular hydrogen abstraction (see equation 3-16).

The cyclopolymerization of diallyl cyanamide was carried out in toluene solution, at a monomer concentration of 3.7 moles/l. with 2% TBPB. Conversion-time results at atmospheric pressure are listed in Table 7-33.

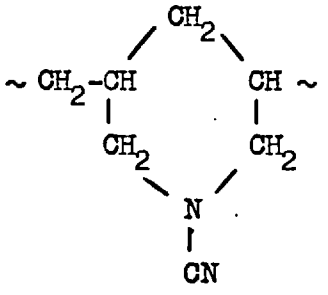
TABLE 7-33

Diallyl Cyanamide Conversion-Time Results in Toluene Solution at 1 atm.†		
Experiment	Time (hrs.)	% Conversion
DC1	16.3	1.0
DC2	47.6	2.2
DC3	95.8	3.7
DC4	144.2	5.0
DC5	166.8	5.5

† [M] = 3.7 moles/l., 2% TBPB, 80°C

As may be seen from the above table, the conversion-time results are normal. The polymerization was heterogeneous and the polymer was precipitated from the reaction medium as a granular solid. The vacuum-dried polymer was a pale, yellowish powder which was insoluble in water or common organic solvents. It was, however, partially soluble in DMF, acetone, pyridine, cyclohexanone and nitrobenzene; and completely soluble in liquid (melted) phenol and m-cresol. A typical sample (DC2) had a molecular weight (cryoscopic) of only 650. Such low molecular weights are typical of allylic polymers.

The cyclic repeating unit of poly(diallyl cyanamide) may be represented:



Because piperidine rings absorb in the far ultraviolet[145], direct

absorption evidence for the cyclopolymer structure was not feasible. However, indirect evidence was available from the observation that infra-red absorptions associated with a terminal methylene group (1645, 990, and 930 $cm.^{-1}$) which were present in the spectrum of the monomer (liquid cell) were greatly reduced in the spectra of the polymers (Nujoll mull) produced at atmospheric pressure and almost absent in the spectra of polymers produced at higher pressures.

The variation of the rate of polymerization of diallyl cyanamide with initiator concentration at atmospheric pressure is given in the following table.

TABLE 7-34

Diallyl Cyanamide Variation of Rate with Initiator Concentration at 1 atm.†		
Experiment	10^2[In] (moles/l.)	$10^7 R_p$ (moles/l./sec.)
DC2	7.3	3.80
DC6	12.4	6.50
DC7	19.0	10.26
DC8	29.2	15.80
DC9	41.9	23.20
DC10	70.7	35.40

† [M] = 3.7 moles/l., 80°c

A logarithmic plot of R_p vs. [In] is linear with a slope of 1.0. This value suggests monoradical (i.e. degradative) termination, and is the same as the results for the catalyst exponent that were found in benzene and m-cresol solutions at 70°C[72].

The variation of the rate of polymerization with monomer concentration at atmospheric pressure is given in the following table.

TABLE 7-35

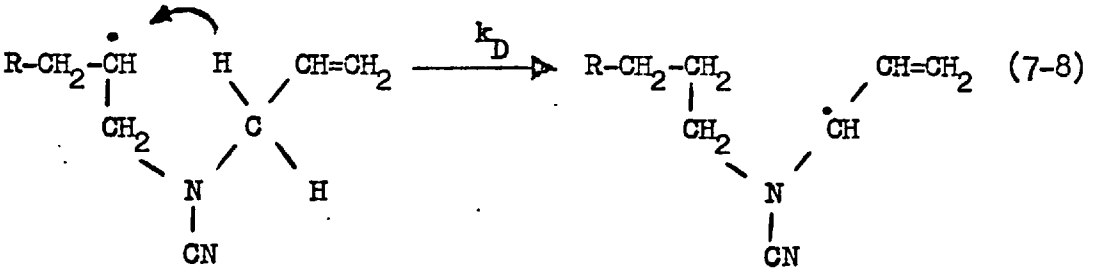
Diallyl Cyanamide Variation of Rate with Monomer Concentration at 1 atm. †		
Experiment	[M] (moles/l.)	$10^7 R_p$ (moles/l./sec.)
DC11	0.9	0.27
DC12	2.1	1.70
DC2	3.7	3.80
DC13	5.1	7.69
DC14	5.6	9.74
DC15	6.3	11.30
DC16	6.6	11.90
DC17	7.3 (bulk)	15.10

† 2% TBPB, 80°C

The logarithmic plot of R_p vs. [M] is linear and has a slope of 2.0. This result is identical to the kinetic dependance of rate on monomer concentration found for the homogeneous polymerization of diallyl cyanamide in m-cresol solution at 70°C[72]. It was also found that the rate varied as the first power of the monomer concentration in benzene solution.

The molecular weights of several of the samples obtained from the polymerization of diallyl cyanamide in toluene at 80°C and at varying monomer and initiator concentrations were determined and all found to have a molecular weight of ~ 650. This is in agreement with the results of Uno et al[72] who found that the specific viscosities of their poly(diallyl

cyanamide) samples varied only slightly for polymers obtained at various initiator and monomer concentrations. Polymers were found to have an average of only one double bond per molecule. Coupled with the first order rate dependence on initiator concentration, these results indicate that $R_1^\bullet + M$ and $R_2^\bullet + M$ termination reactions are unlikely, and suggest that the termination reaction is $R_1^\bullet$ (intramolecular).



(7-8)

XIII XIV

If, as seems highly likely, it is assumed that the noncyclized ($R_1^\bullet$) radicals engage only in intramolecular reactions (cyclization and termination) then linear propagation would proceed by the addition of monomer to the cyclized ($R_2^\bullet$) radicals. In such a case, the theoretical expression for the rate of polymerization is given by equation (4-21).

$$R_p = \frac{2fk_dk_c[In]}{k_D} \qquad (4\text{-}21)$$

However, it has already been seen that $R_p \propto [In][M]$ in benzene solution and $R_p \propto [In][M]^2$ in toluene or m-cresol solutions. Uno and his co-workers have developed a theoretical expression to account for their results, but it does not consider cyclization and it cannot be extended to account for the polymerizations of diallyl cyanamide at higher pressures (which are presented below).

Three possible reasons which, alone or in conjunction with each other, might explain the anomalous kinetic dependence on the monomer concentration are occlusion, cyanide group initiation and induced decomposition.

1) Occlusion - The polymerization of diallylcyanamide is heterogeneous in toluene solution and in benzene solution (although Uno et al[72] do not point this out in their paper). As seen from Section II and from the experimental results for the polymerization of acrylic anhydride, heterogeneous conditions can often cause unusual kinetic results as a result of physical effects. However, such an explanation is considered unlikely as the first order rate dependence on initiator concentration is felt to be the result of degradative termination rather than occlusion. Also, the polymer is readily soluble in m-cresol and the polymerization in that solvent is apparently homogeneous, giving the same overall rate dependence as the heterogeneous polymerization in toluene solution. Since it is not expected that heterogeneous conditions would cause a different integer rate dependence in benzene solution ($R_p \propto [M]$) than in toluene solution ($R_p \propto [M]^2$), such an explanation is not considered to be valid. The short polymer chain lengths, low experimental conversions, normal conversion-time curves, and integer monomer exponents all suggest that chemical, rather than physical, effects are responsible for the results.

2) Cyanide Group Initiation - As pointed out in the discussion of the results for the polymerization of acrylic anhydride (see Section VII-C) a cyanide group initiation reaction was suggested to explain the high degree of chain branching which occurred in the polymerization of methacrylonitrile[36]. If such a reaction were possible with diallyl

cyanamide then this monomer would be capable of forming five radicals in polymerization rather than just two. The kinetics of such a polymerization would probably be extremely complex and might explain the experimental results. This explanation is also considered unlikely for the same reasons as discussed above. Also, the reactivity of a pseudo-halogen cyanide group is not the same as that for a cyanamide cyanide group so there is no reason to suppose that initiation of this latter group will occur even if the initiation of the former group (see equation 7-7) is possible.

3) Induced Decomposition - The most probable explanation for the kinetic dependence on monomer concentration is through complex monomer-initiator-solvent interactions. The following theoretical analysis is suggested as one possible explanation which yields rate expressions which agree, at least quantitatively, with the experimental results.

If the effective initiator decomposition reaction in the polymerization of diallyl cyanamide may be represented:

$$In + M \xrightarrow{k_d'} 2Z^{\bullet} \qquad (7\text{-}9)$$

then the expression derived as equation (4-21) would be raised by a power of [M] and the new expression would agree with the experimental results for the polymerization of diallyl cyanamide in benzene solution[72]. It is well known[161] that in many cases of vinyl polymerization the efficiency of the initiator may vary appreciably with the initiator, monomer, and medium used. Induced chain decomposition (discussed in Sections I-E and V-B-3) has been suggested as a possible explanation and it was noted[11,21,110] that allylic monomers were particularly susceptible to this effect.

Walling[161] has suggested that an induced decomposition involving the simultaneous cleavage of the initiator and bond formation between an initiator fragment and a monomer molecule, often occurs. In the polymerization of styrene initiated by t-butyl hydroperoxide the following reaction was suggested for the decomposition[162].

$$ROOH + CH_2{=}CH{-}\phi \longrightarrow ROO^{\bullet} + CH_3{-}\dot{C}H{-}\phi \qquad (7\text{-}10)$$

Rapid induced decomposition reactions also occur in the presence of many solvents (see equation 1-30 and 1-31). Since solvents with methyl groups which are not part of an aromatic ring are known[163] to be much more reactive than benzene, it might be expected that toluene and m-cresol would be highly susceptible to initiator radical attack[112]. If the resulting solvent transfer radicals were either too inactive to re-initiate chain growth or were effectively lost for this purpose by some complexing reaction, then the transfer reaction could be effectively represented:

$$Z^{\bullet} + SX' \xrightarrow{k_s} \text{inactive products} \qquad (7\text{-}11)$$

In such a case the rate of change of initiator concentration with time becomes:

$$\frac{d[Z^{\bullet}]}{dt} = k_d'[In][M] - k_i[Z^{\bullet}][M] - k_s[Z^{\bullet}][S] = 0 \qquad (7\text{-}12)$$

Using equation (6-3):

$$[Z^{\bullet}] = \frac{k_d'[In][M]}{k_s/10^3 V_s + [M](k_i - k_s V_m/V_s)} \qquad (7\text{-}13)$$

If k_t and $k_s V_m/V_s$ are of about the same order the following approximation is obtained:

$$k_t[Z^\cdot][M] \sim k_z[In][M]^2 \qquad (7\text{-}14)$$

where

$$k_z = 10^3 k_d' k\, Vs/k_s \qquad (7\text{-}15)$$

Using the result obtained in equation (7-14) the expression derived as equation (4-21) becomes instead:

$$R_p = \frac{k_c k_z [In][M]^2}{k_D} \qquad (7\text{-}16)$$

This new expression agrees in overall rate dependence with the results found for the polymerization of diallyl cyanamide in toluene or m-cresol solutions. Thus, it is seen that rapid induced decomposition reactions are one possible explanation for the anomalous monomer dependence found in the experimental results.

The variation of the rate of polymerization of diallyl cyanamide in toluene solution with monomer concentration at 3000 atm. pressure is given in the following table.

TABLE 7-36

Variation of Rate with Monomer Concentration at 3000 atm.†

Experiment	[M] (moles/l.)	$10^6 R_p$ (moles/l./sec.)
DC18	1.2	0.19
DC19	2.4	1.05
DC20	3.7	2.62
DC21	3.7	2.68
DC22	4.8	3.78
DC23	6.1	6.03
DC24	7.3 (bulk)	10.20

† 2% TBPB, 80°C

A logarithmic plot of R_p vs. [M] is linear with a slope of 2.0, the same slope as found for the results at atmospheric pressure.

The variation of the rate of polymerization with initiator concentration at 3000 atm. is given in the following table.

TABLE 7-37

Diallylcyanamide

Variation of Rate with Initiator Concentration at 3000 atm.†

Experiment	10^2 [In] (moles/l.)	$10^6 R_p$ (moles/l./sec.)
DC25	1.4	1.03
DC26	2.5	1.65
DC27	3.6	1.73
DC28	4.8	2.12
DC20	7.3	2.62
DC21	7.2	2.68
DC29	16.1	3.61
DC30	18.6	3.80
DC31	98.8	8.58

† [M] = 3.7 moles/l., 80°C

The results given in Tables 7-34 (1 atm.) and 7-37 (3000 atm.) are illustrated in logarithmic form in Figure 25. The logarithmic plot of R_p vs. [In] at 3000 atm. is linear and has a slope of 0.5. A similar change in the kinetic dependence on initiator concentration, from 1.0 at atmospheric pressure to 0.5 at 5500 kg./cm.^{2}, was noted in the polymerization of allyl acetate[110]. The square root dependence indicates that at 3000 atm. the termination reaction is biradical. Thus, for the cyclopolymerization of diallyl cyanamide at 3000 atm. the overall rate

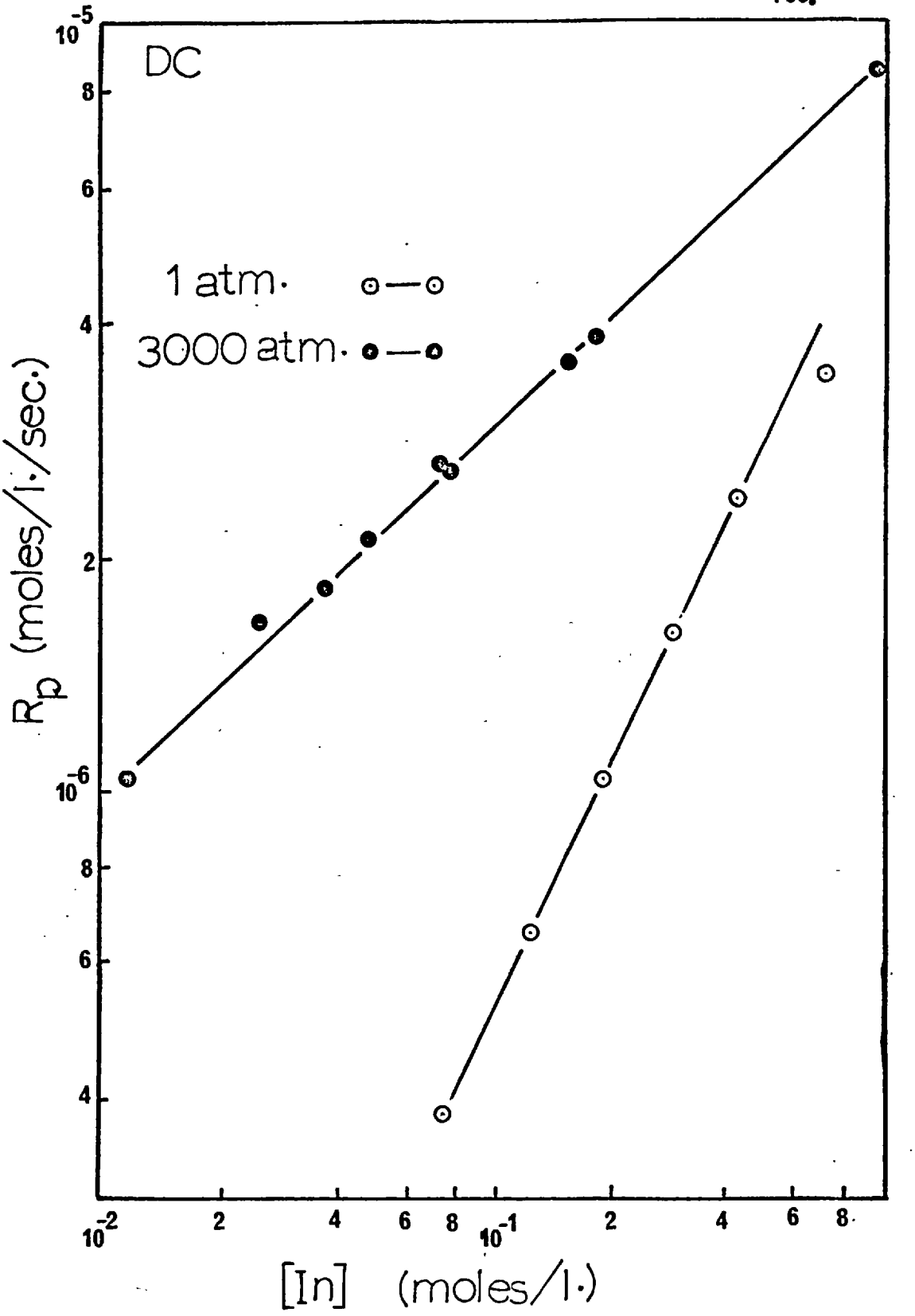

DC
1 atm.
3000 atm.
R_p (moles/l./sec.)
[In] (moles/l.)
10^{-5}
8
6
4
2
10^{-6}
8
6
4
10^{-2}
2
4
6
8
10^{-1}
2
4
6
8

Figure 25

may be represented:

$$R_p = K_{3000}[In]^{\frac{1}{2}}[M]^2 \qquad (7\text{-}17)$$

Applying the same induced decomposition arguments as were described for the atmospheric pressure results, it may be easily shown that equation (4-15) becomes:

$$R_p = k_2(k_z/k_t)^{\frac{1}{2}}[In]^{\frac{1}{2}}[M]^2 \qquad (7\text{-}18)$$

This new theoretical expression agrees with the overall experimental rate dependence found for the polymerization of diallyl cyanamide in toluene solution at 3000 atm. pressure.

The variation of the rate of polymerization with pressure is given in the following table.

TABLE 7-38

Diallyl Cyanamide

Variation of Rate with Pressure at 80°C†

Experiment	Pressure (atm.)	$10^7 R_p$ (moles/l./sec.)	Molecular Weight
DC2	1	3.80	650
DC32	1000	9.94	1150
DC33	2000	20.58	1100
DC20	3000	26.20	1170
DC21	3000	26.80	-
DC34	4000	43.85	1220
DC35	5000	59.57	1350
DC36	6000	115.80	1300

† [M] = 3.7 moles/l., 2% TBPB

The variation of log R_p with pressure is illustrated in Figure 26. The value of ΔV_T^* in the near-linear region of the curve from 1000 - 6000 atm. was found to be - 14.3 cc/mole. This result may be compared with the value of - 13.4 cc/mole obtained by Walling and Pellon[110] in the polymerization of allyl acetate in the region of biradical termination (5500 - 8500 kg./cm.^{2}). It seems likely that biradical termination becomes predominant between 1 and 1000 atm. (see Figure 26) in the polymerization of diallyl cyanamide. This is also evident from the molecular weight results which show a sharp increase in this region. No such increase was observed in the polymerization of allyl acetate in bulk[110], so it seems probable that the biradical termination reaction, when it occurred, in that case, was by disproportionation. In the case of the solution polymerization of diallyl cyanamide, the near doubling of the molecular weight, after biradical termination becomes dominant, probably indicates that the biradical termination reaction is largely by coupling. The polymer produced at high pressures was a white powder in contrast to the yellowish polymer obtained at atmospheric pressure.

In the polymerization of allyl acetate, biradical termination occurred after M^* radicals became active enough to re-initiate chain growth, and k_p increased relative to k_D. In the cyclopolymerization of diallyl cyanamide the DCT reaction does not compete directly with the propagation reaction but rather with the cyclization reaction. (An $R_1^\bullet$ radical may cyclize to form an $R_2^\bullet$ radical or terminate intramolecularily to form a resonance-stabilized R_1^* radical). The results for the cyclopolymerizations of allyl methacrylate and acrylic anhydride show that cyclization is favoured by pressure. Thus, it seems probable that the relatively early change to biradical termination in the

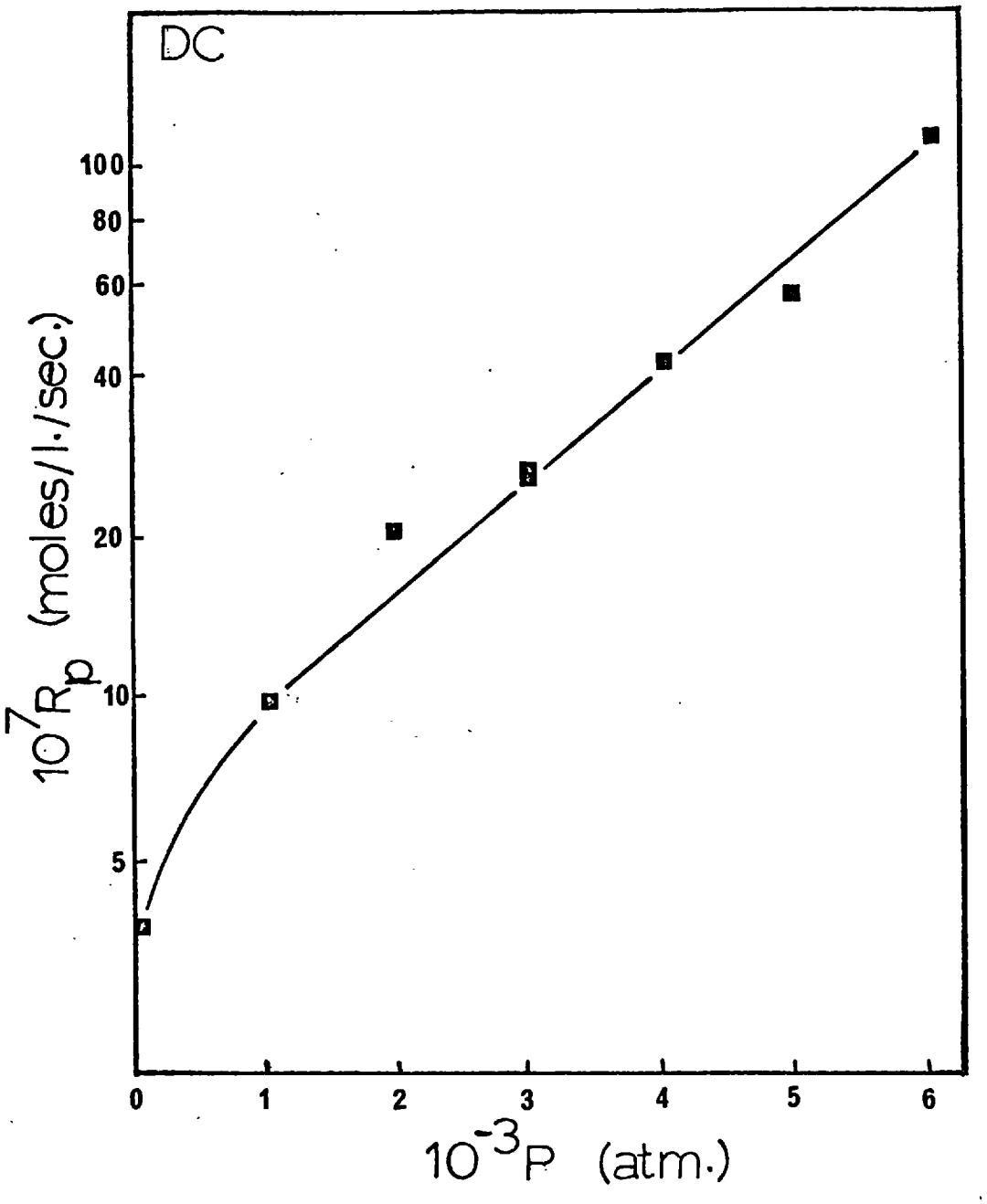


FIG.26: Variation of R_p with Pressure.

cyclopolymerization of diallyl cyanamide under pressure (at 1 - 1000 atm. compared to above 5000 atm. for allyl acetate) is caused as much by a great increase in the rate of cyclization relative to DCT termination, as by the re-initiation of R_1^* radicals.

The variation of the rate of polymerization with temperature at atmospheric pressure and at 3000 atm. is given in the following table.

TABLE 7-39

Diallyl Cyanamide Variation of Rate with Temperature†			
Experiment	Pressure (atm.)	Temperature (°C)	(moles/l./sec.)
DC37	1	60	0.32
DC38		70	1.42
DC2		80	3.80
DC39		90	14.26
DC40	3000	60	5.01
DC41		65	8.68
DC42		70	13.20
DC20		80	26.20
DC43		90	56.20

† [M] = 3.7 moles/l., 2% TBPB

The graphs of log R_p vs. $1/T$ at atmospheric pressure and at 3000 atm. are given in Figure 27. The plots are linear and from their slope the values of E_T at 1 atm. and at 3000 atm. are found to be 29.7 and 19.4 kcal./mole, respectively. This large decrease in the overall activation energy further illustrates the occurrence of biradical termination at higher pressures.

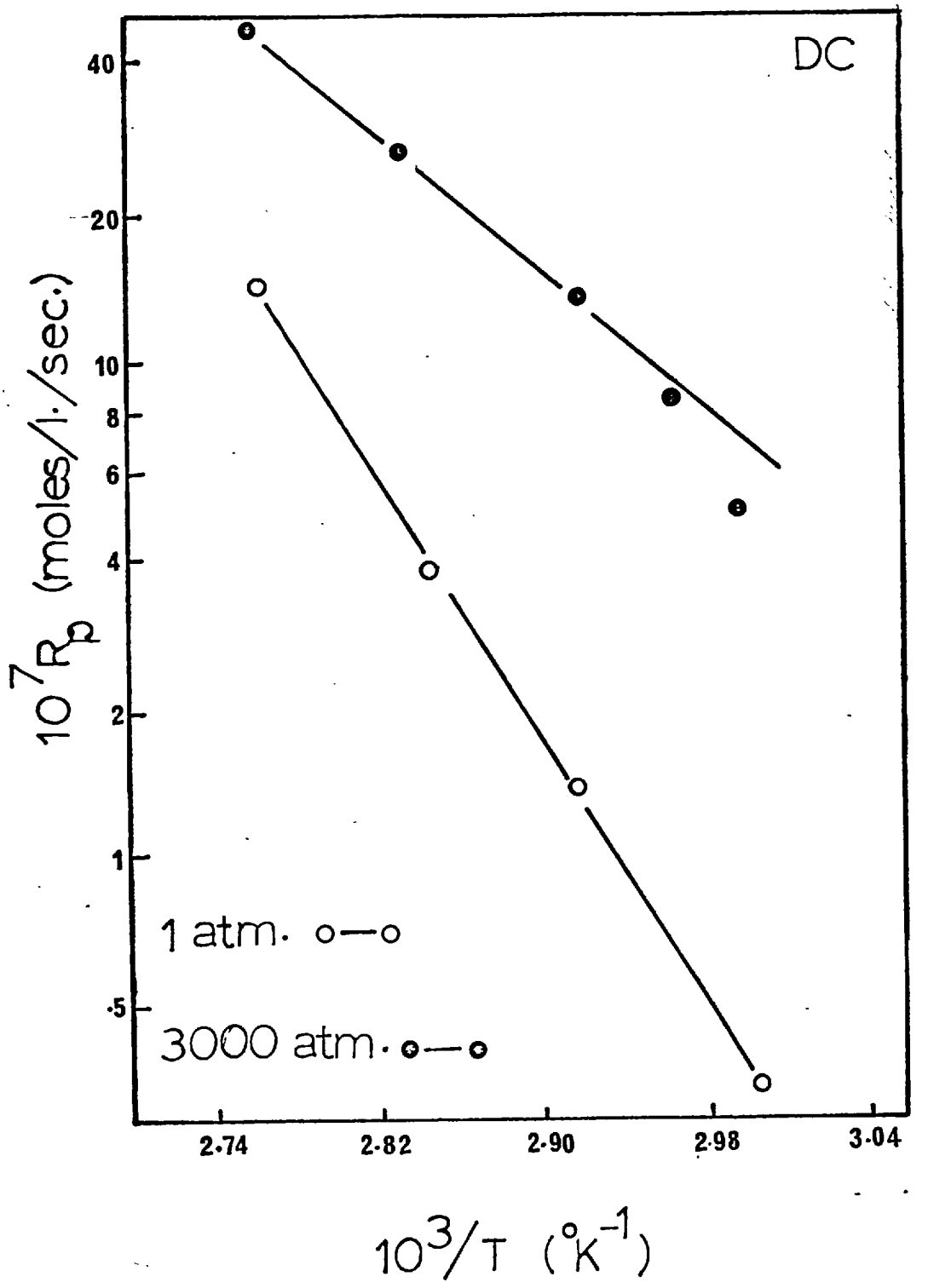
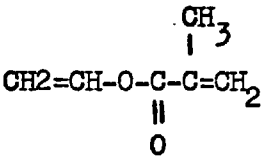

DC
40
20
10
8
6
4
2
1
·5
$10^7 R_p$ (moles/l./sec.)
1 atm. o—o
3000 atm. o—o
2·74
2·82
2·90
2·98
3·04
$10^3/T$ (°K^{-1})

Figure 27

G. VINYL METHACRYLATE

Investigations of the free radical cyclopolymerization of the unsymmetrical 1,5 diene, vinyl methacrylate (XV), were carried out in solution.



XV

Polymerizations were carried out in bulk, in cyclohexanone solution at 50°C and in dioxan solution at 60°C. The initiator was AIBN and the range of monomer concentrations was 0.9 to 8.3 moles/litre.

The cyclopolymerization of this monomer has been reported by Kawai[90] who obtained soluble cyclopolymers at low conversions from the AIBN-catalysed polymerization in toluene solution at 65°C. The polymers were soluble in chloroform and acetone and the percentage of cyclized units in them was estimated to be 50 - 60%.

The cyclopolymerization of this monomer was attempted at 50°C in cyclohexanone solution and at 60°C in dioxan solution using 0.1% AIBN. Under these conditions a large induction period was observed before polymerization began. In attempts to eliminate this inhibition, the monomer was double-distilled and was then pre-polymerized in bulk, to a few percent conversion, before a third distillation. However, it was found that polymerization carried out using this monomer still showed an induction period although its length was greatly reduced. Sample preparation using the vacuum-filling technique had only a small effect on the duration of the induction period so it is felt that absorbed oxygen is not responsible.

The following table shows conversion-time results for the polymerization of vinyl methacrylate in dioxan solution.

TABLE 7-40

Vinyl Methacrylate Conversion-Time Results at Atmospheric Pressure†		
Experiment	Time (mins.)	% Conversion
VM1	20	2.1 *
VM2	20	2.8
VM3	30	1.1
VM4	30	3.1
VM5	31	3.9 *
VM6	45	11.3
VM7	46	9.7
VM8	46	12.0 *
VM9	60	7.8
VM10	60	13.2
VM11	70	17.2 *
VM12	80	20.5 gel

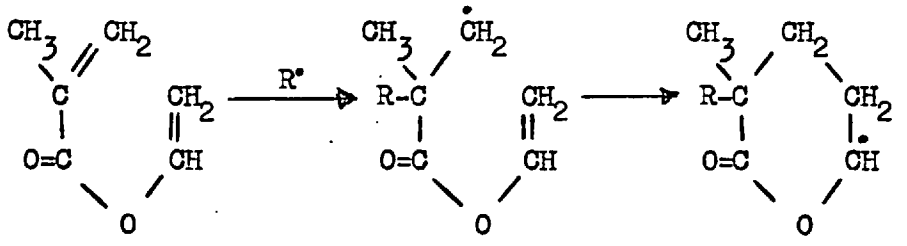
† [M] = 2.1 moles/l., 0.1% AIBN, 60°C, dioxan solution

* Vacuum-filling technique used

The polymers produced below the gel point were soluble in common organic solvents. Like poly(allyl methacrylate) samples, they gradually became insoluble if exposed to air for more than a short time.

Infra-red spectra of the polymers showed no absorption at 1775 $cm.^{-1}$ (five-membered γ-lactone rings) but the -C=O stretch frequency absorption was broadened relative to that of the monomer. These results are in agreement with those of Kawai[90] and indicate[145] the the cyclization reaction proceeds in such a way so as to produce

hexatomic rather than pentatomic rings. The cyclization to produce δ-lactone rings may be represented (for the reaction via the methacrylyl group) by:



(7-19)

As may be seen from the results given in Table 7-40 the induction period is in the region of 10 - 20 minutes. Assuming that this period is relatively constant at varying monomer concentrations, a relation between monomer concentration and rate of polymerization at constant initiator concentration may be obtained. The following table gives the apparent rate of polymerization (R_p') at various monomer concentrations.

TABLE 7-41

Vinyl Methacrylate Variation of Apparent Rate with Monomer Concentration†		
Experiment	[M] (moles/l.)	$10^5 R_p'$ (moles/l./sec.)
VM13	0.9	2.0
VM14	1.5	3.3
VM4	2.1	3.6
VM15	2.8	4.7
VM16	4.2	9.5
VM17	6.2	10.7
VM18	6.5	15.2
VM19	8.3 bulk	24.3

† 0.1% AIBN, 60°C, 1 atm., dioxan solution

Gelation occurred relatively early at higher monomer and initiator concentrations. These results are similar to those obtained by Kawai[90] in toluene solution at 65°C. The reproducibility of the above results and those given in Table 7-40 is very poor.

The following table shows elemental analyses of samples of purified monomer and polymer (VM11).

TABLE 7-42

Vinyl Methacrylate

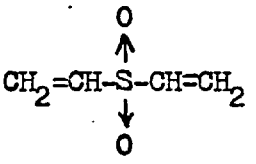
Elemental Analyses of Monomer and Polymer

Percent	Monomer	Polymer	Calculated
Carbon	61.5	60.9	64.3
Hydrogen	7.3	7.4	7.2
Oxygen	29.7	28.9	28.5

The above results seem to indicate that the methods for the preparation and purification of this monomer were unreliable. In view of this, experiments at high pressures were not attempted and a detailed analysis of the kinetics of polymerization of vinyl methacrylate was not attempted.

H. VINYL SULFONE

Investigations of the free radical polymerization of the symmetrical 1,4 diene vinyl sulfone (XVI) were attempted in bulk and in solution



XVI

Experiments were attempted at pressures of up to 5000 atm. and AIBN and Bz_2O_2 were used as initiators.

No homopolymerization results for this monomer have been reported in the literature. The polymerization of vinyl sulfone was attempted in tetrahydrofuran solution at 50°C and a monomer concentration of 6.2 moles/l. with 0.1% AIBN. Experiments carried out at atmospheric pressure, at 1000 atm., and at 5000 atm., for periods of up to 4 days, yielded no polymer. Experiments carried out in bulk at 80°C with 0.5% Bz_2O_2 at atmospheric pressure and at 5000 atm. ended in explosion after a short time.

It was noted, however, that impure monomer would gel if heated at 150 - 180°C for about one hour. An elemental analysis of this polymer is compared with the calculated results in Table 7-43.

TABLE 7-43

Vinyl Sulfone Elemental Analysis of Polymer		
Percent	Polymer	Calculated
Carbon	43.1	40.1
Hydrogen	5.7	5.1
Sulfur	24.3	27.1
Oxygen	-	27.1

From the above results it is apparent that this monomer is unsuitable for kinetic investigations.

SECTION VIII

DISCUSSION AND CONCLUSIONS

In this concluding section the experimental results are summarized and compared with the theoretical derivations and with the published results for the cyclopolymerization of other non-conjugated dienes.

In the free radical cyclopolymerization of most 1,5 and 1,6 dienes, the overall rate of polymerization may be represented by:

$$R_p = K[In]^i[M]^\kappa \qquad (8\text{-}1)$$

The following table shows some of the exponent values in the overall rate equation for cyclopolymerization reactions where biradical termination is expected.

TABLE 8-1

Overall Rate Expressions in Cyclopolymerizations

Diene	Solvent*	i	κ	Reference
Methacrylic Anhydride	DMF	0.5	1.5	70
Methacrylic Anhydride	Cyclohexanone	0.58-0.66	1.0+	100
Acrylic Anhydride	DMF	1.0	0.8-2.3	†
Divinyl Formal	Benzene	0.75	1.5-2.0	71
Allyl Methacrylate	DE	0.69	1.64	†
Vinyl-Trans-Cinnamate	Benzene	0.58-0.93	1.0+	74
Diallyl Cyanamide††	Toluene	0.5	2.0	†

* all except AM and DC, catalysed by AIBN

† this work

†† at 3000 atm. pressure, all others at 1 atm.

As may be seen from Table 8-1, in most cases of cyclopolymerization the catalyst exponent in the overall rate equation has a value greater than the value of 0.5 predicted from the theoretical rate expressions developed in Section IV.

Minoura and Mitch[71] have developed a theoretical expression for simple cyclopolymerization, based on the homogeneous polymerization of divinyl formal at 50°C, and it predicts that $0.5 \leq i \leq 1.0$ and $1.5 \leq \kappa \leq 2.0$. In the derivation of the rate expression it is assumed that all three modes of biradical termination ($R_1^\bullet + R_1^\bullet$, $R_1^\bullet + R_2^\bullet$ and $R_2^\bullet + R_2^\bullet$) occur simultaneously and that the kinetic chain length is low enough for the initiation and termination reactions to be factors determining the stationary state relationships between the various radicals. However, their own measurements of molecular weight for poly(divinyl formal) indicated that $\overline{DP} \sim 100$, so the rate expression cannot be considered valid.

As already noted, Mercier and Smets[99] concluded from ESR and turbidity measurements that the anomalous results found in the apparently homogeneous cyclopolymerization of acrylic anhydride in cyclohexanone solution were due to suspended microgel particles. Similarly, Roovers and Smets[74] detected the occurrence of radical entrapment in the cyclopolymerization of vinyl-trans-cinnamate. It is considered that catalyst exponent values of greater than 0.5 in cyclopolymerization reactions with biradical termination are due, in most cases, to the increasing viscosity of the solution, to the progressive heterogeneity of the reaction medium, and to some trapping of polymer radicals in microgel particles. Indeed, in the cyclopolymerization of diallyl cyanamide at higher pressures, the value of the catalyst exponent is

only 0.5, as might be expected when the cyclopolymer is of low molecular weight and occlusion is unlikely. Unless occlusion is very severe, it is not expected that a value of greater than 0.5 for the catalyst exponent will invalidate the theoretical expressions derived in Section IV.

For the cyclopolymerization of acrylic anhydride in DMF solution, occlusion is so severe that termination is effectively monoradical ($i = 1.0$). However, for the cyclopolymerization of allyl methacrylate in diallyl ether solution, the value of this exponent is only 0.69 at atmospheric pressure despite the fact that the fraction of cyclized units found in poly(acrylic anhydride) is larger than that found in poly(allyl methacrylate). Besides the intrinsic differences in the reactivities of the functional groups and the swelling capabilities of the solvents for the polymers, it is considered that at least part of the difference is due to the following condition. As was previously suggested (see Section VII-B), the residual unsaturation found in the polymers of allyl methacrylate is virtually all due to pendant allyl groups. These groups are relatively unreactive compared to the chain-forming methacrylyl groups; but in the case of the polymers of acrylic anhydride, the pendant groups are identical with the acrylyl groups on the growing chain ends.

Thus, in the cyclopolymerization of the unsymmetrical diene, allyl methacrylate, the effects of chain branching will have much less influence on the kinetics of polymerization than they will for a normal symmetrical diene. Not only may this monomer be regarded as 'pseudo-symmetric'; but because of the relatively unreactive nature of the pendant functional groups in its polymers, its polymerization may be regarded as a model for simple cyclopolymerization.

In the cyclopolymerization of allyl methacrylate in diallyl ether solution, the value of the catalyst exponent falls from 0.69 at atmospheric pressure to 0.62 at 3000 atm.. It is considered that this is due to accelerated chain decomposition and radical recombination reactions of initiator radicals at the higher pressure. A similar effect was observed in the bulk polymerization of indene, where the value of the catalyst exponent fell from 0.5 at atmospheric to 0.4 at 3000 atm. pressure.

In only a few of the examples of cyclopolymerization at atmospheric pressure described in the literature, has the kinetic dependence of both rate and residual unsaturation on monomer concentration been reported (see Table 8-1). In no instance does a straight line relationship exist for only one of the conditions listed in Table 4-3 (i.e. R_p vs. [M], $R_p/[M]$, $R_p/[M]$ vs. [M], or $R_p/[M]^{\frac{1}{2}}$ vs. [M]) or does the resulting slope to intercept ratio obtained from such a relation agree closely with the experimental value of k_1/k_c. In several cases, however, straight line relations were found for more than one condition, (usually $R_p/[M]$ vs. [M] and $R_p/[M]^{\frac{1}{2}}$ vs. [M]) and comparisons of the slope to intercept ratios obtained from such straight lines with the experimental results for k_1/k_c in some cases suggested which of the three possible modes of biradical termination was predominant[93].

In the cyclopolymerization of both acrylic anhydride and vinyl methacrylate suitable straight line relations were not obtained and the kinetic dependence of cyclization on monomer concentration was not determined.

In the cyclopolymerization of allyl methacrylate at atmospheric pressure, excellent agreement of the experimental results with the

theoretical expressions was obtained and the results strongly suggest that the biradical termination reaction was solely between the cyclized radicals ($R_2^{\bullet} + R_2^{\bullet}$). At 3000 atm., straight line relations were obtained in two conditions ($R_p/[M]$ vs. $[M]$ and $R_p/[M]^{\frac{1}{2}}$ vs. $[M]$) and the results suggest that a moderate proportion of cross-termination ($R_1^{\bullet} + R_2^{\bullet}$) is also occurring along with the $R_2^{\bullet} + R_2^{\bullet}$ termination. This result is not unexpected, as it is well known[164] that pressure usually greatly accelerates sterically hindered reactions.

Except for those of diallyl cyanamide, no suitable kinetic results are available for cyclopolymerizations where termination is by degradative transfer. In the cyclopolymerization of diallyl cyanamide at atmospheric pressure, the plot of R_p vs. $[M]$ is linear and has a zero intercept. Since the polymers were only soluble in phenol and m-cresol, determinations of k_1/k_c were not feasible, but other results indicate that the termination reaction is by intramolecular hydrogen transfer.

The derivation of theoretical expressions for the cyclopolymerization of 1,4 dienes is presented elsewhere[91]. Trossarelli and his co-workers[98,165] have also developed theoretical expressions for the cyclopolymerization of unsymmetrical 1,6 dienes. While their results do not include expressions for the overall rate of cyclopolymerization, they do permit, in certain cases, the evaluation of the relative effects of cyclization and intermolecular propagation via each of the two dissimilar functional groups.

Table 8-2 lists a few of the activation energy values for cyclopolymerization at atmospheric pressure for results which have been reported in the literature or determined in this thesis.

TABLE 8-2

Activation Energies for Cyclopolymerizations at 1 atm.

Monomer	System	E_T	$E_1 - E_c$ (kcal./mole)	Ref.
Methacrylic Anhydride	AIBN-DMF	23.0	-	70
Acrylic Anhydride	AIBN-CHO*	-	2.4	99
Acrylic Anhydride	AIBN-DMF	24.5	-	†
Diallyl Cyanamide	TBPB-Toluene	29.7	-	†
Divinyl Formal	AIBN-Benzene	27.7	2.3	71
o-Divinyl Benzene	TMF**-Benzene	-	6.2	166
Allyl Methacrylate	Bz_2O_2-DE	24.4	6.7	†

† this work, * cyclohexanone, ** triphenylmethyl fluoroborate

Data on the individual temperature coefficients of the rate of cyclopolymerization are difficult to interpret as indicated by the complexity of the expressions for the overall activation energies (see Table 4-5). The expression for the overall activation energy for simple cyclopolymerization with $R_2^\bullet + R_2^\bullet$ termination was derived in Section IV as:

$$E_T = \tfrac{1}{2}E_d + E_{1(c)} + E_2 - E_c - \tfrac{1}{2}E_t \qquad (4\text{-}56)$$

This expression was determined by assuming that $E_1 \sim E_c$.

For the cyclopolymerization of allyl methacrylate at atmospheric pressure, $E_1 - E_c$ was found to be 6.7 kcal./mole so in this case, the validity of the above expression may be somewhat limited. Nevertheless, substituting for E_T, E_d (30 kcal./mole[16]), and $E_1 - E_c$, it is found that $E_2 - \tfrac{1}{2}E_t = 2.7$ kcal./mole. This result is in reasonable agreement

with the reported[16] values of $E_p - \frac{1}{2}E_t$ (2 - 5 kcal./mole) for methyl methacrylate, so equation (4-56) probably applies in this case.

Since more than one mode of termination is occurring in the cyclopolymerization of allyl methacrylate at 3000 atm., equation (4-56) will not be expected to apply. Indeed, the substitution of the values for E_T (22.4 kcal./mole), and $E_1 - E_c$ (8.0 kcal./mole) yields a negative value for $E_2 - \frac{1}{2}E_t$. These results give additional support to the theoretical interpretations of the experimental results.

The values of $E_1 - E_c$ obtained in the cyclopolymerization of allyl methacrylate are higher than the reported values for any other non-conjugated diene. However, since only a few results have as yet been published for cyclopolymerizations at atmospheric pressure and none for cyclopolymerizations at higher pressures, no conclusions may be drawn from these experimental results. Results for the cyclopolymerization of methacrylic anhydride under similar conditions (not available) would be useful for comparative purposes.

For the cyclopolymerization of diallyl cyanamide at atmospheric pressure, E_T was found to be 29.7 kcal./mole. This value is typical of values obtained for the overall activation energies of allylic monomers[11]. From equation (7-16) the overall activation energy may be derived as:

$$E_T = E_z + E_c - E_D \qquad (8\text{-}2)$$

No exact value can be ascribed to E_z, but it is probably approximately equal to E_d. Since cyclization and termination may be regarded as competitive reactions in the cyclopolymerization of diallyl cyanamide at atmospheric pressure, a reasonable assumption would be that $E_c \sim E_D$.

Thus, from the above equation, it might be expected that the value of E_d (34.5 kcal./mole for TBPB[17]) would give a rough estimate of E_T and this is in fair agreement with the experimental result.

Similarly, for the cyclopolymerization of diallyl cyanamide at 3000 atm. where termination is biradical, the following approximate expression may be obtained using equation (7-18):

$$E_T \sim \tfrac{1}{2}E_d + E_2 - \tfrac{1}{2}E_t \qquad (8\text{-}3)$$

From the reported results for the polymerization of several monovinyl monomers at atmospheric pressure, it is found[16] that the value of $E_p - \frac{1}{2}E_t$ is usually in the range 0 - 5 kcal./mole. Since it is probable that $E_2 - \frac{1}{2}E_t$ for the cyclopolymerization of diallylcyanamide at 3000 atm. also falls in this range, the expected value of E_T would be 17.3 kcal./mole, plus 0 to 5 kcal./mole and this is in good agreement with the experimental result (19.4 kcal./mole).

The following table lists the volumes of activation found for the monomers examined in this work.

TABLE 8-3

Overall Volumes of Activation	
Monomer	ΔV_T^* (cc/mole)
Allyl Methacrylate	- 15.9
Acrylic Anhydride	+ 1.5 and - 13.8
Diallyl Cyanamide	- 14.3 (birad. Term.)
Indene	- 21 to - 8
Styrene	- 17.8

The results obtained for the overall volume of activation in the polymerizations of acrylic anhydride and indene do not permit the estimation of values for the individual activation volume coefficients.

For the cyclopolymerization of allyl methacrylate at atmospheric pressure, equation (4-7) applies and the overall volume of activation is given by:

$$\Delta V_T^* = \tfrac{1}{2}\Delta V_d^* + \Delta V_{1(c)}^* + \Delta V_2^* - \Delta V_c^* - \tfrac{1}{2}\Delta V_t^* \qquad (5\text{-}5)$$

However, by 3000 atm. pressure, cross-termination reactions ($R_1^\bullet + R_2^\bullet$) are occurring as well, and equation (4-7) will no longer apply. Also, in the determination of equation (5-5) it was assumed that $\Delta V_1^* \sim \Delta V_c^*$ but for the cyclopolymerization of allyl methacrylate it was determined that $\Delta V_1^* - \Delta V_c^* = 7.1$ cc/mole. Thus, the use of equation (5-5) to estimate the individual activation volumes will probably not yield accurate results. Indeed, substituting into equation (5-5) for ΔV_T^*, ΔV_d^* ($\sim +5$ cc/mole), ΔV_t^* ($\sim +12$ cc/mole), and $\Delta V_1^* - \Delta V_c^*$, it is found that $\Delta V_2^* \sim -20$ cc/mole. This result is about double the probable value. Thus, in the case of the cyclopolymerization of allyl methacrylate, the individual volumes of activation of the rate of cyclopolymerization cannot be estimated using the theoretical derivations because of the complexity of the true expression for the overall volume of activation.

In the cyclopolymerization of diallyl cyanamide at high pressures an expression for the overall volume may be obtained using equation (7-18) as before:

$$\Delta V_T^* \sim \tfrac{1}{2}\Delta V_d^* + \Delta V_2^* - \tfrac{1}{2}\Delta V_t^* \qquad (8\text{-}4)$$

Substituting into equation (8-4) for ΔV_T^*(- 14.3 cc/mole), ΔV_d^* and ΔV_t^*, it is found that $\Delta V_2^* \sim$ - 11 cc/mole. This is about the value predicted in Section V. If it is assumed that this value is approximately equal to the value of ΔV_1^* in the cyclopolymerization of allyl methacrylate, then a reasonable value for ΔV_c^* is about - 18 cc/mole.

It is stressed that the values of the individual volumes of activation and activation energy determined above are only to be regarded as rough estimates and probably have only limited accuracy.

A separate discussion has already been given for each monomer in Section VII and previously in this section, but the main features will be summarized below to provide a general outline of the results and conclusions.

(1) In the range of experimental conditions studied, the rate of free radical homopolymerization of the symmetrical 1,6 diene, diallyl ether, was negligible.

(2) The unsymmetrical 1,6 diene, allyl methacrylate, was found to cyclopolymerize in diallyl ether solution to yield soluble cyclopolymers at monomer concentrations and conversions not previously achieved. It is considered that cyclopolymerization proceeds primarily via the methacrylyl groups. It was found that $R_p \propto [In]^{0.69}[M]^{1.64}$ at atmospheric pressure and $R_p \propto [In]^{0.62}[M]^{1.53}$ at 3000 atm. The rate of polymerization is accelerated by pressure and ΔV_T^* was found to be - 15.9 cc/mole.

The cyclization reaction was found to be highly favoured by pressure and $\Delta V_1^* - \Delta V_c^*$ was determined to be + 7.1 cc/mole. The overall activation energies for cyclopolymerization of allyl methacrylate were found to 24.4 and 22.4 kcal./mole at atmospheric pressure and 3000 atm., respectively. The degree of cyclization was found to decrease as the

temperature increased, and $E_1 - E_c$ was found to be 6.7 kcal./mole at atmospheric pressure and 8.0 kcal./mole at 3000 atm. pressure.

Very good agreement between the experimental results and the derived theoretical expressions was found. It was shown that the biradical termination reaction was solely between cyclized radicals for polymerizations at atmospheric pressure while cross-termination reactions between cyclized and noncyclized radicals occurred as well at higher pressures.

(3) The symmetrical 1,6 diene, acrylic anhydride, was found to undergo free radical cyclopolymerization in toluene and dimethylformamide solutions. Using polymers produced in toluene solution, the relation between intermolecular propagation and cyclization, k_1/k_c, was found to be 0.13 l./mole.

The cyclopolymerizations of this monomer were heterogeneous in toluene solution and ostensibly homogeneous in DMF solution at low monomer concentrations. In DMF solution at higher monomer concentrations, popcorn polymerization occurred. The rate of polymerization was determined to vary as the first power of the initiator concentration. It was shown that the homogeneous polymerization of acrylic anhydride in DMF solution had many features in common with the heterogeneous bulk polymerization of acrylonitrile, and the anomalous results were attributed to occlusion in suspended microgel particles.

The rate of polymerization was found to decrease slightly with pressure up to 2500 atm. and in this range ΔV_T^* was found to be + 1.5 cc/mole. The degree of cyclization and the molecular weight increased steadily in the region of rate decrease. Above 2500 atm., the rate increased normally with pressure and both the degree of cyclization and the molecular weight levelled off. In this region, ΔV_T^* was found

to be - 13.8 cc/mole. These results were attributed to decreased penetrability and monomer diffusion in microgel particles.

The activation energy at atmospheric pressure was calculated to be 24.5 kcal./mole.

(4) Indene was found to polymerize by free radical methods and to yield low molecular weight polymers. It was determined that ΔV_T^* was a function of pressure; varying from about - 21 cc/mole below 2000 atm. to about - 8 cc/mole in the range 2000 - 5000 atm.. The termination reaction was shown to be biradical and the kinetic dependence of rate on initiator concentration was found to be 0.5 at atmospheric pressure and 0.4 at 3000 atm. pressure.

The activation energy at atmospheric pressure was determined to be 23.2 kcal./mole.

(5) It was determined that the symmetrical 1,6 diene, diallylamine hydrochloride, could be cyclopolymerized at atmospheric and higher pressures to yield solid polymers which were virtually 100% cyclized.

(6) The symmetrical 1,6 diene, diallyl cyanamide, was found to undergo heterogeneous cyclopolymerization in toluene solution to yield soluble, low molecular weight polymers. It was determined that $R_p \propto [In][M]^2$ at atmospheric pressure and $R_p \propto [In]^{\frac{1}{2}}[M]^2$ at 3000 atm. pressure. The termination was determined to be by intramolecular hydrogen transfer at atmospheric pressure and by the biradical coupling of cyclized radicals at 3000 atm. pressure.

It was considered that the kinetic dependence of rate on the square of the monomer concentration was due to complex initiator-monomer-solvent interactions and theoretical expressions were developed which agreed, at least quantitatively, with the experimental results.

The rate of polymerization increased sharply in the region 1 - 1000 atm. and normally thereafter. It was shown that above 1000 atm. the termination reaction was biradical and in this range ΔV_T^* was found to be - 14.3 cc/mole.

The activation energy was found to be 29.7 kcal./mole at atmospheric pressure and 19.4 kcal./mole at 3000 atm. pressure.

(7) The unsymmetrical 1,5 diene, vinyl methacrylate, was found to undergo free radical cyclopolymerization in cyclohexanone and dioxan solutions, and to yield soluble cyclopolymers containing six-membered lactone rings. Because of induction, kinetic investigations of the polymerization of this monomer were not carried out.

(8) Attempts to cyclopolymerize the symmetrical 1,4 diene, vinyl sulfone, were not successful.

(9) From a few experiments on the effect of pressure on the free radical polymerization of styrene in benzene solution, ΔV_T^* was calculated to be - 17.8 cc/mole.

In addition to the previous results and conclusions for particular monomers the following general conclusions about cyclopolymerization were obtained.

(10) On the basis of the experimental results, it appears that the alternating inter-intramolecular reaction mechanism which was originally proposed by Butler and Angelo[3] generally describes the free radical polymerization of many non-conjugated dienes at atmospheric and higher pressures.

(11) The theoretical expressions developed in Section IV give a reasonable interpretation of the experimental results for cyclopolymerization and their use permits the evaluation of the relative importance of cyclization and intermolecular propagation, and in some cases the

determination of the probable termination reaction(s).

(12) A tendency to microgel formation is probably a factor in the cyclopolymerization of most non-conjugated dienes which yield high molecular weight polymers.

(13) The rate of cyclopolymerization is usually increased by pressure.

(14) In cyclopolymerization, pressure greatly increases the rate of cyclization relative to the rate of intermolecular propagation.

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