ORGANOMETALLIC INITIATORS OF FREE-RADICAL POLYMERIZATION:

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SYNOPSIS:

The potentialities of certain organometallic complexes as initiators of free-radical polymerization have been investigated by dilatometric techniques. The systems studied are based on metal(II) acetylacetonates in the absence or presence of a reductant or an oxidizer.

The Bamford initiator, which consists of cupric acetylacetonate and ammonium trichloracetate, does not initiate the polymerization of vinyl acetate at 65°C. Consequently, the kinetics of polymerization of methyl methacrylate previously investigated by Bamford et.al. at 80°C, have been re-examined at 65°C. The kinetics at 65°C were different from that at 80°C. A modified or alternative mechanism at 65°C, which involves a linear termination reaction in addition to the Bamford mechanism, is discussed together with a problem involved in the initiation process.

Certain acetylacetonato complexes initiate the polymerization of certain monomers by themselves. Ferrous acetylacetonate polymerizes styrene and methyl methacrylate, but not vinyl acetate. The mechanism in these cases probably involves the formation of a complex between monomer and initiator. The important role of the unassociated or associated form of the ferrous acetylacetonate under various experimental conditions is discussed.

The kinetics of the polymerization of methyl methacrylate at 25°C initiated by a mixture of ferrous acetylacetonate and cumene hydroperoxide are discussed.

This thesis contains no material previously submitted for a degree of diploma in any University and, to the best of my knowledge and belief, contains no material previously written by another person, except when due reference is made in the text.

GOH TONG HONG

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PART I GENERAL INTRODUCTION:

Organometallic initiators for vinyl polymerizations fall roughly into three classes:

A. ALKYL, ARYL OR ALKOXYL METAL COMPOUNDS, TYPICALLY, BUT NOT EXCLUSIVELY, OR GROUPS I, II, XII OF THE PERIODIC TABLE.

B. HETEROGENEOUS OR SOLUBLE COMPLEX CATALYSTS FORMED BY REACTING CLASS 1 ORGANOMETALLIC COMPOUNDS WITH CERTAIN TRANSITION METAL COMPOUNDS.

C. COORDINATION COMPLEXES, e.g. Carbonyl and acetylacetonate complexes of transition metals.

A. CLASS 1 INITIATORS:

The organometallic complexes of Class 1 may be either salt-like or covalent.

1. Anionic Polymerisation:

The 'typical' polymerization is anionic in character. In systems where free ions are formed, the alkyl, aryl, or alkoxide anion is the effective initiator and a growing free carbanion is the propagating species, e.g.

$$\sim\!\sim\!\sim CH_2.CH\overset{-}{:} + CH_2 = CHX \longrightarrow \sim CH_2.CHX.CH_2CHX\overset{-}{:}$$

Where free ions are not present, initiation occurs by insertion of the monomer into the metal-carbon or metal-oxygen bond of an ion-pair or covalent compound and propagation consists of repeated insertions of monomer into the self-renewing metal-carbon bond. For ion pairs:

$$\sim\!\sim\!\sim CH_2.CHX\overset{-}{:}, Mt^+ + CH_2 = CHX \longrightarrow \sim CH_2.CHX.CH_2.CHX\overset{-}{:} Mt^+$$

and for polar, but essentially covalent bonds:

$$\sim CH_2\overset{\delta-}{C}HX - \overset{\delta+}{Mt}^+ + CH_2 = CHX \longrightarrow \sim CH_2.CHX.CH_2.\overset{\delta-}{C}HX - \overset{\delta+}{Mt}^+$$

Example of Class 1 initiators are sodium and potassium alkyls, [1] n-butyllithium,[2-6] sodium naphthalene, [7,8] and lithium tertiary alkoxide.[9]

Over the past few years, considerable work has been carried out on the polymerization of various monomers using n-butyllithium. However, these studies have yielded many kinetic results which appear to be contradictory[2-6, 10-23] Kinetic orders with respect to monomer have varied from 1 to 2 and with respect to initiator from 0 to 1, even with similar systems. Unlike sodium and potassium alkyls, n-butyllithium tends to associate in hydrocarbon solvents. Evidence showed that n-butyllithium exists almost entirely in the hexameric[24] form in non-polar solvents. Worsfold[25] offered evidence that $(BuLi)_6$ yields only BuLi, and that no intermediate species could be formed. Initiation involves the addition of the monomeric form, BuLi to the monomer:

$$(BuLi)_6 \rightleftharpoons 6\ BuLi \qquad K$$

$$BuLi + M \longrightarrow BuM^-Li^+ \qquad k_i$$

Perhaps, the most unusual and fascinating aspect of anionic polymerization initiated by the alkali alkyls and aryls is that the polymeric molecules can 'live' for a long period of time until the supply of monomer is exhausted. Szwarc[7] named such polymers "living" polymers. The rediscovery of a polymerization process without any termination by Szwarc[7,8] in 1956 started a new era in the history of anionic polymerization. Szwarc, Levy and Milkovich[8] succeeded in preparing a living polystyrene in tetrahydrofuran using sodium naphthalene as an initiator. The initiation step involves electron transfer with the formation of a naphthalene radical ion.

$$\text{Na} + \text{naphthalene} \longrightarrow \text{Na}^+ + \text{naphthalene}^-$$

where $(CH_2 = CHX)^-$ has resonating structures

$$\cdot CH_2 - \bar{C}HX \longleftrightarrow :\bar{C}H_2 - CHX\cdot$$

The further addition of one monomer unit yields a dimer

$$:\bar{C}HX - CH_2 - CHX - CH_2\cdot \longleftrightarrow :CHX - CH_2 - CH_2 - C\;\;\cdot$$

Since the radical end is not stable, it dimerizes into dianions

$$:\bar{C}HX - CH_2 - (CH_2CHX) - CH_2 - \bar{C}HX$$

The dianions will grow over a period of several days until depletion of monomer. Such carbanions are called "living" polymers.

2. Free Radical Polymerization

Besides the 'typical' polymerization which is anionic in character, there is, however, the 'untypical' mechanism, which is free-radical in character and is believed to arise from the homolytic decomposition of the metal-organic bond. Silver alkyls have been studied quite extensively by several groups of workers.[26-31] One such compound is ethylsilver, AgEt, which has been shown to decompose into silver and ethyl radicals at temperatures much below 0°C. Bawn, Janes and North[32] have recently studied the low temperature polymerization of methyl meth~~yl~~acrylate using ethylsilver. The observed rate equation is

$$R_p = K\,[M]^{3/2}\,[Ag]^{1/2}$$

The dependence of the rate on the square root of the initial silver concentration is indicative of a free-radical chain reaction initiated by first-order decomposition of the ethylsilver and termination by a bimolecular reaction between the growing chains. The most interesting feature is the production of single ethyl radicals in the presence of a relatively inactive silver atom and the absence of primary termination effects.

The dependence of rate upon monomer concentration suggests that a monomer-initiator complex is formed which then decomposes.

A possible mechanism for the reaction is:

$$\begin{array}{llll}
\text{AgEt} + \text{M} & \rightleftharpoons & \text{COMPLEX} & K \\
\text{COMPLEX} & \longleftrightarrow & \text{Et.} + \text{Ag} + \ldots & k_d \\
\text{Et.} + \text{M} & \longrightarrow & \text{Et M.} & k_i \\
\text{M.} + \text{M} & \longrightarrow & \sim\!\!\sim \text{M.} & k_p \\
2 \sim\!\!\sim \text{M.} & \longrightarrow & \text{Polymer} & k_t
\end{array}$$

B. CLASS 2 INITIATORS

The active centre here is a metal-carbon bond and the basic CHEMICAL processes are similar to those of Class 1 initiators. Both the 'typical' and 'untypical' mechanisms are known.

1. Ziegler-Natta Catalysts:

The initiators involving a 'typical' mechanism are the well-known Ziegler-Natta catalysts. The Ziegler-Natta catalyst is essentially a crystalline transition metal salt activated by an organometallic compound of Groups I, II, III. The most widely investigated Ziegler-Natta catalysts consist of titanium halides in conjunction with alkylaluminium compounds. These are heterogeneous catalyst systems. Natta et al[33,34], and Breslow and Newburg[35,36] found that when titanium tetrachloride is replaced by bis(cyclopentadienyl) titanium dichloride in the reaction with alkylaluminium compounds, soluble complexes are formed which have some initiating power.

The mechanism of polymerization initiated by Ziegler-Natta catalysts is undoubtedly still an open one. Allen[37] has recently made a very critical survey of several current theories (e.g. Patat-Sinn mechanism, coordination mechanism proposed by Ziegler, Cossee mechanism) of the action of catalytic surfaces in vinyl polymerization, pointing out the strengths and weaknesses of each in relation to current work. Allen is of the opinion that whoever proposed a new mechanism should pay proper attention to the physical factors involved. Allen and his associates[38,39] have shown that the rate of polymerization is a physical process and not that of a chemical process in one system where the rate of polymerization of styrene initiated by a heat-cured Grignard reagent - $TiCl_4$ catalyst decelerated with the catalyst particles becoming encased in polymer gel. The problem of physical restrictions on the polymerization rate in systems of this type is discussed by Allen, Gill and Patrick.[40] The mechanism of Rodriquez[41] undoubtedly meets most of the objections raised to earlier mechanisms.

2. Free Radical Initiators

Class 2 initiators which proceed via a free-radical mechanism[42,43] are also known. When aluminium or mercury alkyl is one of the two components, most of the reaction systems remain homogeneous. However, when zinc or cadmium alkyl is used, the system becomes heterogeneous.

Furukawa and co-workers[42,43] observed that for vinyl polymerizations catalyzed by Class 2 initiators, the polymerizations proceeded through a radical mechanism. The radical mechanism occurs when the monomer is added to one catalyst components (the metal halide), prior to the addition of the other catalyst component (metal alkyl). If the monomer is added last, as is usual in Ziegler polymerizations, very little catalytic activity is obtained. This suggests that the interaction between the metal halide and monomer forms a complex which upon addition of a Class 1 organometallic compound (metal alkyl) liberates transient radicals which immediately attack the vinyl monomers present.

C. CLASS 3 INITIATORS:

The carbonyls and acetylacetonato complexes of transition metals have received considerably less attention that the Class 1 and 2 initiators but have now become one of the most expanding fields in vinyl polymerization. The majority of the catalysts studied appear to initiate by a free-radical mechanism, but the mechanisms are complicated and in a number of instances monomer-initiator complexes may be involved.

1. Metal Carbonyls:

The use of metal carbonyls (together with a low concentration of a suitable organic halide e.g. CCl_4) as initiators of vinyl polymerization was first reported by Bamford and Finch.[44,45] Bamford[46] later reported the use of a wide range of organometallic compounds, particularly the metal carbonyls, as initiators of vinyl polymerization. The mechanism proposed for the metal carbonyls is rather complicated.

2. Metal Acetylacetonates:

Several groups of workers have recently shown that certain metal acetylacetonates can function as initiators of vinyl polymerization.

Kastning and co-workers[47] have shown that a number of metal chelates, at concentrations of the order of 10^{-2} mole $l.^{-1}$, are active initiators for the polymerization of styrene at temperatures in excess of 100°C. The order in reactivity of the acetylacetonates studied was found to be

$$Mn^{III} > Co^{III} > Ni^{II} > Mn^{II} > Ce^{IV}$$

as judged by conversions of styrene after one hour at 120°. A marked increase in catalytic activity was found when various additives, namely organic halogen compounds, were added to the system in approximately the same concentrations as the metal chelate. For polystyrene polymerization at 110°C, both in the presence and absence of carbon tetrachloride, a half order dependence of rate on cobalt(III) acetylacetonate concentration was found. There was no evidence of a change in the valency of the metal atom during the polymerization.

Bamford and Lind[48] have studied the polymerization of methyl methacrylate at 80°C in the presence of various metal acetylacetonates at concentrations of the order of 10^{-3} mole l^{-1}. Their results differ somewhat from those reported by Kastning et al.[47] Under their conditions, Bamford and Lind found that $Mn^{III}(acac)_3$ was an active initiator, but $Co^{III}(acac)_3$ was completely inactive. The initial rate of polymerization was found to be first order in monomer and half-order in catalyst concentration. This supports the view of Arnett and Mendelsohn[50] that a first order decomposition of the chelate occurs by a simple fission of a ligand as follows:

$$Mn^{III}(acac)_3 \longrightarrow Mn^{II}(acac)_2 + CH_3CO\dot{C}HCOCH_3$$

This mechanism, contrary to that of Kastning et al.[47] involves a valency change of the metal atom, and is supported by the colour changes observed by Arnett and Mendelsohn[50] during the polymerization of styrene with $Ce^{IV}(acac)_4$ and $Co^{III}(acac)_3$. Riches[49] also observed that during the polymerization of butadiene and isoprene with $Co^{III}(acac)_3$ the characteristic dark green colour of the catalyst faded to pale pink.

A more recent paper by Riches[49] reported that $Co^{III}(acac)_3$ is an active catalyst for the solution polymerization of butadiene and isoprene at 130°C. This agrees with Kastning et al.[47] but is contrary to that of Bamford and Lind[48] who find the chelate completely inactive for the polymerization of methyl methacrylate at 80°C. However, a half order dependence on the catalyst concentration and an approximate first order dependence on the monomer concentration have been found, similar to the kinetic results of Bamford and Lind.[48] In accordance with Bamford and Lind[48] and contrary to Kastning et al.[49] Riches found that carbon tetrachloride does not enhance the activity of the chelate under his conditions. Diphenylpicrylhydrazyl and p-benzoquinone had no significant effect on the rates of the diene polymerization although the styrene polymerization was strongly inhibited under similar conditions.

The results, so far reported, are most contradictory and confusing. Despite the kinetic evidence favouring a radical mechanism involving a valency change of the metal as suggested by Arnett and Mendelsohn,[50] there is also the possibility that a monomer-initiator complex may be involved. The kinetic runs were conducted by

Kastning et al.[47] and Riches[49] at rather high temperatures (in excess of 100°C). One would expect in normal dilatometric and gravimetric procedures, to carry out experiments at temperatures $\leqslant$ 80°C. The kinetic work of Kastning et al.[47] ought to be re-examined at 80°C for $Mn^{III}(acac)_3$ and $Co^{III}(acac)_3$ in styrene using dilatometry instead of a gravimetric technique where their rates quoted are merely mean rates. Most important is a thorough investigation of the valency state of the metal atom of manganese and cobalt after reacting the chelates with styrene and other vinyl monomers at 80°C. The possiblity of monomer complexing to the chelate ought to be examined since a valency change of the metal atom can arise not only from a straightforward fission of the ligand as a radical but also from participation of the monomer concerned. The simple free-radical mechanism postulated[48,50] is, therefore, by no means the only explanation.

One of the interesting aspects of Class 3 initiators arises from the recognition[51] that they are capable of SELECTIVE initiation of radical polymerization. Bamford and Lind[51] found that the fluorinated chelate, $Mn^{III}(facac)_3$, initiates the polymerization of methyl methacrylate and acrylonitrile, is a relatively ineffective initiator with vinyl acetate but is a strong retarder of the free-radical polymerization of styrene.

3. Redox Initiators:

Acetylacetonato complexes have been used for many years in conjunction with hydrogen peroxide or alkyl or aryl hydroperoxides as redox pairs for production of free radicals. These reactions are probably far more complicated than is often assumed. Two groups of workers[52, 53] have recently reported the low initiator efficiencies in styrene polymerization initiated by a combination of an alkyl or aryl hydroperoxide with one of a series of acetylacetonato complexes.

Burnett and North[52] have reported the polymerization of styrene initiated by the reaction between ferrous acetylacetonate and cumene hydroperoxide. The observed kinetic equation is

$$Rp = K\left[Fe(acac)_2\right]^{0.29}\left[CHP\right]^{0.32}$$

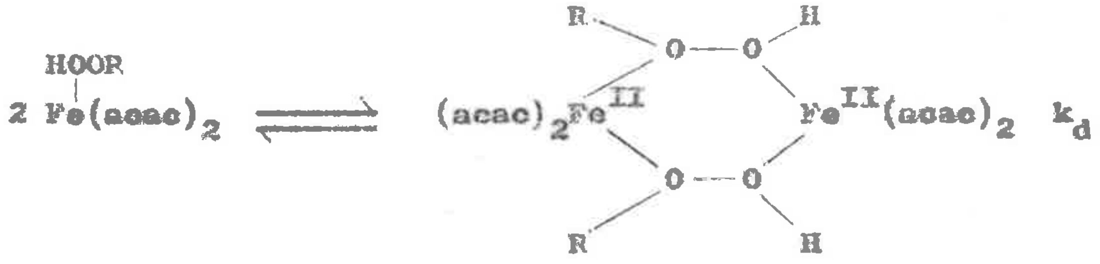
at 25°C and 40°C. It is most unfortunate that they did not give a detailed quantitative data of the initial rates together with the concentration range of ferrous acetylacetonate and cumene hydroperoxide. The rate law suggests that the two reagents rapidly form a 1:1 complex

$$ROOH + Fe^{II}(acac)_2 \rightleftharpoons \overset{HOOR}{\overset{|}{Fe^{II}}}(acac)_2 \qquad K$$

which yields RO. radicals by a one-electron transfer reaction in the complex

$$\overset{HOOR}{\overset{|}{Fe^{II}}}(acac)_2 \longrightarrow \overset{HO}{\overset{|}{Fe^{III}}}(acac)_2 + RO. \qquad k_1$$

The initiation mechanism is, however, more complicated. Burnett and North[52] observed a decreased in polymerisation rate with time. This decrease, as suggested by Burnett and North, arises as a result of the 1 : 1 complex undergoing a second order reaction leading to a binuclear complex



which yields free-radicals more slowly than the initial intermediate. Molecular weight studies[54] indicated that the termination by ferrous chelate is unimportant and that mutual termination of two free radicals is the more important termination mechanism. This is most unexpected since the low order of the two reagents is indicative of a case of mixed primary radical termination.

In a recent paper, Indictor and Lindner[53] assayed the initiator efficiencies in styrene polymerization of the system tert-butylhydroperoxide-metal acetylacetonate for a number of different metals. Their kinetic data indicate that Al(III), Zr(IV), TiO(II), Ni(II), and Zn(II) have little or no effect on tert-butylhydroperoxide as polymerization initiators, that small quantities of Cu(II), Co(III), Cr(III), and Fe(III) promote tert-butylhydroperoxide polymerization initiation, and that V(III), Mn(II), Vo(II), Fe(II) and Co(II) enhance tert-butylhydroperoxide decomposition but do not promote polymerization initiation.

The present study deals with redox initiators, one of the two-component system being a metal(II) acetylacetonate.

Part II is concerned with the re-investigation of the ammonium trichloracetate-cupric acetylacetonate system previously reported by Bamford, Eastmond and Rippon.[55] This was brought about as a result of findings that Bamford's initiator does not initiate the polymerization of vinyl acetate.

Part III deals with the initiating power of ferrous acetylacetonate without any additive. This was discovered in the process of examining the ferrous acetylacetonate-cumene hydroperoxide-methyl methacrylate system. Ferrous acetylacetonate alone polymerizes styrene and methyl methacrylate, but not vinyl acetate.

Part IV is a study of the polymerization of methyl methacrylate (which is a more polar solvent than styrene) initiated by ferrous acetylacetonate and cumene hydroperoxide.

PART II INITIATION OF VINYL POLYMERIZATION BY AMMONIUM TRICHLORACETATE IN THE PRESENCE OF CUPRIC ACETYLACETONATE

CHAPTER I EXPERIMENTAL

A. VACUUM LINE

Since molecular oxygen has been found to be a strong inhibitor of free-radical polymerization, all the polymerizations of the vinyl monomer were carried out under high vacuum conditions.

The apparatus used for degassing and distillation of the monomers and solvents is shown in figure II/1.1.

The vacuum line was constructed of Pyrex glass tubing. It was evacuated by means of a two-stage mercury diffusion pump backed by a rotary oil pump. The former is capable of producing the high vacuum needed (10^{-5}Torr.) and the latter produces a rough vacuum (10^{-2} - 10^{-3} Torr) necessary for proper operation of the diffusion pump. A liquid trap L_1 prevented contamination of the pump whilst the air trap L_2 acted as a reservoir for any liquid that may distil over during the process of

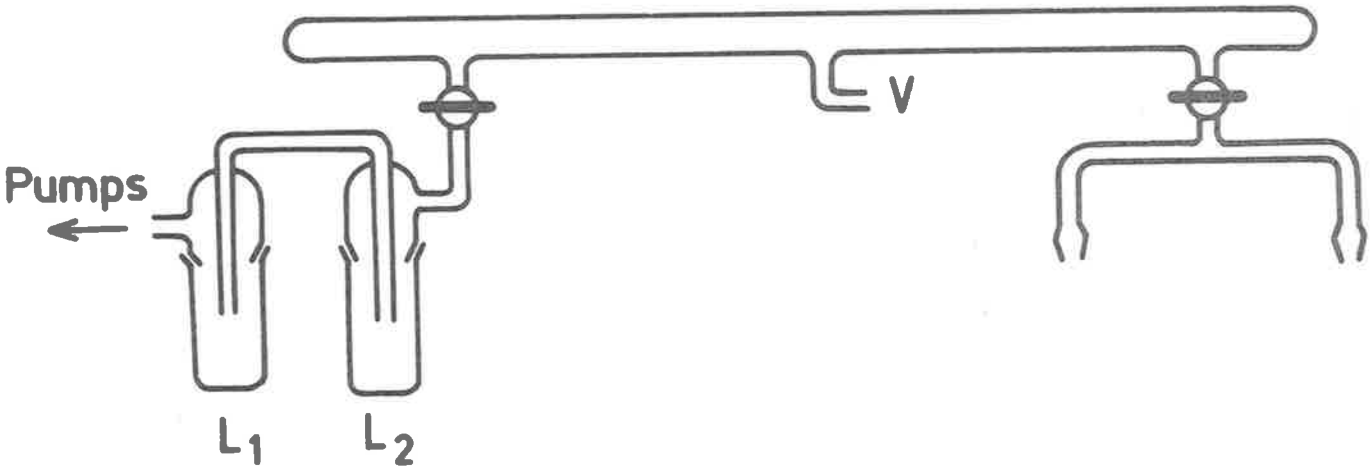


FIG. II/1·1 High Vacuum Line

degassing. The number of ground glass taps and joints were kept to a minimum. All taps and joints were greased with Dow Corning High Vacuum silicone lubricant. The criterion adopted for a good vacuum was that of the mercury 'sticking' to the closed limb of the vacuostat V when inverted. This is probably equivalent to a pressure of $10^{-4} - 10^{-5}$ Torr.

B. MATERIALS:

1. Vinyl acetate

Commercial vinyl acetate was freed of inhibitor by shaking up with seven lots of 10% sodium hydroxide solution. This was washed with distilled water until it was neutral to litmus, and dried overnight, over anhydrous magnesium sulphate. The dried monomer was filtered and distilled under reduced pressure of nitrogen, the initial and final 20% of the distillate being rejected. The middle fraction was collected in a reservoir vessel and further dried by the addition of calcium hydride. Vigorous reaction was observed at first. When the evolution of hydrogen had subsided, the vessel was attached to the high vacuum line. The monomer was degassed several times, prepolymerized with uV irradiation to 10-15% conversion, and vacuum distilled into another vessel containing a fresh lot of calcium hydride. The pure monomer was degassed a few more times, removed from the vacuum line and stored in the refrigerator until required for use.

2. Methyl Methacrylate:

Methyl methacrylate was purified by the same procedure adopted for the purification of vinyl acetate.

3. Cupric Acetylacetonate:

Cupric acetylacetonate was prepared by reacting an alcoholic solution of cupric acetate with an alcoholic solution of acetylacetonate. The crude product was recrystallized from benzene.

4. Ammonium Trichloracetate:

Ammonium trichloracetate was prepared by neutralizing a concentrated aqueous solution of trichloracetic acid with ammonia and recrystallizing the product from water. The salt was dried in vacuum at room temperature.

C. DILATOMETERS:

The process of polymerization involves a decrease in volume of the system. The use of a dilatometer, which measures small volume contractions at various time intervals in a polymerizing system, is a convenient and accurate tool for studying the kinetics of vinyl polymerization.

1. Construction:

The conventional dilatometer consists of a 26 cm. length of thin-walled 3 mm. bore Pyrex capillary tubing, one end of which was closed and thickened in an oxygen-gas flame, then blown into a bulb of approximately 3 ml. capacity. The dilatometer was carefully annealed. A line A was scratched on the undisturbed capillary immediately above the bulb and another mark B was made half-way up the capillary tube, as shown in figure II/1.2.

2. Calibration:

The dilatometer was weighed. By means of a syringe to which was attached a 30 cm. stainless steel needle of narrow bore, distilled water was introduced just up to makk A. The dilatometer was wiped dry and reweighed.

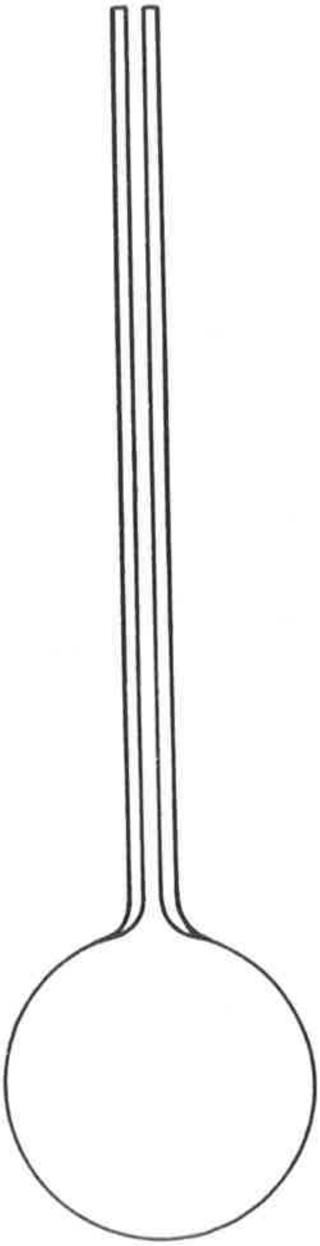


FIG. II/1·2 Dilatometer

Additional water was introduced, taking care to avoid air bubbles, until its level was at mark B. The dilatometer was reweighed. The height of the capillary between A and B was measured by a cathetometer. From the known density of water at room temperature, the volume of the dilatometer up to mark B and the cross-sectional area of the capillary were calculated.

3. Measurement of Conversion for Monomers:

The conversion of monomer was followed dilatometrically. The percentage contraction in volume for 100% conversion at a particular temperature t°C can be calculated from the relationship:

$$\% \text{ contraction } = \left(\frac{V_{m_t} - V_{p_t}}{V_{m_t}}\right) \times 100$$

where V_{m_t} and V_{p_t} are the respective volumes of the monomer and polymer at a certain temperature t°C. The above relationship can be reduced to

$$\% \text{ contraction } = \left(\frac{1 - \rho m_t}{\rho p_t}\right) \times 100$$

assuming the mass of the monomer to be the same as that of the polymer. ρm_t is the density of monomer at t°C and ρp_t is the density of polymer at t°C.

For vinyl acetate, the values of ρm_t, and ρp_t found by Matheson et al.[56] For methyl methacrylate, the constants were those quoted by Matheson et al.[57] For styrene, the data of Patnode and Scheiber[58] were used.

The experimental percentage contraction in volume at a given time and temperature t°C can be determined by the equation

$$\% \text{ contraction} = \left(\frac{\pi r^2 \Delta h}{V_{m_t}}\right) 100$$

where Δh is the contraction of the meniscus at a given time, πr^2 is the cross-sectional area of capillary and V_{m_t} the volume of original monomer at t°C.

D. FILLING OF DILATOMETERS:

The polymerizations of the monomer were followed dilatometrically under high vacuum conditions.

By means of a 1 ml. syringe to which was attached a 30 cm. stainless needle, initiator and suitable solvent were introduced into the calibrated dilatometer. Ammonium trichloracetate was found to be soluble in a chloroform-ethanol mixture. Solutions of cupric acetylacetonate of known concentration were prepared in chloroform. The solvent was then pumped off by means of an ordinary water suction pump, leaving behind the initiator in the dilatometer. Four dilatometers, each containing initiator of a different concentration, were sealed to flask R_2. Flask R_2 was then attached to the high vacuum line, as shown in figure II/1.3. Any leaks, that may arise when the dilatometers were joined to the flask, may be located by the high frequency spark discharge coil known as the Tesla coil. The highly purified monomer, after a further degassing, was distilled under vacuum from flask R_1 to flask R_2. The monomer in flask R_2 was frozen by placing a Dewar bowl containing liquid nitrogen beneath flask R_2. When sufficient monomer had distilled into flask R_2, the Dewar bowl was removed to allow the monomer to thaw. Flask R_2 was detached from the high vacuum line. Each of the dilatometers was filled up to the upper mark B with monomer by tilting flask R_2 and sealed off under vacuum. The contents of the dilatometer were later thoroughly mixed by inverting and shaking the dilatometer. The dilatometer was placed in the 65°C (or 80°C) thermostat. The maximum height reached by the meniscus during warming-up period was

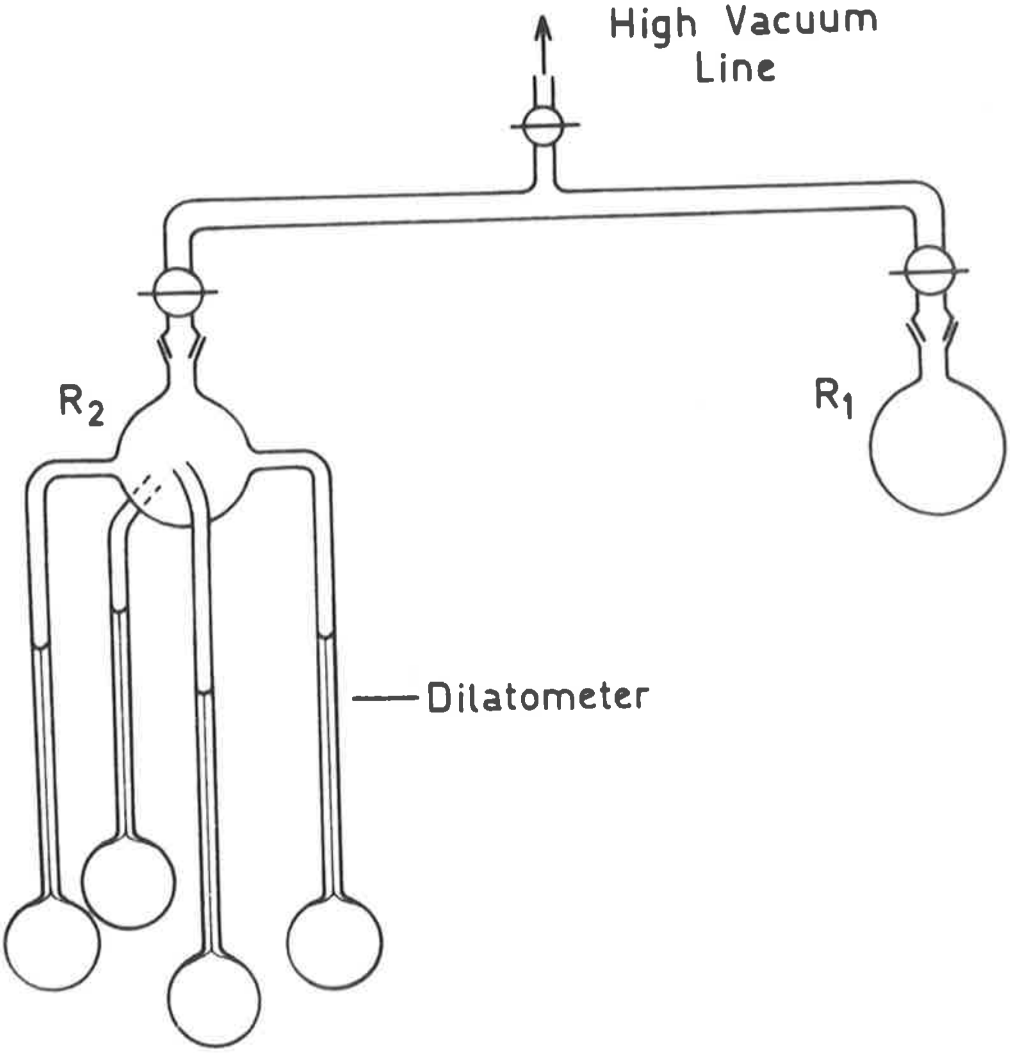


FIG. II/1·3 Dilatometer filling assembly.

noted by a cathetometer. This was normally 3 minutes or less after immersion. Time and contraction were measured from the moment the thermal expansion of the dilatometer contents ceased.

E. THERMOSTAT:

The thermostat consisted of a lagged Pyrex vessel filled with water. Stirring was done by a mechanical stirrer. The water-bath was heated to a temperature slightly less than 65°C by a main heater of 100 watts and a bulb heater. The final temperature of 65°C was achieved and controlled by using a toluene-mercury regulator and a thyratron valve relay controlling a 75 watt heater.

For a 80°C thermostat, a toluene-mercury regulated oil-bath was used.

CHAPTER 2 INTRODUCTION, RESULTS AND DISCUSSION:

A. INTRODUCTION:

Ammonium trichloracetate together with cupric acetylacetonate was first reported by Bamford, Eastmond, and Rippon[55] as an effective initiator of free-radical polymerization of methyl methacrylate at 80°C. The unusual feature of this initiator is the production of single $\dot{C}Cl_3$ radicals which have since been confirmed by[59] a tracer techhique. The mechanism appears to involve the formation of a complex between the two initiator components which decompose to give a trichloromethyl radical:

Initiation:

$$Cu(acac)_2 + CCl_3COONH_4 \rightleftharpoons I \qquad K \qquad (II2.1)$$

$$I \longrightarrow \dot{C}Cl_3 + II \qquad k_d \qquad (II2.2)$$

$$CCl_3 + M \longrightarrow CCl_3M. \qquad k_i \qquad (II2.3)$$

Propagation:

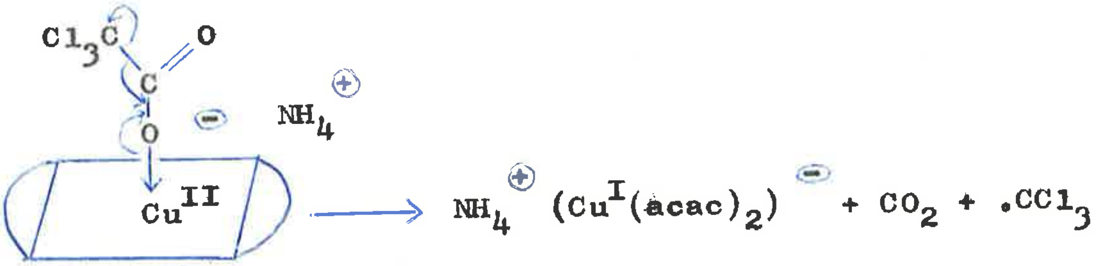
$$CCl_3M. + M \longrightarrow CCl_3MM.$$

$$M. + M \longrightarrow \sim\!\sim\!\sim M. \qquad k_p \qquad (II2.4)$$

Termination:

$$2 \sim\!\sim\!\sim M\cdot \longrightarrow \text{Polymer} \qquad 2k_t \qquad \text{(II2.5)}$$

Complex I and complex II have the following possible structures:



(I) (II)

At 80°C and at low ammonium trichloracetate concentrations ($< 6.00 \times 10^{-4}$M) with a constant $[Cu(acac)_2]_0 = 1.92 \times 10^{-3}$M, Bamford and his co-workers[55] found that the initial rate of polymerization is proportional to $[CCl_3COONH_4]_0^{\frac{1}{2}}$. The equilibrium constant K is large (2706 mole^{-1} l. at 80°C). Bamford's results fit reasonably well to an equation:

$$R_p = k\,[CCl_3COONH_4]_0^{\frac{1}{2}} \qquad \text{(II2.6)}$$

when $[CCl_3COONH_4]_0 \ll [Cu(acac)_2]_0$ and $[Cu(acac)_2]_0$ is constant. These results are consistent with the mechanism above, the stationary state rate being:

$$R_p = \frac{k_p}{(2k_t)^{\frac{1}{2}}} \; (k_d \; I)^{\frac{1}{2}} \left[M\right] \qquad (II2.7)$$

where $[I] = [CCl_3COONH_4]_o$ if K is large and $[CCl_3COONH_4]_o \ll [Cu(acac)_2]_o$

The approximation

$$[I] = [CCl_3COONH_4]_o$$

can be shown to be true under these conditions by a more rigorous mathematical treatment, with the assumption that the equilibrium (II2.1) is not significantly affected by reaction (II2.2):

$$I = K(C_o - 1)(S_o - I)$$

Rearranging, $KI^2 - \left\{(KC_o + KS_o) + 1\right\}I + KC_oS_o = 0$

or $$I^2 - (C_o + S_o + 1/K)I + C_oS_o = 0$$

The two roots of I are given by

$$\begin{aligned}
I &= \tfrac{1}{2}\left(\pm\sqrt{(C_o + S_o + 1/K)^2 - 4C_oS_o} + C_o + S_o + 1/K\right) \\
&= \tfrac{1}{2}\left(\pm\sqrt{(C_o - S_o + 1/K)^2 + 4S_o/K} + C_o + S_o + 1/K\right) \\
&= \pm\tfrac{1}{2}\sqrt{(C_o - S_o + 1/K)^2 + 4S_o/K} + C_o/2 + S_o/2 + 1/2K \\
&= S_o \pm \tfrac{1}{2}\sqrt{(C_o - S_o + 1/K)^2 + 4S_o/K} + C_o/2 - S_o/2 + 1/2K \\
&= S_o - \tfrac{1}{2}\left\{\pm\sqrt{(C_o - S_o + 1/K)^2 + 4S_o/K} - (C_o - S_o + 1/K)\right\} \qquad (II2.8)
\end{aligned}$$

The real root of I is, from equation (II2.8), given by

$$I = S_o - \tfrac{1}{2}\left\{ + \sqrt{(C_o - S_o + 1/K)^2 + 4S_o/K} - (C_o - S_o + 1/K)\right\}$$

$$= S_o - \tfrac{1}{2}\ \{(C_o - S_o + 1/K)^2 + 4S_o/K\}^{\frac{1}{2}} - (C_o - S_o + 1/K)\} \qquad (II2.9)$$

Equation (II2.9) is of a better and more convenient form than the equation

$$I = S_o - \frac{1}{2K}\left[\{K^2(C_o - S_o)^2 + 2K(C_o + S_o) + 1\}^{\frac{1}{2}} - K(C_o - S_o) - 1\right] \qquad (II2.10)$$

given by Bamford et al.[55]

If K is large (2706 mole^{-1} l. at 80°C) and $S_o \ll C_o$, equation (II2.9) is reduced to

$$[I] = [S]_o \qquad (II2.11)$$

Values of $[I]$ calculated using equation (II2.9) are shown in table II/2.1

Table II/2.1:

$[Cu(acac)_2]_o = C_o$	$[ATCA]_o = S_o$	
$10^3 \times C_o$ mole l^{-1}	$10^3 \times S_o$ mole l^{-1}	$10^3 \times [I]$ mole l^{-1}
1.92	0.555	0.444
1.92	0.277	0.227
1.92	0.125	0.104
1.92	0.0555	0.0464
1.92	0.0277	0.0232
1.92	0.0125	0.0100

It was originally intended to use Bamford's initiator (which yields single CCl_3 radicals) on the vinyl acetate system to study the kinetics of radical polymerization at high conversion.

B. RESULTS

1. Dilatometric Measurements of Vinyl Acetate at 65°C:

Dilatometers were filled as described previously. At the low ammonium trichloracetate concentration range (3.94×10^{-5} - 3.39×10^{-4} M) with constant cupric acetylacetonate concentration of 1.92×10^{-3}M in vinyl acetate at 65°C, no significant contraction of the solution was observed, even when the dilatometers were placed in the thermostat for several hours. Furthermore, polymerization did not occur when the salt concentration range was increased to 1.00×10^{-2} - 5.55×10^{-2} M at constant cupric acetylacetonate concentration of 1.92×10^{-3}M The blue-green colour of the cupric complex was destroyed, the solution becoming light brown and a precipitate formed. At room temperature, the same changes occurred over a period of several weeks ($[Cu(acac)_2]_o = 1.92 \times 10^{-2}$M, $[CCl_3COONH_4]_o = 4.50 \times 10^{-4}$M).

The results were contrary to what were expected. If the primary single radical as postulated by Bamford and co-workers[55] is $\dot{C}Cl_3$, it should also initiate the polymerization of vinyl acetate. This conclusion is substantiated by the work of Melville, Robb and Tutton[60] on the photolysis of bromotrichloromethane. Using this technique, they calculated the propagation step k_2 for the addition of a $\dot{C}Cl_3$ radical to vinyl acetate. Part of their mechanism is as follows:

Initiation $CCl_3Br \xrightarrow{hv} \dot{C}Cl_3 + Br$

Propagation $\dot{C}Cl_3 + CH_2 = Ch\text{-}O\text{-}COCH_3 \xrightarrow{k_2}$

$CCl_3 - CH_2 - \dot{C}H - O - COCH_3$

The value of k_2 (at 30°C) is

$$k_2 = 112.0 \text{ l. mole}^{-1} \text{ sec}^{-1}$$

Melville and his colleagues showed that a $\dot{C}Cl_3$ radical initiates the polymerization of vinyl acetate. A significant rate of polymerization should, therefore, be observed with vinyl acetate using a mixture of cupric acetylacetonate and ammonium trichloracetate. Results indicated no polymerization with vinyl acetate. Several explanations are possible.

(a) The $\dot{C}Cl_3$ radical is not the primary radical but a less reactive radical which does not react with vinyl acetate. This explanation has been disproved by Bamford and Robinson[59] who have recently identified the $\dot{C}Cl_3$ radical by a tracer technique.

(b) Methyl methacrylate initiation involves specific mechanism, e.g. the monomer complexing with adduct I (ca.II2.1)

$$I + MMA \rightleftharpoons I,MMA \qquad (II2.12)$$

$$I,MMA \longrightarrow R. \qquad (II2.13)$$

(c) Vinyl acetate complexes with salt, cupric chelate or the adduct

$$S + VA \rightleftharpoons \text{product} \qquad (II2.14)$$

$$C + VA \rightleftharpoons \text{product} \qquad (II2.15)$$

$$\text{or } I + VA \rightleftharpoons \text{stable product} \qquad (II2.16)$$

Steps (II2.14, II2.15, II2.16) may interfere with equilibrium (II2.1) and reduce the rate of initiation R_i.

If complexing is strong, $R_i \Longrightarrow 0$

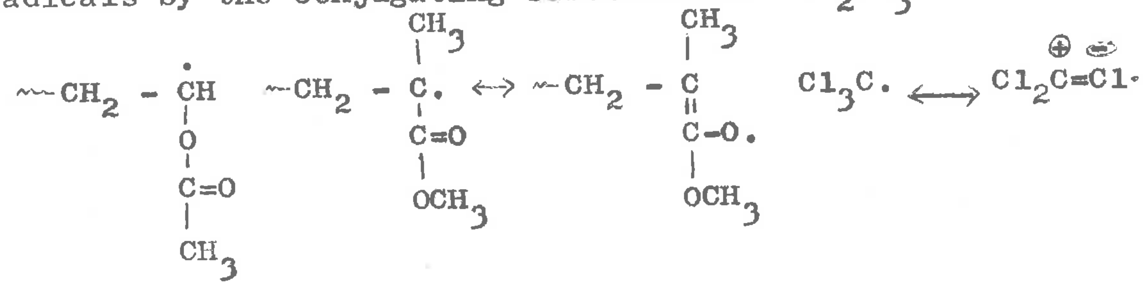
(d) The salt, cupric chelate, or adduct inhibits polymerization by scavenging propagating radicals.

$$P_n\cdot + S \longrightarrow \text{inactive product} \qquad (II2.17)$$

$$P_n\cdot + C \longrightarrow \text{inactive product} \qquad (II2.18)$$

$$P_n\cdot + I \longrightarrow \text{inactive product} \qquad (II2.19)$$

This is quite feasible since a polyvinyl radical is believed to be more reactive than a polymethyl methacrylate or a $\dot{C}Cl_3$ radical. There is considerable experimental evidence to support this belief. From the point of view of reactivity theory, the effect could be attributed to the stabilization of the PMMA and CCl_3 radicals by the conjugating substituents $-CO_2CH_3$ and $-Cl$.



$$\sim CH_2-\underset{\underset{\underset{\underset{CH_3}{|}}{C=O}}{\underset{|}{O}}}{\overset{\bullet}{C}H} \qquad \sim CH_2-\underset{\underset{OCH_3}{\underset{|}{C=O}}}{\overset{CH_3}{\overset{|}{C}}}\cdot \longleftrightarrow \sim CH_2-\underset{\underset{OCH_3}{\underset{|}{C-O\cdot}}}{\overset{CH_3}{\overset{|}{C}}} \qquad Cl_3C\cdot \longleftrightarrow Cl_2\overset{\ominus}{C}=\overset{\oplus}{Cl}\cdot$$

PVA radical PMMA radical CCl_3 radical

To test explanation (d), the effects of the ammonium salt and the cupric chelate on the polymerization of vinyl acetate initiated by $1.30 \times 10^{-3}M$ benzoyl peroxide were examined at 65°C. The results are shown in figure II/2.1. Ammonium trichloracetate ($4.50 \times 10^{-4}M$) had no significant effect. Cupric acetylacetonate ($1.90 \times 10^{-3}M$) reduced the rate thirteen-fold. A mixture of both substances, at these concentrations, suppressed polymerization completely. The characteristic colour of the cupric complexes persisted in the last two cases. These tests favour explanation (d) strongly,

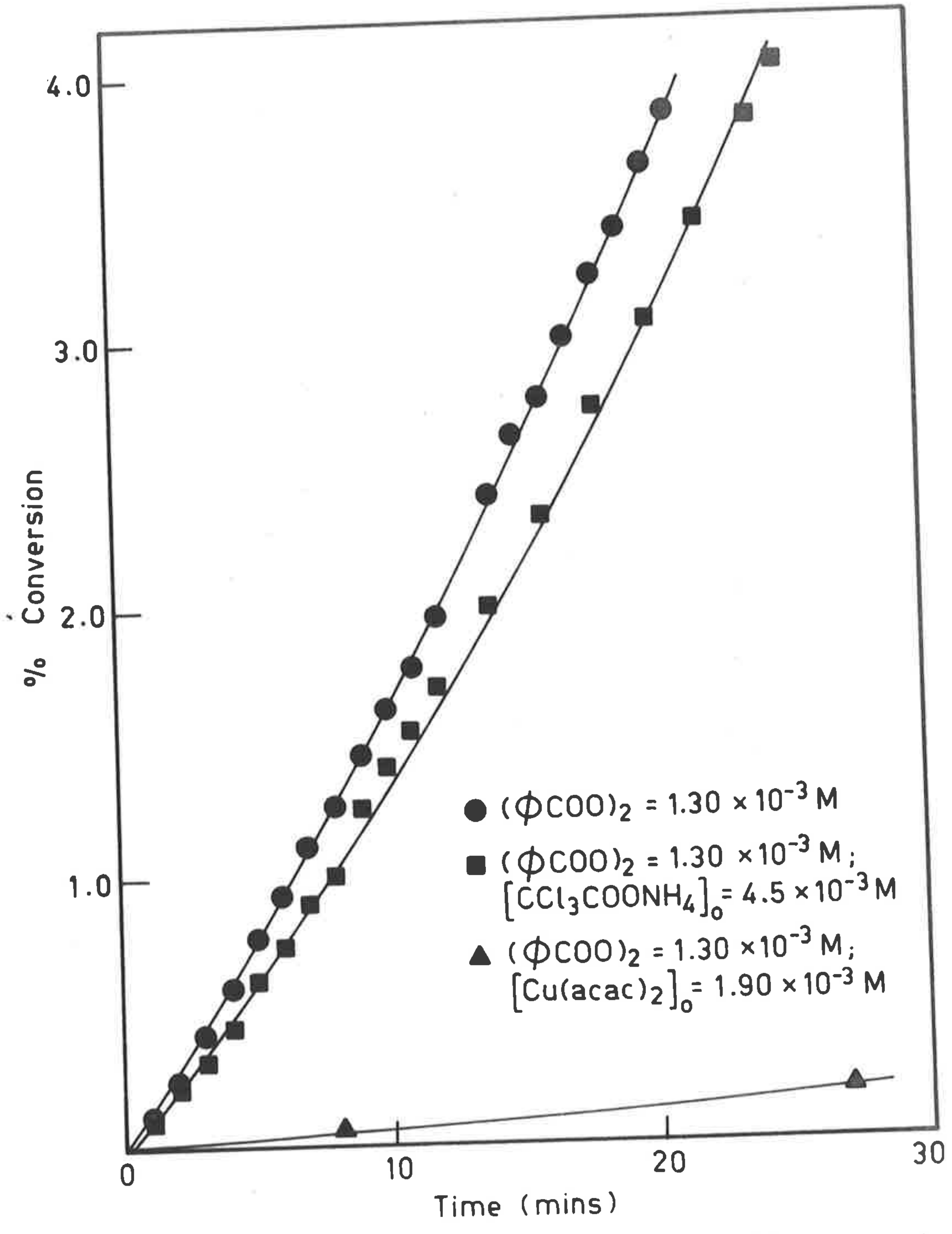


FIG. II/2·1 Effects of $Cu(acac)_2$ and CCl_3COONH_4 on the polymerization of vinyl acetate initiated by 1.30×10^{-3} M $(\phi COO)_2$ at 65°C.

particularly step (II2.19). They do not however, eliminate (b) and (c) as an explanation.

2. Polymerization of Methyl Methacrylate Initiated by Ammonium Trichloracetate and Cupric Acetylacetonate:

The rather unexpected results obtained for the CCl_3COONH_4 - $Cu(acac)_2$ - vinyl acetate system at 65°C seemed to indicate that the reaction mechanism is not kinetically simple as that proposed by Bamford and his associates.[55] The kinetics of the polymerization of methyl methacrylate at 65°C (and 80°C) were re-investigated over a wide concentration range of ammonium trichloracetate (1.00×10^{-5} - 5.00×10^{-2}M) at constant $Cu(acac)_2 = 2.00 \times 10^{-3}$M

(a) Dilatometric Measurements:

Rates of polymerizations were determined dilatometrically. In all cases conversions were about 4%. Plots of monomer conversion against time at 65°C for the low ammonium trichloracetate concentration range ($< 6.00 \times 10^{-4}$M) and the high salt concentration range (1.00×10^{-3} - 5.00×10^{-2}M) at constant $[Cu(acac)_2]_o = 2.00 \times 10^{-3}$M are illustrated respectively in figures II/2.2 and

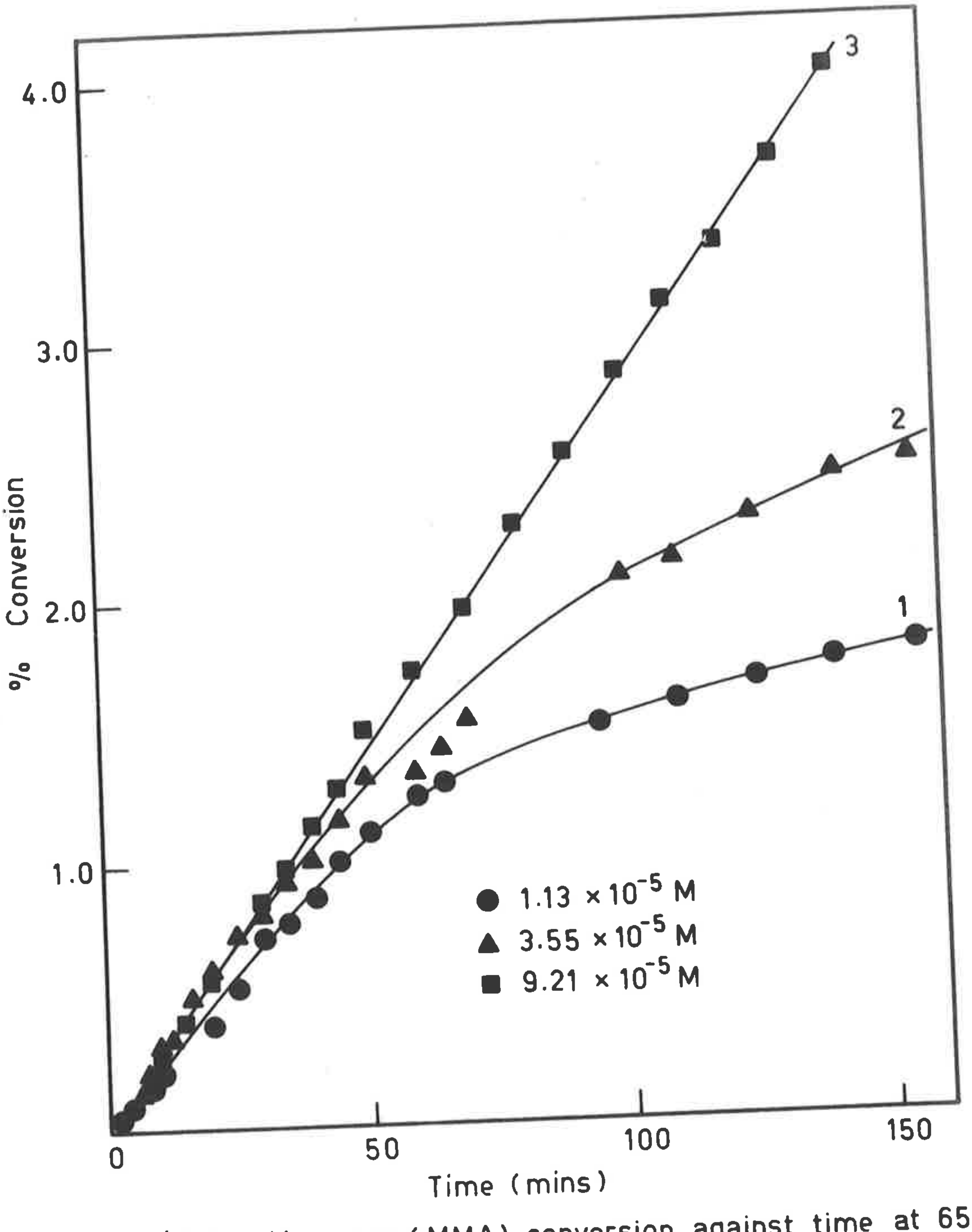


FIG. II/2·2 Monomer (MMA) conversion against time at 65°C for low $[CCl_3COONH_4]_0$ at constant $[Cu(acac)_2]_0 = 1.98 \times 10^{-3}$ M

II/2.3, and figure II/2.4. Figure II/2.5 shows the monomer conversion against time at 80°C for the high salt concentration ($5.00 \times 10^{-3} - 6.00 \times 10^{-2}$M) at constant concentration of the cupric chelate.

(b) Conversion-Time Curves:

Bamford, Eastmond and Rippon[55] determined their initial rates of polymerization at 80°C gravimetrically, having demonstrated that the conversion-time curve was linear up to 8% conversion. At 65°C, this technique is inadmissable. Dilatometric conversion curves are reasonably linear (Curve 3, Figure II/2.2 and Fig. II/2.3) only when the ammonium trichloracetate concentration is in the range $9.00 \times 10^{-5} - 6.00 \times 10^{-4}$M. At lower concentrations the rate of reaction decelerates more rapidly than accountable for by consumption of monomer (Curves 1 and 2, Fig. II/2.2). At higher concentrations significant and irreproducible induction periods were observed (Fig. II/2.4). This has been noted by Bamford in a more recent paper.[59] No extensive data at 80°C was obtained but the variation in the induction periods at high ammonium trichloracetate was noted (Fig.II/2.5). These were short when concentrations of the two initiator

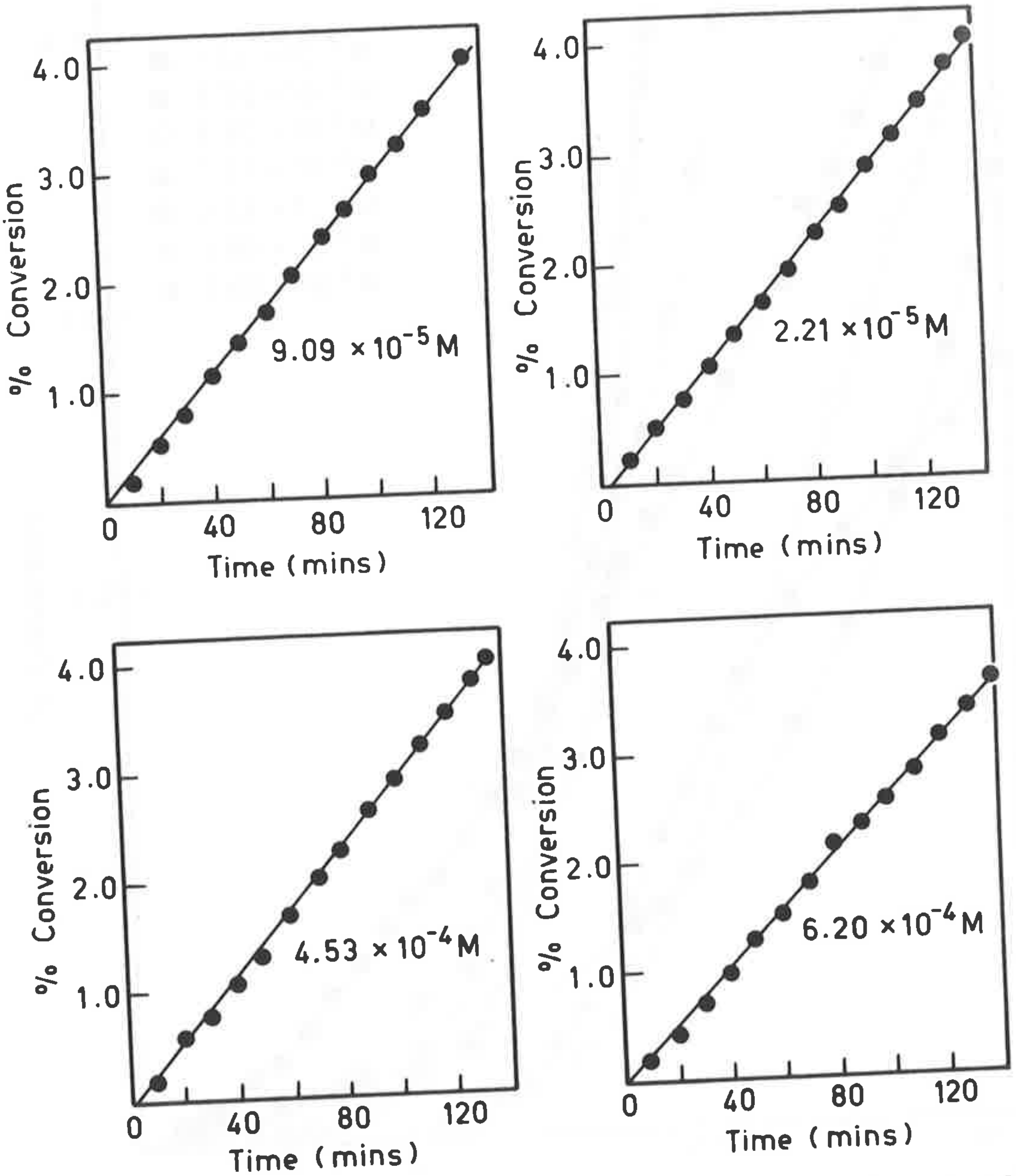


FIG. II/2·3 Monomer (MMA) conversion against time at 65°C for low $[CCl_3COONH_4]_0$ at constant $[Cu(acac)_2]_0 = 1.98 \times 10^{-3}$ M components were of the same order (curves 1-2, Fig. II2.5) but were long when ammonium trichloracetate was in significant excess (Curves 3-5, Fig.II/2.5). Initial rates of polymerization can be determined unambiguously from dilatometric runs at low and intermediate ammonium trichloracetate concentration range. Above this range, a steady-state rate may be cited, though there are serious doubts about its relevance.

(c) Low Salt Concentrations

$[CCl_3COONH_4]_0 \ll [Cu(acac)_2]_0 = (1.98 \pm 0.03) \times 10^{-3} M.$

The rates of polymerization obtained from the dilatometric runs at 65°C are, as cited, initial rates. The initial rates Rp are listed in table II/2.2

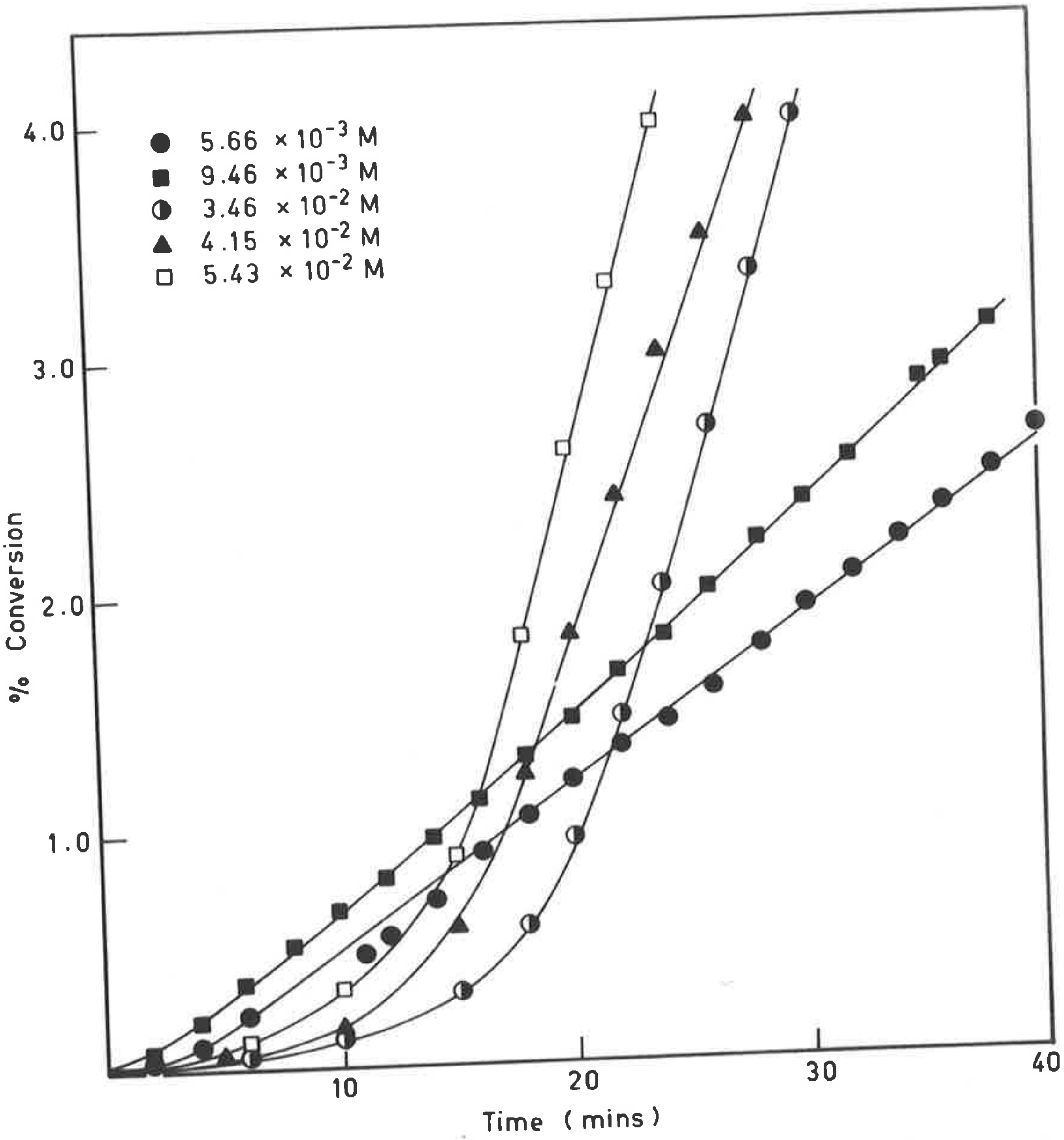


FIG. II/2·5 Monomer (MMA) conversion against time at 80°C for high $[CCl_3COONH_4]_o$ at constant $[Cu(acac)_2]_o = 1.95 \times 10^{-3}$ M.

Table II/2.2 Polymerization at 65°C initiated by $Cu(acac)_2$ and CCl_3COONH_4 at low $[CCl_3COONH_4]_0$

$10^3[Cu(acac)_2]_0$ mole l^{-1}	$10^4[CCl_3COONH_4]_0$ mole l^{-1}	$10^2[CCl_3COONH_4]_0^{\frac{1}{2}}$ mole$^{\frac{1}{2}}$, $l^{-\frac{1}{2}}$	$10^5.Rp$ molel^{-1} sec.$^{-1}$	$10^{-4}(1/Rp)$ mole^{-1} l.sec	$Rp/[CCl_3COONH_4]_0$ sec.$^{-1}$	$10^{-2}(1/[CCl_3COONH_4]_0^{\frac{1}{2}})$ mole$^{-\frac{1}{2}}$ $l^{\frac{1}{2}}$
1.98	0.109	0.330	3.28	3.05	3.01	3.03
1.98	0.113	0.336	3.13	3.20	2.77	2.98
1.98	0.355	0.596	3.73	2.68	1.05	1.68
1.98	0.909	0.953	4.25	2.35	0.498	1.05
1.98	0.921	0.960	4.18	2.39	0.454	1.04
1.98	2.16	1.47	4.40	2.27	0.204	0.680
1.98	2.21	1.49	4.45	2.25	0.201	0.671
1.98	4.53	2.13	4.52	2.21	0.100	0.469
1.98	6.20	2.49	4.03	2.48	0.065	0.402

A comparison of the variation in the rate of polymerization as a function of the square root of the salt concentration at constant cupric chelate concentration at 65°C with that by Bamford et al.[55] at 80°C is shown in figure II/2.6. At 65°C, the rate does not conform to a half order dependence on the salt concentration (equation II/2.6)

At low chelate concentration the rate fits the equation

$$Rp = k\,[CCl_3COONH_4]_o^{0.13} \qquad \text{(II2.20)}$$

but the order decreases with increase of concentration (Fig. II/2.8). There is really no basis for assuming the rate equation has a simple $k[CCl_3COONH_4]_o^n$ form.

(d) <u>High Salt Concentrations</u> (1.00 x 10^{-3} - 5.00 x 10^{-2} mole l^{-1}.)

For this concentration range the rates cited (Tables II/2.3 and II/2.4) are steady rates following the induction period as did Bamford and Robinson.[59] The rates at 80°C given by Bamford et al.[55] are gravimetrically determined and will be lower than the steady rate by an amount depending on the duration of the induction period.

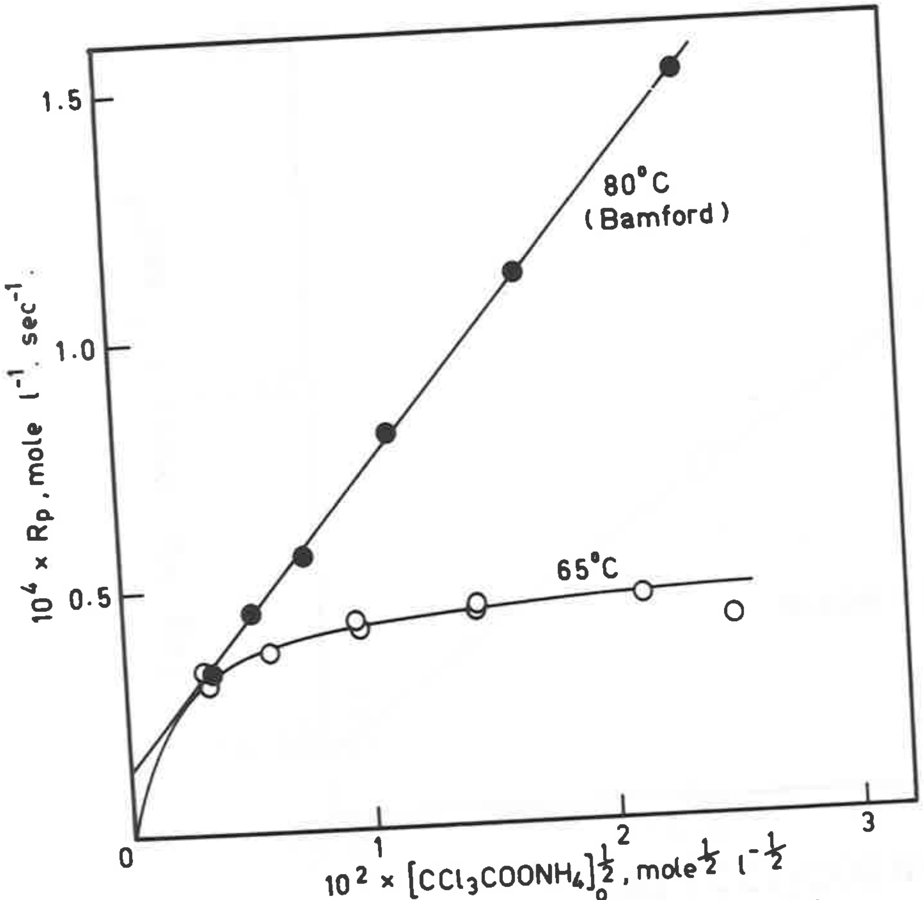


FIG. II/2·6 Initial rate of polymerisation of methyl methacrylate initiated by $Cu(acac)_2$ and CCl_3COONH_4. $[Cu(acac)_2]_0 = (1.98 \pm 0.03) \times 10^{-3}$ M

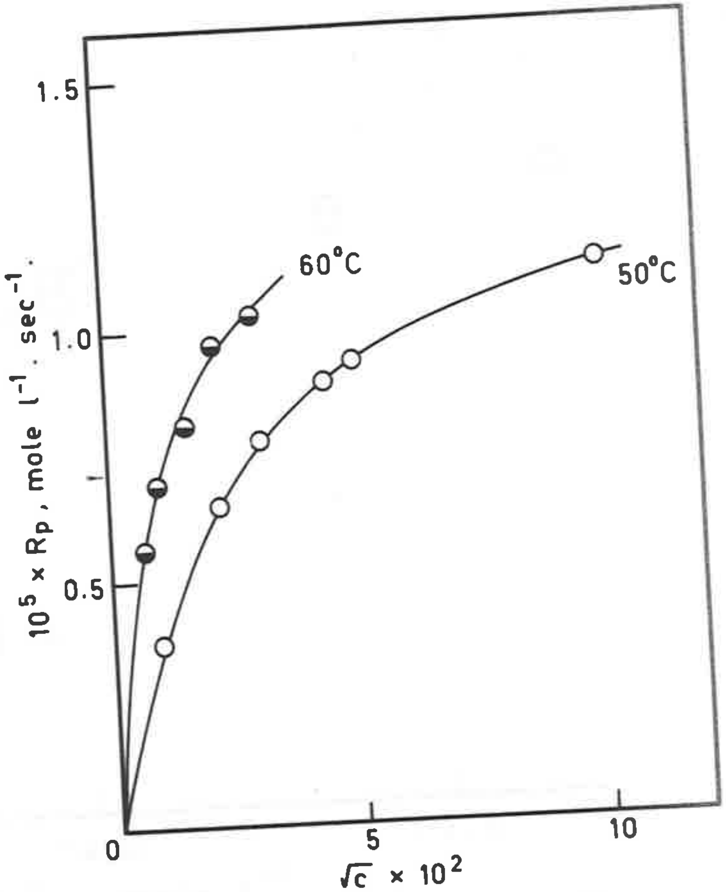


FIG. II/2·7 The curves of Misra et.al.[62] showing the rate of polymerisation of styrene as a function of phenylazotriphenylmethane concentration.

Table II/2.3 Polymerisation at 65°C initiated by $Cu(acac)_2$ and CCl_3COONH_4 at high $[CCl_3COONH_4]_0$

$10^3\,[Cu(acac)_2]_0$ mole l^{-1}	$10^2\,[CCl_3COONH_4]_0$ mole l^{-1}	$10^4 R_p$ mole l^{-1} sec.$^{-1}$
1.98	0.162	0.522
1.98	0.324	0.895
1.98	0.590	0.790
1.98	1.27	0.559
1.98	2.54	0.906
1.98	3.84	1.64
1.98	5.00	1.74

Table II/2.4 Polymerization at 80°C initiated by $Cu(acac)_2$ and CCl_3COONH_4 at high $[CCl_3COONH_4]_0$

$10^3[Cu(acac)_2]_0$ mole l^{-1}	$10^2[CCl_3COONH_4]_0$ mole l^{-1}	10^4Rp mole l^{-1} sec^{-1}
1.95	0.566	1.14
1.95	0.946	1.34
1.95	1.50	1.28
1.95	3.46	4.61
1.95	4.15	4.24
1.95	5.43	5.20

The results obtained by Bamford et.al.[55] at 80°C and those determined dilatometrically at 65°C and 80°C are shown in figure II/2.9. At 80°C the results obtained by dilatometry follow the pattern observed by Bamford etâ. up to a point. The rate of polymerization was relatively insensitive to ammonium trichloracetate concentration when it was in excess of the cupric chelate concentration up to less than a tenfold excess. In greater excess,increase in ammonium trichloracetate produced a significant increase in rate. Bamford et al[55] claimed that the rate of polymerization in this region increased linearly with the ammonium trichloracetate concentration. The results obtained dilatometrically indicate an order of lower than unity and it is a moot point whether Bamford's results would fit better to a lower order equation. The rates obtained from dilatometric runs compared favourably with Bamford's below ten-fold excess of the salt over the cupric chelate, but above this point they are significantly lower. The deviation may in fact be greater than shown, as significant induction periods were observed in this region. If this is the case Bamford's rates would be significantly less than the actual steady-state rate: e.g. with curve 3, figure II/2.5 a rate determined gravimetrically at 5% conversion would be half the steady-state rate.

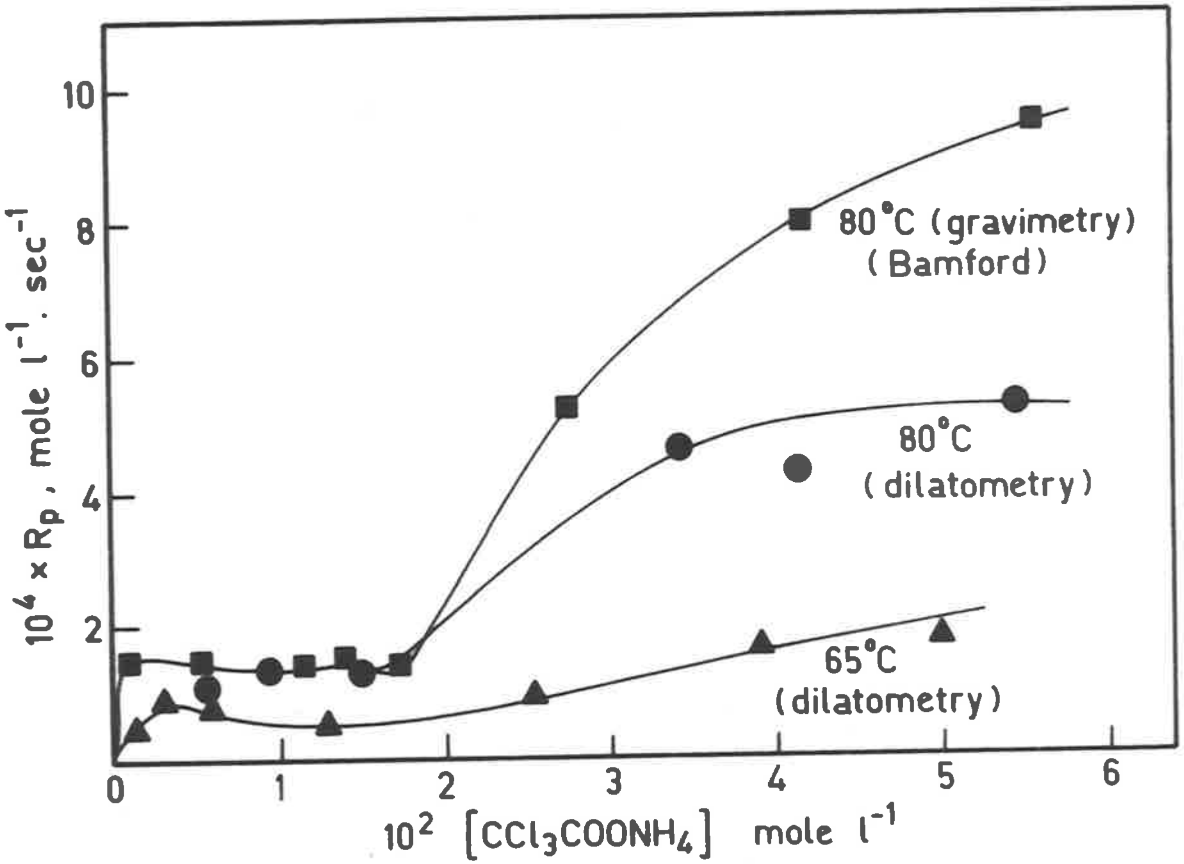


FIG II/2·9 Polymerisation of methyl methacrylate at high $[CCl_3COONH_4]_o$ in presence of constant $[Cu(acac)_2]_o$ = $(1.98 \pm 0.03) \times 10^{-3}$ M at 65°C and 80°C.

At 65°C the steady-state rate of polymerization increased only very slightly (ca. figure II/2.9) with increase of ammonium trichloracetate concentration when this salt is in excess of the cupric chelate.

(e) The Effects of Each Initiator Component on Methyl Methacrylate Polymerization:

Cupric acetylacetonate was not an initiator at 65°C. Ammonium trichloracetate initiated a slow polymerization. The initial rates were 10^{-5} mole l^{-1} sec.$^{-1}$ at an initiator concentration of 1.30×10^{-2} mole l^{-1} and 5.00×10^{-5} mole l^{-1} sec.$^{-1}$ at 5.13×10^{-2} mole l^{-1}. (Fig. II/2.10), in comparison with 10^{-4} mole l^{-1} sec.$^{-1}$ at 5.55×10^{-2} mole l^{-1} reported by Bamford et al[55] at 80°C.

At concentrations used in the dilatometric experiments, neither the cupric chelate nor the salt retarded the polymerization of methyl methacrylate initiated by 1.40×10^{-3} mole l^{-1} benzoyl peroxide at 65°C (Fig. II/2.11).

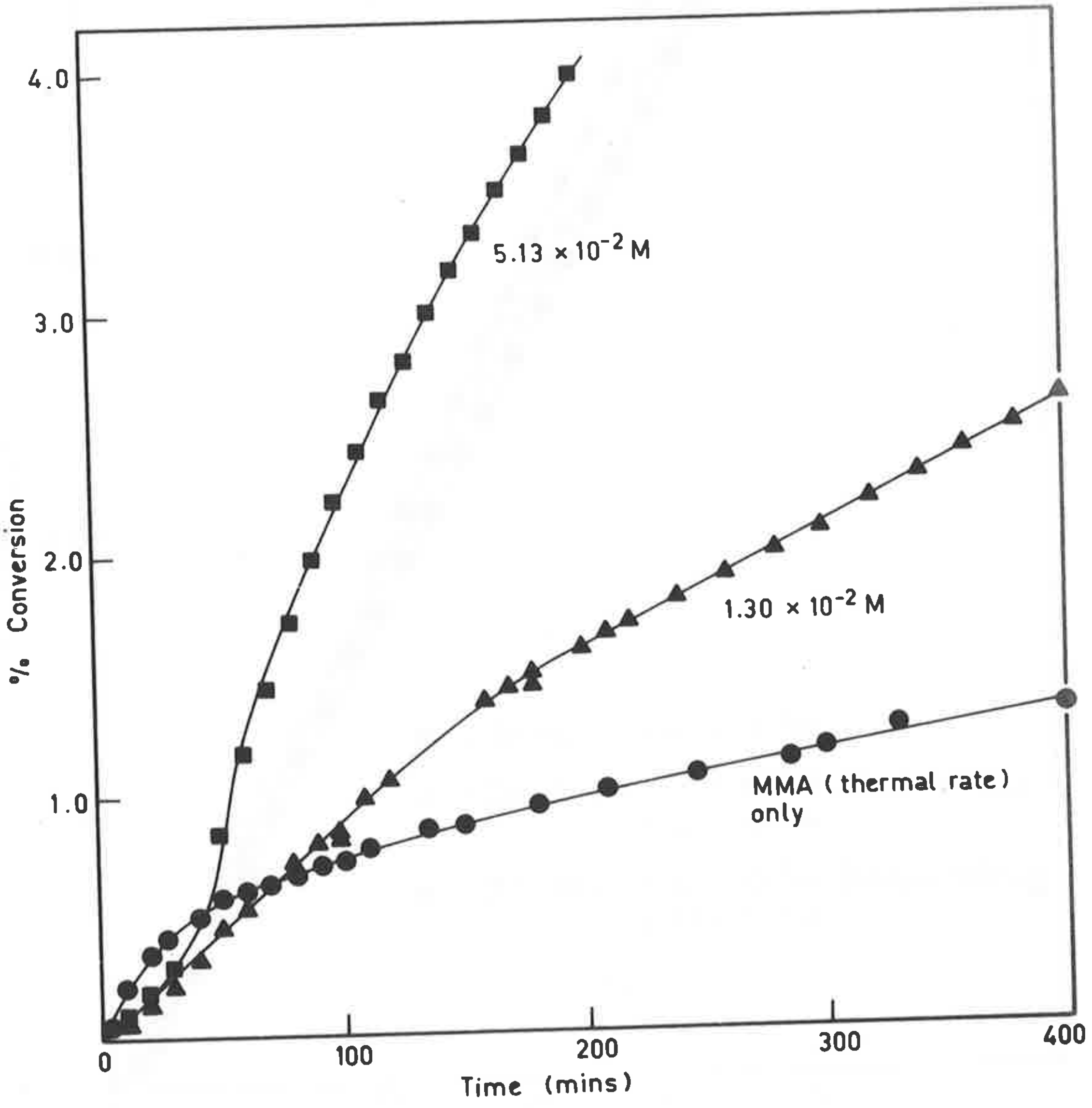


FIG. II / 2·10 Effect of CCl_3COONH_4 on methyl methacrylate polymerisation at 65°C .

C. DISCUSSION:

1. High Salt Concentrations:

The kinetics of the polymerization of methyl methacrylate at high salt concentrations are very complicated. The increase in rate of polymerization with time to a steady rate after the long and irreproducible induction period at 65°C and 80°C (Figs. II/2.4 and II/2.5) suggests that a complex, different from that at low salt concentrations, is formed during the induction period. The stationary-state rates listed in table II/2.3 and table II/2.4 and the 'initial' rates (Fig/ II/2.9) quoted by Bamford et al[55] should be based on this unknown complex. The conflicting results at 80°C obtained gravimetrically by Bamford et al[55] and those determined dilatometrically are illustrated in figure II/2.9. Serious doubts are therefore raised about the relevance of computing the kinetics of the reaction at high salt concentrations based on results obtained by gravimetric and dilatometric techniques. This is because the concentration of the unknown complex formed during the induction period is not known. The mechanism proposed by Bamford et al[55] at high salt concentrations should be treated with caution.

2. Low Salt Concentrations:

The kinetics at the low salt concentrations at 65°C can be formulated since the rates of polymerization are unambiguous initial rates. The kinetics at 65°C are, however, different from that at 80°C (Fig. II/2.6). The low order of reaction with respect to the ammonium trichloracetate (ca. 0.13) is symptomatic of mixed order termination. Neither the salt nor the cupric chelate (Fig. II/2.11) is a retarder of the polymerization of methyl methacrylate at 65°C. At 80°C the salt is a retarder.[55] The important role of the adduct (equation II2.19) was stressed in the vinyl acetate system.

(a) Modified Mechanism:

At 65°C, the Bamford mechanism is inadequate and is replaced by a modified mechanism. To the Bamford mechanism (equations II2.1, II2.2, II2.3, II2.4, and II2.5) is added a linear termination reaction by complex I:

$$\sim\!\!\sim M\cdot + I \longrightarrow III + \text{Polymer} \qquad k_I \qquad (II2.21)$$

The modified stationary state equation is

$$k_d[I] = k_I[I][\sim M\cdot]_{s.s.} + 2k_t[\sim M\cdot]^2_{s.s.} \qquad \text{(II2.22)}$$

Substituting $[\sim M\cdot]_{s.s.} = R_p/k_p[M]$ into equation (II2.22) gives

$$k_d[I] = \frac{k_I[I]\,R_p}{k_p[M]} + \frac{2k_tR_p^2}{k_p^2\,[M]^2}$$

or

$$\frac{1}{R_p} = \frac{k_I}{k_dk_p[M]} + \frac{2k_t}{k_dk_p^2\,[M]^2}\,\frac{R_p}{[I]} \qquad \text{(II2.23)}$$

where $[I] = [CCl_3COONH_4]$.

The modified mechanism predicts a linear relationship between $1/R_p$ and $R_p/[I]$. Values of $1/R_p$ and $R_p/[I]$ at 65°C are listed in table II/2.2. Figure II/2.12 shows that the experimental rates fit this law for methyl methacrylate, particularly at 65°C. The slope $2k_t/k_dk_p^2[M]^2$ gives a measure of the extent of second order termination, while the intercept $k_I/k_dk_p[M]$ shows termination by complex I. The intercept was found to be 2.2×10^4 and 4.0×10^3 mole^{-1}l.sec at 65 and 80°C respectively, while the slope gave values of 3.3×10^3 and 1.25×10^4 mole^{1}l.sec^{2} at 65 and 80°C respectively.

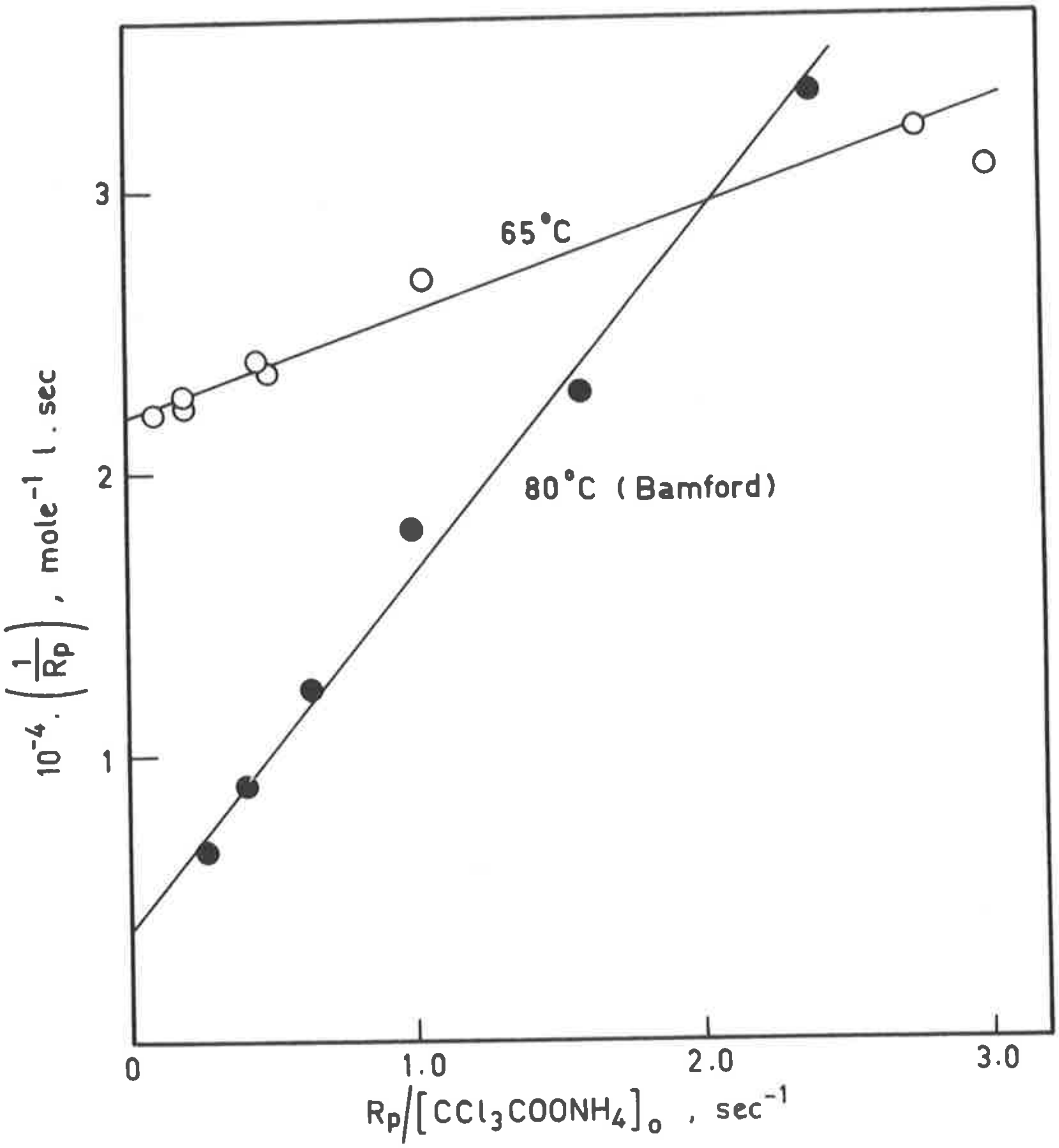


FIG. II/2·12 Test of modified mechanism.

(b) Alternative Mechanism:

There is an alternative mechanism where termination could occur by

$$\sim\!\!\sim M\cdot + II \longrightarrow IV + \text{Polymer} \qquad k_{II} \qquad (II2.24)$$

in addition to reactions (II2.1), (II2.2), (II2.3), (II2.4) and (II2.5). This is a special case of primary radical termination. However, it is kinetically intractable involving quintic equations in stationary state concentrations[61] since there are insufficient, precise data available to make any fit meaningful. It would, however, give a rate curve of the type found (figure II/2.7), as observed by Misra et al[62], using phenyl-azo-triphenyl-methane. The $\dot{C}Cl_3$ radical would be the reactive radical analogous to the phenyl radical produced from the decomposition of the phenyl-azo-triphenyl-methane, while the complex II would be the inhibitor analogous to the triphenylmethane $\dot{C}Ph_3$ radical which is a stable radical known to inhibit the polymerization of styrene at 100°C.

It should be noted that the experimental results at 65°C fitted the empirical equation.

$$\frac{1}{R_p} = a + \frac{b}{[I]^{\frac{1}{2}}} \qquad (II2.25)$$

obeyed by systems showing primary radical termination as shown in figure II/2.13. This equation was derived by Bamford, Jenkins and Johnston,[23] and Misra et al.[62] using the geometric mean treatment

$$k_{12} = \sqrt{k_{11}k_{22}} \qquad (II2.26)$$

This approach was criticised by Allen and Patrick[61] on the grounds that it is inappropriate to diffusion-controlled termination reactions. Recently, however, Cullinan[64] using the absolute rate theory of Eyring have developed an expression which predicts the concentration dependence of the <u>binary</u> mutual diffusion coefficient in terms of the two infinite dilute coefficients and a thermodynamic factor

$$D_{ij} = (D^{o}_{ij})^{X_j}(D^{o}_{ji})^{X_i}\left(1 + \frac{d\ln \gamma_i}{d\ln X_i}\right) \qquad (II2.27)$$

where X_i and X_j are the mole fractions of species i and j respectively, and γ_i is the activity coefficient of species i. This relationship has been tested by Vignes[65] and shown to be valid in all binary liquid and solid systems measured to date with the exception of associated mixtures.

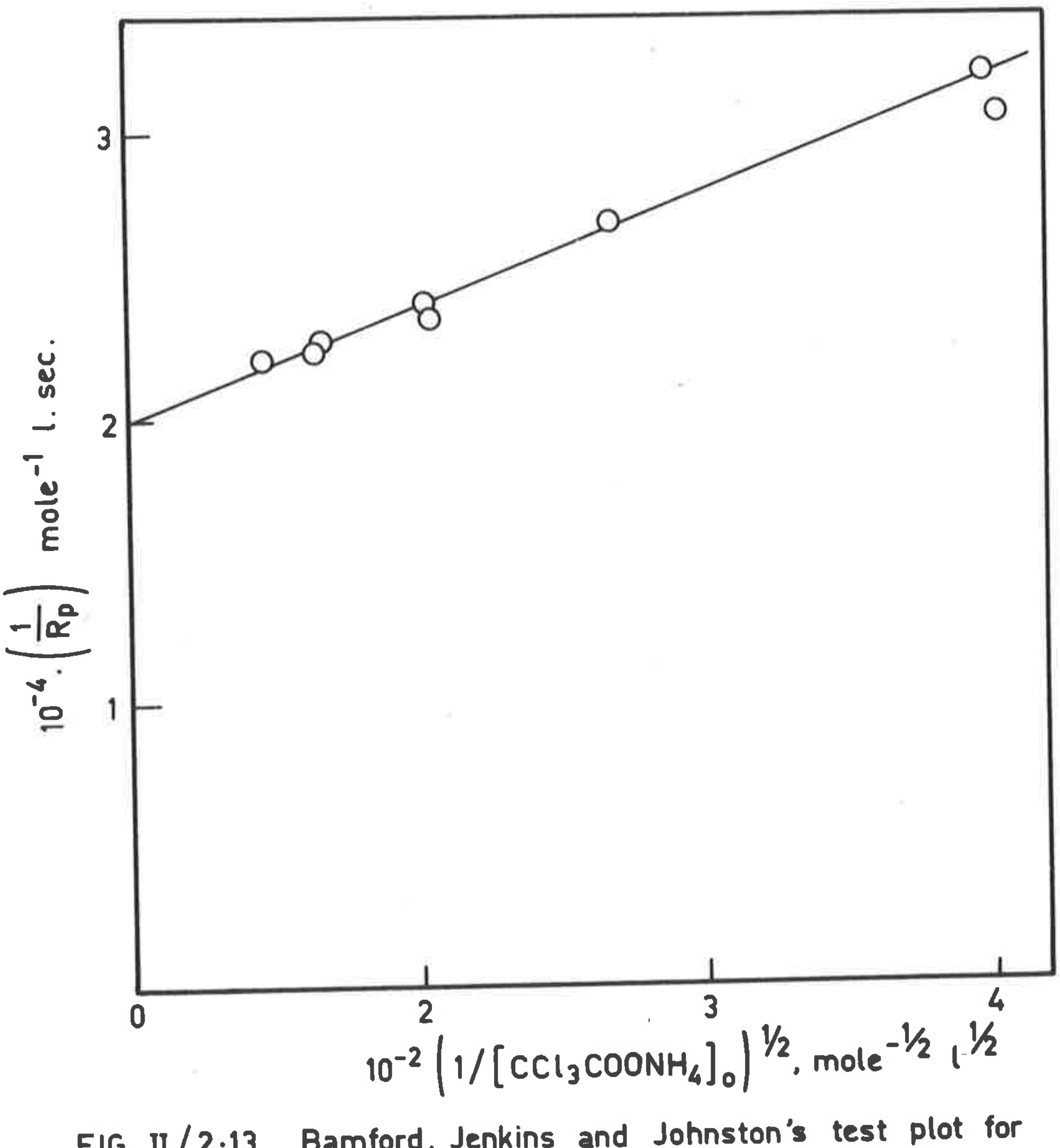


FIG. II/2·13 Bamford, Jenkins and Johnston's test plot for primary radical termination.

Cullinan and Cusick[66] have extended the lattice model of Eyring to the case of diffusion in a multi-component system. More recently, the work of Cullinan and Cusick[66] was criticised by Mortimer[67] who showed that the Eyring model is inadequate for a theory of multicomponent diffusion.

O'Driscoll[68] has cited equation (II2.27) as justification for using the relationship

$$k_{12} = k_{11}^{X_1} k_{22}^{X_2} \qquad (II2.28)$$

to estimate the termination constant for unlike radicals. He further claims that this approximates to equation (II2.26) over a wide range of relative concentrations. If this is valid then the theoretical status of equation (II2.25) is restored. However, there are considerable doubts about the applicability of equation (II2.27) for a binary system to a multi-component system.

Allen and Patrick[61] rejected equation (II2.26) in favour of

$$k_{12} = k_{11} + k_{22} \qquad (II2.29)$$

for standard controlled reactions. This relationship is based on

$$D_{12} = D_1 + D_2 \tag{II2.30}$$

an expression derived by Chandrasekhar[69] for a system in which D_{12} is the diffusion coefficient governing the separation of two particles moving independently and randomly with individual diffusion constants D_1 and D_2. The original application was to Brownian motion, but the Brownian-motion model is a reasonable one to apply to the problem of two radicals moving in solvent.

The question of a suitable model for multi-component diffusion is still an open one.

(c) Nature of Linear Termination:

In the case of the modified mechanism, the values of the ratio intercept/slope given by

$$\frac{\text{intercept}}{\text{slope}} = \frac{k_I k_p}{2k_t}[M] \tag{II2.31}$$

are 6.7 and 0.24 mole^{-1} 1. at 65 and 80°C respectively as calculated from figure II/2.12. By defining the apparent "energy of activation" $E_{I/S}$ for the ratio of intercept over slope as

$$\frac{\text{intercept}}{\text{slope}} = Ae^{-E_{I/S}/RT} \qquad (II2.32)$$

it was found that $E_{I/S} = -52.3$ kcal.mole^{-1}. Since $E_{I/S} = E_I + E_p - E_t$ (eqn. (II2.31)) and if $E_p - E_t = 3$ kcal. mole^{-1}, then $E_I = -55.3$ kcal.mole^{-1} E_I has an unusual high negative value.

In the alternative mechanism, deviation from $R_p \propto [I]^{\frac{1}{2}}$ diminishes rapidly with increasing temperature. E_{II} must be negative.

Thus k_I and k_{II} are not simple rate coefficients. A possible explanation of the negative value of E_I is to add to the modified mechanism a reaction

$$\text{III (or IV)} + M \longrightarrow \text{Radical} \quad k_{III} \qquad (II2.33)$$

$$\text{or} \quad \text{III (or IV)} \longrightarrow \text{Radical (s)}$$

At 65°C, k_I (or k_{II}) is a genuine termination constant and k_{III} is negligible. At 80°C,k_I(or k_{II}) is a non-terminating constant and k_{III} is important - reinitiation occurs. The normal $R_p \propto [I]^{\frac{1}{2}}$ kinetics is therefore observed at 80°C. Whichever reaction is responsible for reinitiation of chains, it has a high energy of activation.

(d) A Problem about Initiation:

The initiation mechanism is more complicated than that proposed by Bamford et al.[55] The values of the slope given by

$$\text{slope} = 2k_t/k_d k_p^2 \left[M\right]^2 \qquad (II2.34)$$

are 3.3×10^3 and 1.25×10^4 $\text{mole}^{-1}\text{l. sec.}^2$ at 65 and 80°C respectively. By defining the apparent "energy of activation" E_{slope} for the slope as

$$\text{slope} = A_e^{-E_{slope}/RT} \qquad (II2.35)$$

it was found that $E_{slope} = 20.5$ kcal.mole^{-1}. Since $E_{slope} = E_t - 2E_p - E_d$ (eqn. (II2.34) and if $E_p - \frac{1}{2}E_t = 4.5$ kcal.mole^{-1}, then $E_d = -25$ kcal.mole^{-1}.

The negative value of E_d indicates that the rate constant k_d must be complex and contain an equilibrium constant:

$$\begin{array}{ccc} CCl_3COONH_4\text{(or I)} + ? & \overset{\Delta H}{=\!=\!=} & \text{Complex} \\ & & E_d{}' \\ & & \text{Radical(s)} \end{array}$$

$$\text{where } E_{d_{obs}} = E_d{}' - \Delta H \qquad (II2.36)$$

Bamford et al.[55] found that at low salt concentration range (1.00 - 6.00 x 10^{-4}M) the equilibrium constant K = 2706 mole^{-1} l. at 80°C and $[I] = [CCl_3COONH_4]_o$. If this is true, then K $\gg$ 2706 mole^{-1} l. at 65°C and $[I] = [CCl_3COONH_4]_o$. Under these conditions, the rate equation for initiation becomes

$$R_i = k_d[CCl_3COONH_4]_o \qquad (II2.37)$$

K does not appear in the rate coefficient and E_{obs} will not, therefore, include ΔH for this equilibrium.

One is forced to make one of the following conclusions: Either (i) The equilibrium constant (K = 2706 $\text{mole}^{-1}\ l^{+1}$) is incorrect and is much smaller. This is unlikely in view of the kinetics observed, particularly $R_p \propto S_o^{\frac{1}{2}}$. Also Bamford et al.[55] has found that under conditions where the kinetics were observed at 80°C, the deviations from $S_o^{\frac{1}{2}}$ dependence are explicable in terms of an equilibrium constant of 2706 $\text{mole}^{-1}\ l^{+1}$ and equation (II2.10)

or (ii) The equilibrium constant for which K = 2706 $\text{mole}^{-1}\ l^{+1}$ at 80°C, is not the one (or only one) involved in the initiation. There are possibilities of monomer involvement, 2:1 complexes, etc.

Of the two explanations, the first one is the less likely. It is very simple in principle to determine the role of monomer in an initiator equilibrium by looking at the variation of R_p on $[M]$. If monomer is involved, the order should obviously be 1.5, but if monomer does not enter into the initiation process a value of unity would be anticipated. It is very difficult in practice to determine the order in $[M]$ of the overall reaction. The difficulties are:

(i) An inert solvent (diluent) must be found that can maintain the polar medium of methyl methacrylate which is a polar monomer, and avoid any specific solvation effects or participation in the radical chain reaction. It is very difficult to find such a nonreactive diluent.

(ii) $[M]$ will or will not appear in the function for the rate of initiation depending on the position of the equilibrium.

A good example is the work of Bamford and Lind[48] on the polymerisation of methyl methacrylate initiated by $Mn^{III}(acac)_3$. The observed rate equation is

$$R_p = K'[Mn^{III}(acac)_3]^{\frac{1}{2}}[M] \qquad (II2.38)$$

where the first order in monomer was obtained by using ethyl acetate as diluent. The conclusion was that the monomer did not participate in the initiation step. It must be pointed out that the viscosity of ethyl acetate is, unfortunately, 16% lower than that of the monomer and a viscosity correction must be applied to monomer + ethyl acetate mixtures since the termination reaction in the free-radical polymerization of methyl methacrylate is diffusion-controlled.[70] It can be deduced that, even if the monomer is involved in the equilibrium, a stationary-state rate equation can be formulated similarly to the observed rate equation (II2.38). Consider the initiation mechanism

$$\mathrm{Mn^{III}(acac)_2 + M \rightleftharpoons Complex} \qquad K \qquad \text{(II2.39)}$$

$$\mathrm{(Complex) \longrightarrow Radical} + \text{--} \qquad k_d \qquad \text{(II2.40)}$$

If $[M] \gg [\mathrm{Mn^{III}(acac)_3}]_o$ or if the equilibrium lies predominantly to the right, i.e. if K is large, then

$$[\mathrm{Complex}] = [\mathrm{Mn^{III}(acac)_3}]_o \qquad \text{(II2.41)}$$

where $[\mathrm{Mn^{III}(acac)_3}]_o$ is the concentration of $\mathrm{Mn^{III}(acac)_3}$ added.

The rate of initiation becomes

$$R_i = k_d \left[Mn^{III}(acac)_3 \right]_o \qquad (II2.42)$$

Substituting equation (II2.42) into the stationary state equation

$$R_p = k_p \sqrt{\frac{R_i}{2k_t}} \left[M \right] \qquad (II2.43)$$

gives

$$R_p = k_p \sqrt{\frac{k_d}{2k_t}} \left[Mn^{III}(acac)_3 \right]_o^{\frac{1}{2}} \left[M \right] \qquad (II2.44)$$

which is in agreement with the observed rate equation (II2.38).

Thus, the observed kinetic rate equation is not conclusive in the sense that it cannot predict with 100% certainty whether the monomer is involved in the initiation process.

D. A SUMMARY OF THE SYSTEM: $Cu^{II}(acac)_2/CCl_3COONH_4/MMA$:

The results and discussion, as cited earlier, lead to the following conclusions:

(i) Bamford mechanism explains results at 80°C, except that

(ii) initiation is more complicated

(iii) The complex ($K = 2706$ mole^{-1} l. at 80°C) determined by Bamford is probably not the initiator.

(iv) At 65°C, Bamford mechanism is inadequate

(v) Must add a linear termination reaction,

(vi) which diminishes in importance at higher temperatures.

Two problems remain unsolved:

(i) The exact nature of the initiation process and

(ii) the mechanism of reinitiation of chains at higher temperatures.

PART III : INITIATION OF VINYL POLYMERIZATION BY FERROUS ACETYLACETONATE:

CHAPTER I: EXPERIMENTAL:

A. INTRODUCTION

Several groups of workers[47-49] have shown that certain metal (III) acetylacetonates are effective initiators of vinyl polymerization (ca.Part I, C2). However, no extensive work has been carried out on metal (II) acetylacetonates as effective polymerization initiators. It was decided to investigate whether ferrous acetylacetonate alone could initiate the polymerization of styrene, methyl methacrylate and vinyl acetate, before examining the kinetic consequences of the polymerization of methyl methacrylate initiated by the redox pair which consists of a combination of ferrous acetylacetonate and cumene hydroperoxide.

B. MATERIALS

1. Purification of Monomers:

The procedure for the purification of styrene, methyl methacrylate and vinyl acetate was similar to that described in Part II, Chapter IB.

2. Anhydrous Ferrous Acetylacetonate, $Fe(acac)_2$

Hydrated ferrous acetylacetonate, $Fe(acac)_2.2H_2O$, was prepared as described by Emmert and Jarcyznski.[71] The hydrate was then dehydrated and sublimed to the anhydrous orange-brown complex, $Fe(acac)_2$, under vacuum at 165-175°C/10^{-3} Torr.

C. DILATOMETER AND FILLING OF DILATOMETER:

The introduction of ferrous acetylacetonate into the dilatometer by the method described in Part II, Chapter ID may result in contamination of the ferrous chelate by spurious impurities and oxidation of the chelate. The dilatometer and dilatometer-filler apparatus were therefore redesigned.

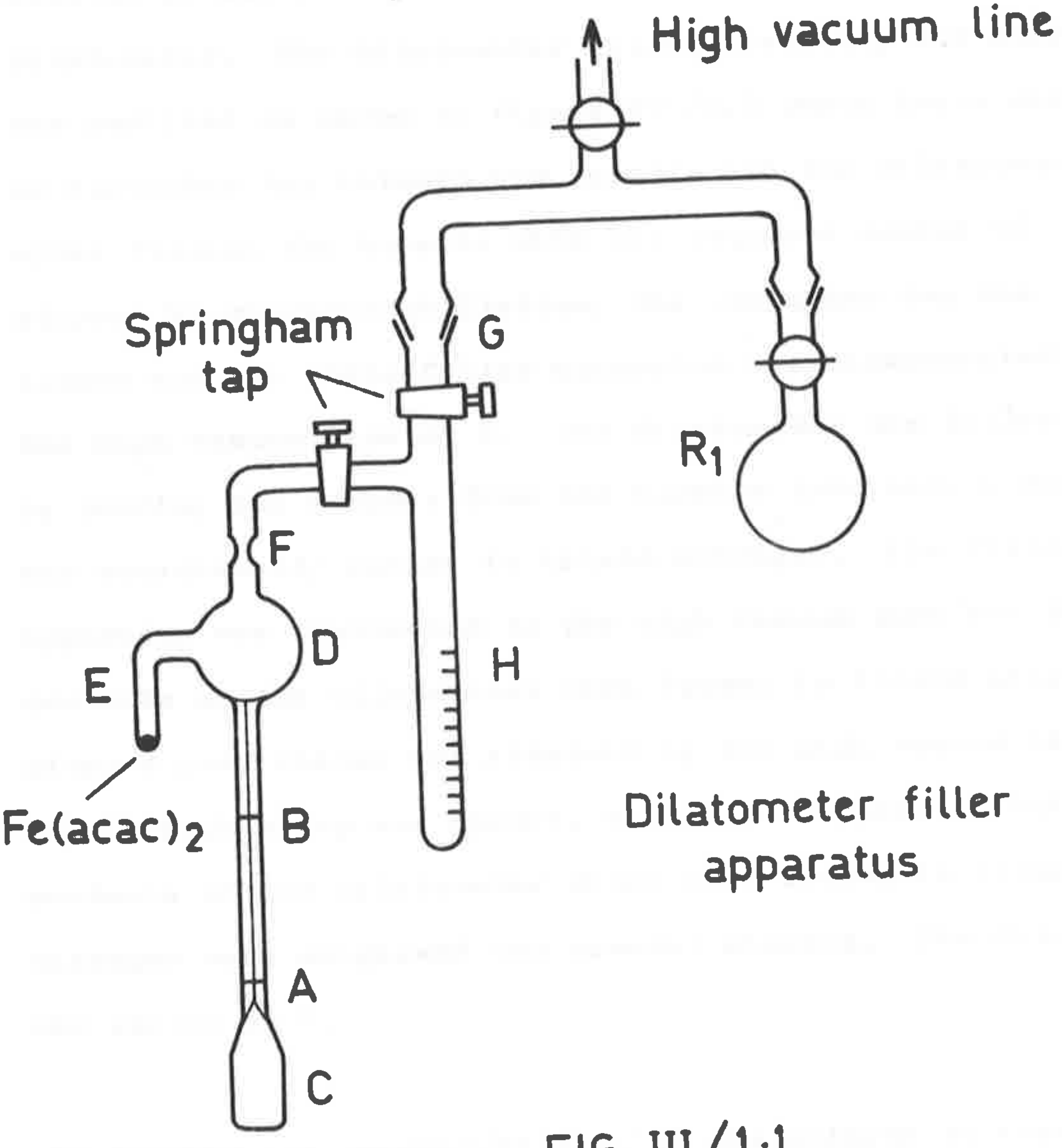
The dilatometer (10 ml. capacity) was of a larger and different type to that described in Part II, Chapter 1C. It consisted of a cylindrical bulb (10 ml. capacity), rounded off at one end and sealed at the other onto an approximately 30 cm. length of 1 mm. or 2 mm. bore capillary tubing. Onto the other end of the capillary tube was sealed a larger mixing bulb (about 20 ml. capacity), with a side arm. The dilatometer was calibrated as described in

Part II, Chapter 1C.

The dilatometer and the filling apparatus for monomers, methyl methacrylate and vinyl acetate, is shown in figure III/1.1 Springham greaseless stopcocks with fluorocarbon rubber (Viton A) diaphragms were used to minimise the amount of adsorbed moisture that may be present. A known weighed amount of anhydrous ferrous acetylacetonate in a pyrex semi-micro tube was sealed to the side-arm at E. The filler was attached to the high vacuum line at G, evacuated and flamed with a smoky flame to remove traces of adsorbed moisture. Any leaks that may arise in the dilatometer filler apparatus may be located by the Tesla coil. The whole apparatus and the ferrous chelate was outgassed for at least three hours. The required amount of monomer was vacuum-distilled from the reservoir vessel R_1 into the graduated burette H, given another good outgassing and distilled under vacuum into bulb C by freezing the bulb in liquid nitrogen. The monomer in the bulb was further outgassed until a 'sticky' vacuum was attained. The dilatometer was sealed at F.

The dilatometer-filler apparatus of the type shown in figure III/1.1 was not suitable for styrene. It was found that it took too long (about four hours) to vacuum distill 10 ml. of styrene from the burette into the dilatometer. The dilatometer filling assembly for styrene was modified as shown in figure III/1.2 where there was no Springham tap between the burette and the dilatometer. After filling the burette with the required amount of styrene by vacuum-distillation, the Springham tap was closed and the whole filler apparatus was disconnected from the high vacuum line at G. The dilatometer was filled by pouring the monomer from the burette into bulb C which was occasionally cooled in liquid nitrogen. The filler apparatus was reattached to the high vacuum line and the contents of the dilatometer were frozen in liquid nitrogen. After a good vacuum was attained by the high vacuum line, the Springham tap was opened, the filler apparatus and contents of the dilatometer which were frozen in liquid nitrogen were outgassed for several minutes. The dilatometer was sealed at F.

The monomer (or monomer/Fe(acac)$_2$) was allowed to thaw and warmed to room temperature by placing the dilatometer in a vessel containing water at room temperature. The



Dilatometer filler apparatus

FIG. III/1·1

complex and the monomer was thoroughly mixed by inverting the dilatometer and shaking its contents in the larger mixing bulb D. The monomer solution was allowed to flow back into bulb C and up the capillary. The dilatometer was placed in a thermostat bath. At 25°C, no adjustment of the level of the meniscus in the capillary was required. At temperatures above 25°C, the dilatometer, after placing in the thermostat bath for less than a minute, was quickly removed from the bath, and the height of the solution in the capillary was adjusted to a suitable level between the lower mark A and the upper mark B by tipping some of the solution into the side arm tube. The dilatometer was replaced immediately into the thermostat bath. The meniscus should rise to a level either below B or above B depending on the temperature of the thermostat. The extent of the polymerization could be followed down this full length as the solution contracted. The maximum height reached by the meniscus during warming-up period was noted with a cathetometer. This steady value was taken as the "zero height" and "zero time" for the run. The meniscus began to fall as polymerization commenced. The difference between the maximum height and the height at any subsequent time is a direct measure of the amount of polymerization that had taken place.

The polymerization was followed up to about 1% conversion. The dilatometer was removed from the thermostat, the side-arm broken and the polymer was precipitated by pouring the polymerizing medium into methanol.

The rates of polymerization quoted in subsequent chapters are either initial rates or steady-state rates depending on the duration of the induction period. If the induction period is short (from one to five minutes) the rates cited are initial rates. However, when the induction period is long (from 15 minutes onwards), the rates are strictly stationary rates.

D. THERMOSTAT:

The 25°C water bath was controlled by a 10K thermistor-controlled unit. The 65-80°C mercury-toluene controlled bath as described in Part II, Chapter IE was replaced by a new heating unit. The 60°C water-bath was maintained at that temperature by a control unit consisting of four heating rods with a total heating capacity of 400 watts and a 100K thermistor probe. The 80°C thermostat consisted of an oil-bath maintained at the required temperature by another control unit consisting of four heating rods with a total heating power of 800 watts and a 100K thermistor probe.

E. CLEANING OF USED DILATOMETERS AND DILATOMETER-FILLING APPARATUS:

The dilatometer history affect is quite novel, depending on the particular cleaning technique used. Of the three cleaning methods employed for used dilatometers - R.B.S. 25 treatment, standard chromic acid method, and the nitric acid method - the nitric acid treatment was found to be most ideal in cleaning used dilatometers since this method gave good reproducible results (ca. Table III/2.1). All subsequent used dilatometers were cleaned by the nitric acid treatment which is described as follows:

The used dilatometers were rinsed several times with chloroform, soaked overnight in chloroform, dried in the oven at 110°C and finally cleaned in 50% warm nitric acid.

The cleaned dilatometers were washed with plenty of distilled water and roasted at 600°C for about two hours to remove traces of organic materials and residues of nitric acid.

The dilatometer filler was cleaned by soaking in 1% HF for several minutes. The cleaned filler was washed several times with distilled water and dried in the oven at 110°C.

CHAPTER II: INITIATION OF POLYMERIZATION OF STYRENE BY FERROUS ACETYLACETONATE-RESULTS AND DISCUSSION:

A. RESULTS:

1. Polymerization at 60°C

Two preliminary dilatometric runs of the type discussed earlier, were carried out on styrene at 60°C using thermal initiation and ferrous acetylacetonate (5.00×10^{-4}M) alone. The results are shown in figure III/2.1. The induction period was slightly less than 5 minutes. The initial rate of polymerization of styrene at 60°C initiated by ferrous acetylacetonate alone is about 3 times faster than the uncatalyzed thermal rate which has a value of 0.1014% conversion per hour. The thermal rate is in very good agreement with the literature[72] value of 0.1% conversion per hour. The preliminary results are in contrast to the finding of Burnett and North[52] at 40°C. Burnett and North[52] found that the rate of thermal polymerization was slightly higher than the rate in the presence of the ferrous complex. The results at 60°C showed that ferrous acetylacetonate initiates the polymerization of styrene, although it may not be an efficient initiator. A series of dilatometric runs were

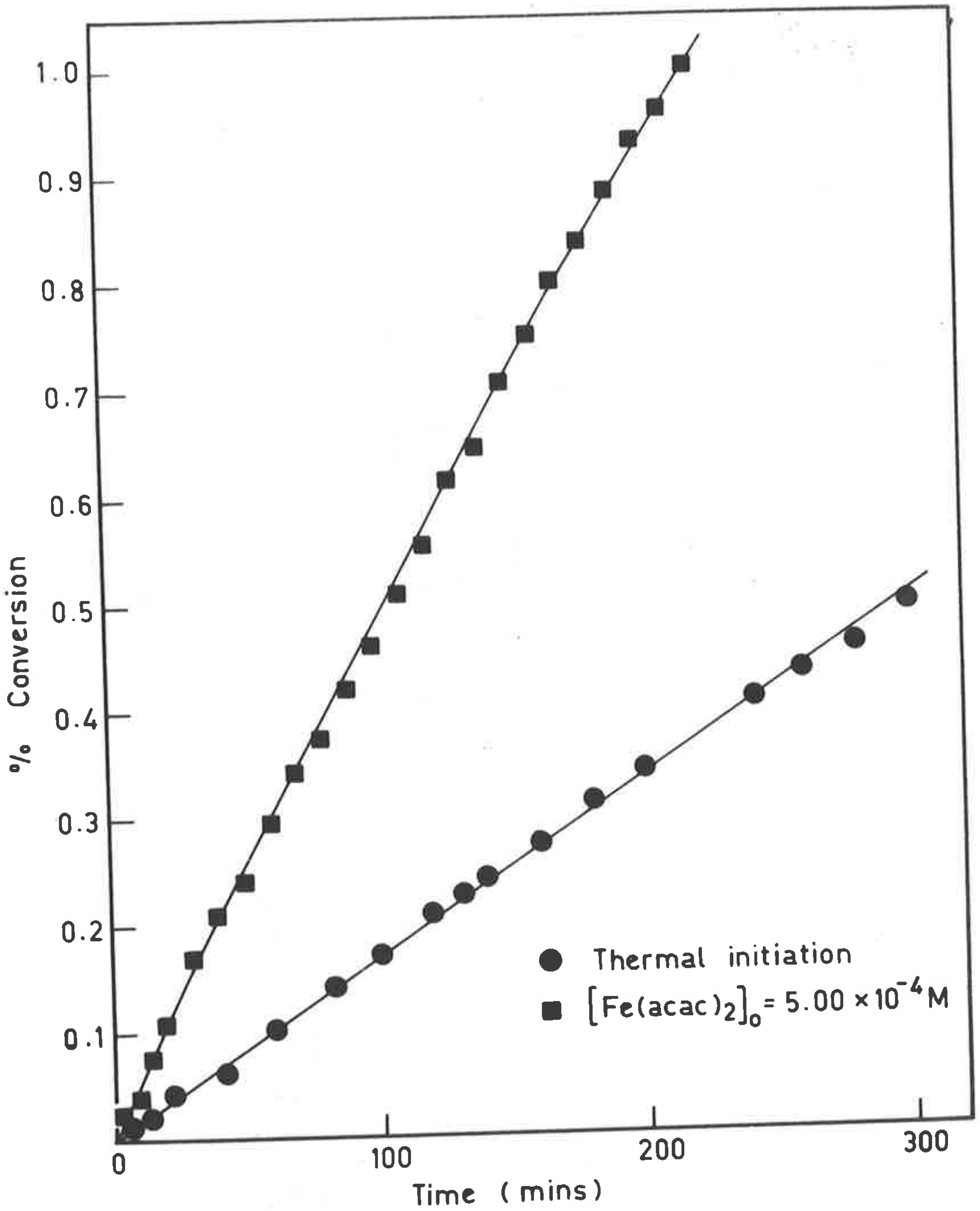


FIG. III/2·1 Effect of ferrous acetylacetonate on the initial rate of polymerisation of styrene at 60°C.

further carried out on styrene at 60°C by varying the concentration of the ferrous complex. The kinetic runs are shown in figure III/2.2. The induction period was in the range 3-5 minutes. The rates of polymerization are initial rates which were obtained from the initial slope of a plot of % conversion against time (figure III/2.2). The initial rates R_p are listed in table III/2.1. The variation in rate with concentration of the ferrous chelate is shown in figure III/2.3. The conventional dependence of the initial rate of polymerisation upon the square root of the ferrous acetylacetonate concentration no longer holds under the existing conditions.

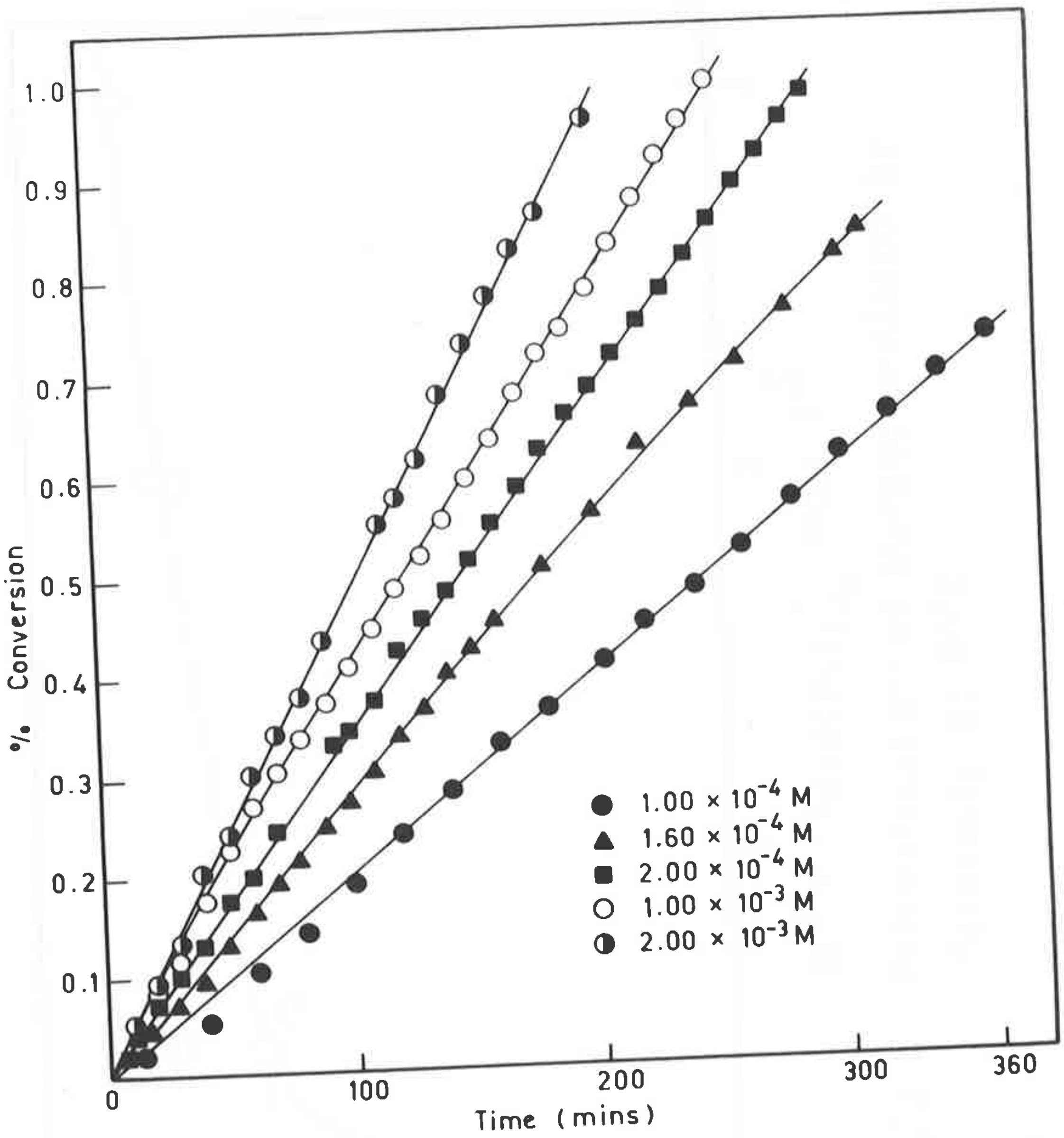


FIG. III/2·2 Effect of ferrous acetylacetonate on the initial rate of polymerisation of styrene at 60°C.

Table III/2.1 Polymerization of styrene initiated by $Fe(acac)_2$ at 60°C.

$10^4[Fe(acac)_2]_0$ mole l^{-1}	10^6 x Rp mole l^{-1} sec^{-1}	$10^{-5}(1/Rp)$ $mole^{-1}l.sec$	$10^2Rp/[Fe(acac)_2]_0$) sec^{-1}
-	2.45	4.08	-
1.00	3.06	3.27	3.06
1.60	3.95	2.53	2.47
2.00	4.85	2.06	2.43
2.50	4.97	2.01	1.98
4.00	5.94	1.68	1.49
5.00	6.16	1.62	1.23
5.00	7.17	1.39	1.43
6.00	5.81	1.72	0.97
10.00	6.53	1.53	0.65
20.00	7.27	1.38	0.36
20.00	7.31	1.37	0.37
30.00	7.76	1.29	0.26

2. Energy of Activation Experiments:

A series of polymerizations were carried out to find out how temperature affected the initial rate of styrene. The concentration of ferrous acetylacetonate was kept constant at 5.00×10^{-4}M. At 40°C, the polymerization was found to be so slow that it could not be measured with any accuracy. Fairly linear straight lines were observed for plots of % conversion against time in the temperature range 50 - 80°C as illustrated in figure III/2.4. The induction period for kinetic runs at temperatures 60, 70 and 80°C was less than 5 minutes, but the induction period at 50°C was about 40 minutes. The rates of polymerization at 60-80°C are therefore initial rates, but that at 50°C is the steady-state rate. These are listed in table III/2.2. Figure III/2.5 shows the Arrhenius plot of $-\ln R_p$ against $1/T$°K. The rates of polymerization of styrene measured over the range 50-80°C for constant $Fe(acac)_2 = 5.00 \times 10^{-4}$M conform satisfactorily to the Arrhenius plot, the overall activation energy being 11 kcal.mole^{-1}. This value is unusually low for an initiation process, especially when compared to those for $Mn^{III}(acac)_3$ - methyl methacrylate[48] system and $Co^{III}(acac)_3$-diene systems[49].

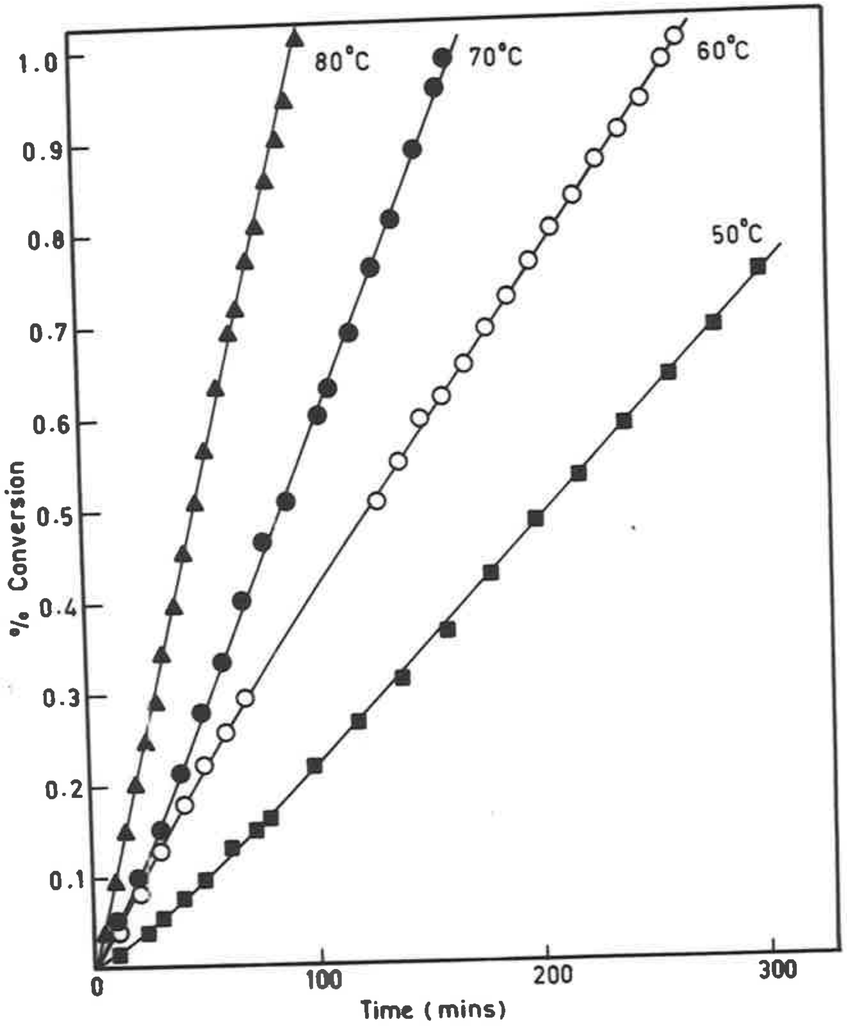


FIG. III/2·4 Effect of temperature on the rate of polymerization of styrene at constant $[Fe(acac)_2]_0 = 5.00 \times 10^{-4}$ M.

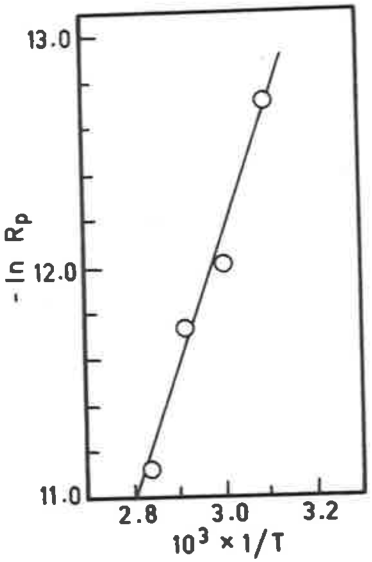


FIG. III/2·5 Arrhenius plot.

Table III/2.2 Effect of temperature on initial rate of polymerization of styrene at constant $[Fe(acac)_2]_o = 5.00 \times 10^{-4}M$

Temp. °C	Temp. °K	$10^6 \times Rp$ mole l^{-1} sec.$^{-1}$	$-\log_{10}Rp$	$-\ln Rp$	$10^3 \times 1/T°K$
40	313	v.v.slow	-	-	3.195
50	323	3.01	5.5214	12.72	3.096
60	333	6.16	5.2104	11.99	3.003
70	343	7.96	5.0991	11.74	2.915
80	353	14.70	4.8327	11.13	2.833

Bamford and Lind[48] found that the rates of polymerization of methyl methacrylate measured over the range 60-80°C for constant $[Mn^{III}(acac)_3]$ gave a satisfactory Arrhenius plot leading to an activation energy for initiation of 26 kcal.mole^{-1}. More recently, Riches[49] found that the rates of polymerization measured over the temperature range 110-140°C for constant $[Co^{III}(acac)_3]$ conform approximately to the Arrhenius plot, the apparent activation energy being approximately 13 k cal. mole^{-1} for isoprene and approximately 20 kcal. mole^{-1} for butadiene.

Under the present conditions, the observed energy of activation for the $Fe^{II}(acac)_2$-styrene system can, from equation (III2.6), be approximately equal to

$$E_{obs.} = E_p + E_d - E_t'$$

Since $E_{obs.}$ = 11 kcal.mole^{-1} and if E_p = 6 kcal.mole^{-1}, then $E_d - E_t'$ = 5 kcal.mole^{-1}. The present conditions are thus limited in giving information about individual E_d(eqn. (III2.1)) and E_t'(eqn.(III2.5)), and also about the extent of termination of the propagating radicals by the associated form of ferrous acetylacetonate $(Fe(acac)_2)_n$ or its complex with monomer as a function of temperature (eqn. (III2.6)). To obtain these data a series of rates of polymerization of styrene should be measured over a concentration range of ferrous acetylacetonate (2.50×10^{-4} - 2.00×10^{-3}M) as a function of temperature (50 - 80°C). These have not been done at the time of writing this thesis.

B. DISCUSSION:

The breakdown of the dependence of the initial rate of polymerization upon the half order in concentration of ferrous acetylacetonate suggests that the termination process is not just a simple bimolecular termination between two propagation radicals. In non-polar solvents, e.g. benzene, $Fe(acac)_2$ is reported to associate to a hexamer.[73] In styrene, the species may be the associated form $(Fe(acac)_2)_n$ where n is possibly 6. The postulated mechanism is as follows:

Initiation:

Either
$$(Fe(acac)_2)_n + M \rightleftharpoons \text{Complex} \qquad K$$
$$\text{Complex} \longrightarrow \text{Radicals} \qquad k_d \qquad (III2.1)$$

or
$$(Fe(acac)_2)_n \longrightarrow \text{Radicals} \qquad k_d$$
$$\text{Radicals} + M \longrightarrow \sim\!\sim\!\sim\cdot \qquad k_i \qquad (III2.2)$$

Propagation:

$$\sim\sim\sim\cdot \quad + M \longrightarrow \sim\sim\sim\cdot \qquad k_p \qquad \text{(III2.3)}$$

Termination:

$$2 \sim\sim\sim M\cdot \longrightarrow \text{Polymer} \qquad 2k_t \qquad \text{(III2.4)}$$

$$\sim\sim\sim\cdot \quad + (Fe(acac)_2)_n \longrightarrow \text{Polymer} \quad k_t' \qquad \text{(III2.5)}$$

This mechanism is similar to the modified mechanism proposed for the earlier system, $Cu(acac)_2$ —— CCl_3COONH_4 —— methyl methacrylate (Part II, Chapter 2). The stationary state equation is therefore

$$\frac{1}{R_p} = \frac{k_t'}{k_dk_p[M]} + \frac{2k_t}{k_dk_p^2[M]^2}\,\frac{R_p}{[Fe(acac)_2]_0} \qquad \text{(III2.6)}$$

where the concentration of the ferrous chelate is strictly $[(Fe(acac)_2)_6]$.

For the uncorrected rates a plot of $1/R_p$ against $R_p/[Fe(acac)_2]_0$ gave a straight line (Fig. III/2.6) which deviates at low $Fe(acac)_2$ concentration. The deviation is entirely due to neglect of the thermal rate which is very significant at the lowest $Fe(acac)_2$ concentration. The intercept $\frac{k_t'}{k_dk_p[M]}$ shows termination fy $(Fe(acac)_2)_n$ or its complex with monomer while the slope $\frac{2k_t}{k_dk_p^2[M]^2}$ gives a measure of the extent of bimolecular termination. The linear plot corrected for the thermal rate is shown in figure III/2.6. The reciprocal of the rate corrected for the thermal rate i.e. $1/R_{P\,corr.}$, at low $Fe(acac)_2$ can be evaluated by considering the initiation of styrene by a complex of $(Fe(acac)_2)_6$ with monomer and by thermal polymerization, followed by mixed termination. The kinetic scheme is as follows:

Initiation	$(Fe(acac)_2)_6 + M \rightleftharpoons$	C		(III2.7)
	$C \longrightarrow$	$R. + ?$	k_d	(III2.8)
	$nM \longrightarrow$	$R.$	k_{th}	(III2.9)
	$R. + M \longrightarrow$	$P_1\cdot$	k_i	(III2.10)
Propagation	$P_{\dot{1}} + M \longrightarrow$	$P_2\cdot$		
	$P_{\dot{n}} + M \longrightarrow$	$P_{\dot{n}+1}$	k_p	(III2.11)
Termination	$2P_{\dot{n}} \longrightarrow$ polymer		$2k_t$	(III2.12)
	$P_{\dot{n}} + C \longrightarrow$ polymer		k_t''	(III2.13)

Here $R.$ and $P_{\dot{n}}$ are the primary and propagating radicals respectively. Since the concentration of the monomer is in great excess compared to the concentration of the ferrous chelate, the concentration of complex C can be assumed to be approximately equal to the concentration of the ferrous chelate, i.e.

$$[C] = [Fe(acac)_2]_0 \qquad (III2.14)$$

For the thermal polymerization alone,

$$k_{th}[M]^n = 2k_t[P\cdot]^2_{th} \qquad (III2.15)$$

assuming stationary state approximation.

The thermal rate is given by

$$R_{th} = k_p[P\cdot]_{th}[M] \qquad (III2.16)$$

Substituting for $[P\cdot]_{th}$ into equation (III2.13),

$$k_{th}[M]^n = 2k_tR^2_{th}/(k_p[M])^2 \qquad (III2.17)$$

For the initiated polymerization given in the kinetic scheme (equations III 2.7 - III 2.13),

$$k_{th}[M]^n + k_d[C] = 2k_t[P\cdot]^2_{s.s.} + k'_t[C][P\cdot]_{s.s.} \qquad (III2.18)$$

assuming steady-state approximation.

Substituting for $k_{th}[M]^n$ as given in equation (III2.17) and for

$$[P\cdot]_{s.s.} = R_p/k_p[M] \qquad (III2.19)$$

into equation (III2.18) gives

$$\frac{1}{R_p} = \frac{2k_t}{(k_p[M])^2}\frac{1}{k_d}\frac{R_p}{[C]} + \frac{k_t'}{k_p[M]}\cdot\frac{1}{k_d} - \frac{2k_t}{(k_p[M])^2}\frac{1}{k_d}\frac{R_{th}^2}{R_p[C]} \qquad (III2.20)$$

or

$$\frac{1}{R_p} = a\frac{R_p}{[C]} + b - \delta(R_p, [C]) \qquad (III2.21)$$

where $a = 2k_t/(k_p[M])^2k_d$

$b = k_t^1/k_p[M]\ k_d$

$$\delta = \lim_{R_p/[C]\to 0}\frac{d(1/R_p)}{d(R_p/[C])}\ \frac{R_{th}^2}{R_p[C]} \qquad (III2.22)$$

From figure III/2.6,

$$\lim_{R_p/[C]\to 0}\frac{d(1/R_p)}{d(R_p/[C])} = 5.6 \times 10^6 = a$$

and $aR_{th}^2 = 3.36 \times 10^{-5}$ mole 1^{-1}.sec.^{2}

The deviation δ can thus be calculated from equation (III2.22) and feed back into the equation

$$\frac{1}{R_{p_{corr.}}} = \frac{1}{R_{p_{uncorr.}}} - \delta \qquad (III2.23)$$

as shown in table III/2.3 until a constant value for $1/R_{p_{corr.}}$ is obtained. The linear relationship between $1/R_{p_{corr.}}$ and $R_p/[Fe(acac)_2]$ is shown in figure III/2.6.

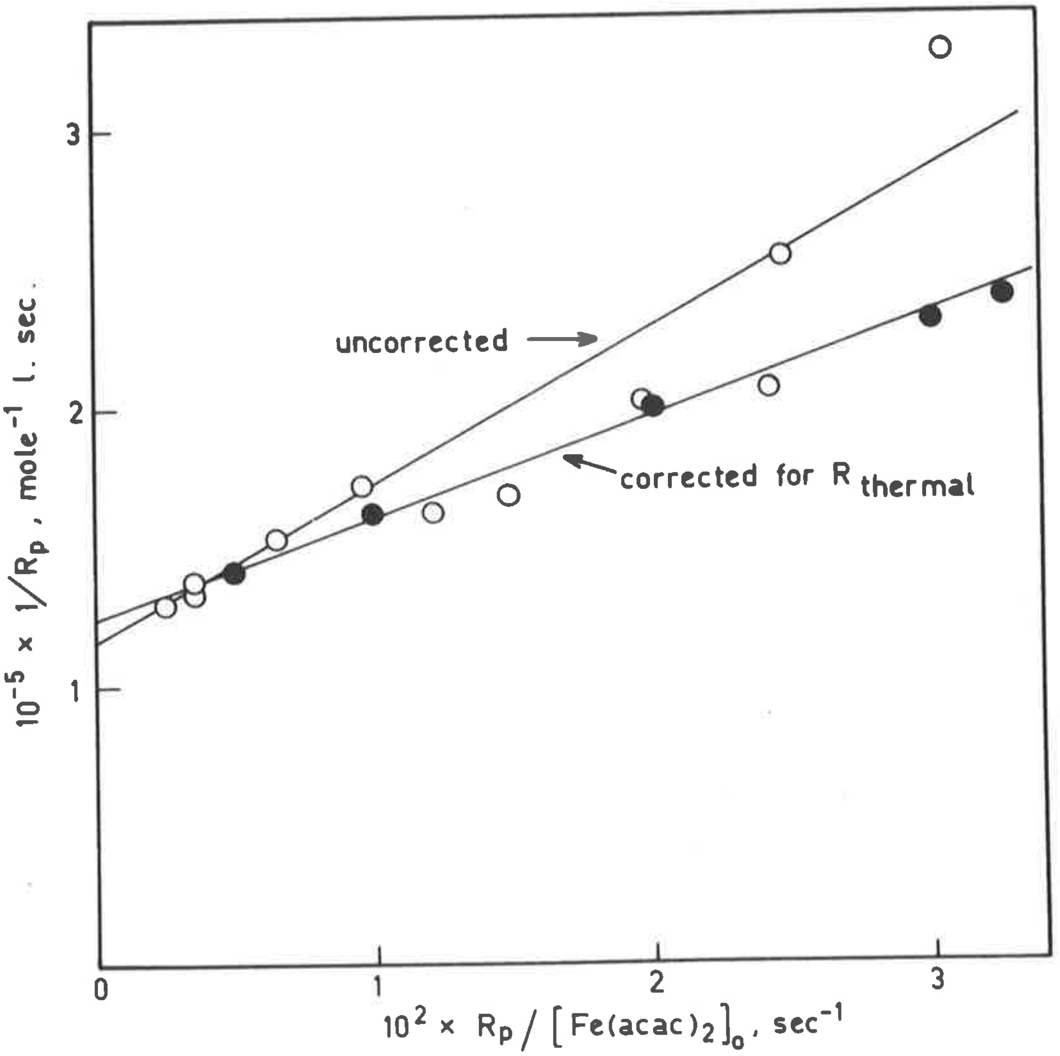


FIG. III/2·6 Test plot of mechanism where complex initiates styrene and terminates chains.

Table III/2.3 Deviation from $1/R_p$ vs. $R_p/[C]$ uncorrected = δ

$R_p/[C]$ from uncorr. $1/R_p$ vs R_p/C l^{1} sec	$1/R_{p\,uncorr.}$ from graph mole^{-1} l. sec.	$1/[C]$ mole^{-1} l.	$\delta' = \frac{aR^2_{th}}{R_p[C]}$ mole sec.^{3}	$\frac{1}{R'_p} = \frac{1}{R_{p\,uncorr.}} - \delta'$ mole^{-1} sec.
3.0×10^{-2}	2.85×10^{5}	8.55×10^{3}	0.82×10^{5}	2.03×10^{5}
2.0×10^{-2}	2.28×10^{5}	4.56×10^{3}	0.35×10^{5}	1.93×10^{5}
1.0×10^{-2}	1.72×10^{5}	1.72×10^{3}	0.10×10^{5}	1.62×10^{5}
0.5×10^{-2}	1.44×10^{-5}	0.72×10^{3}	0.03×10^{5}	1.41×10^{5}
3.26×10^{-2}	3.00×10^{-5}	9.78×10^{3}	0.98×10^{5}	2.02×10^{5}

$R_p/[C]$	$\frac{1}{R'_{p\,corr.}}$	$\delta'' = aR^2_{th} \frac{R_p}{[C]} \left(\frac{1}{R'_{p\,corr.}}\right)^2$	$\frac{1}{R''_{p\,corr.}} = \frac{1}{R_{p\,uncorr.}} - \delta''$
3.0×10^{-2}	2.03×10^{5}	0.42×10^{5}	2.43×10^{5}
2.0×10^{-2}	1.93×10^{5}	0.25×10^{5}	2.03×10^{5}
1.0×10^{-2}	1.62×10^{5}	0.09×10^{5}	1.63×10^{5}
0.5×10^{-2}	1.41×10^{5}	0.03×10^{5}	1.41×10^{5}
3.26×10^{-2}	2.02×10^{5}	0.45×10^{5}	2.55×10^{5}

$R_p/[C]$	S'''	$\frac{1}{R'''_{p\,corr.}}$	S^{IV}	$\frac{1}{R^{IV}_{p\,corr.}}$	S^{V}
3.0×10^{-2}	0.59×10^{5}	2.26×10^{5}	0.51×10^{5}	2.34	$0.55z10^{5}$
2.0×10^{-2}	0.28×10^{5}	2.00×10^{5}	0.27×10^{5}	2.01	0.27×10^{5}
1.0×10^{-2}	0.09×10^{5}	1.63×10^{5}	0.09×10^{5}	1.63	———
0.5×10^{-2}	0.03×10^{5}	1.41×10^{5}	0.03×10^{5}	1.41	———
3.26×10^{-2}	0.71×10^{5}	2.29×10^{5}	0.57×10^{5}	2.43	0.64×10^{5}

$R_p/[C]$	$\frac{1}{R^{V}_{p\,corr.}}$	S^{VI}	$\frac{1}{R^{VI}_{p\,corr.}}$	S^{VII}	$\frac{1}{R^{VII}_{p\,corr.}}$
3.0×10^{-2}	2.30×10^{5}	0.53×10^{5}	2.32×10^{5}	0.54×10^{5}	2.31×10^{5}
2.0×10^{-2}	2.01×10^{5}	———	———	———	———
1.0×10^{-2}	———	———	———	———	———
0.5×10^{-2}	———	———	———	———	———
3.26×10^{-2}	2.36×10^{5}	0.61×10^{5}	2.39×10^{5}	0.63×10^{5}	2.37×10^{5}

$R_p/[C]$	S^{VIII}	$\frac{1}{R^{VIII}_{p\,corr.}}$	S^{IX}	$\frac{1}{R^{IX}_{p\,corr.}}$	$\frac{1}{R_{p\,corr.}}$
3.0×10^{-2}	0.54×10^{5}	2.31×10^{5}			2.31×10^{5}
2.0×10^{-2}	———	———	———	———	2.01×10^{5}
1.0×10^{-2}	———	———	———	———	1.63×10^{5}
0.5×10^{-2}	———	———	———	———	1.41x105
3.26x10	0.62 x105	2.38x105	0.62x105	2.38x105	2.38x105

CHAPTER 3 - INITIATION OF POLYMERIZATION OF METHYL METHACRYLATE AND VINYL ACETATE BY FERROUS ACETYLACETONATE - RESULTS AND DISCUSSION

A. RESULTS:

1. Polymerization of Methyl Methacrylate Initiated by Ferrous Acetylacetonate

(a) Preliminary Dilatometric Experiments at 25°C

The discovery that ferrous acetylacetonate alone initiates the polymerization of styrene at temperatures $\geqslant 50^\circ$C led to further investigation of the kinetic consequences arising from using a more polar monomer solvent than styrene - in this case, methyl methacrylate was used. Preliminary kinetic runs at 25°C using thermal initiation and ferrous acetylacetonate (7.70×10^{-4}M) alone showed that the ferrous chelate initiates the polymerization of methyl methacrylate. A further series of 17 dilatometric runs were carried out at 25°C by varying the concentrations of the complex. It was found that reproducibility in results were poor and irreproducible induction period varied from several minutes to an hour. The steady-state rates of polymerization were about the same (3.00×10^{-6} mole 1^{-1} sec^{-1}) in the concentration range (3.00×10^{-4} - 8.00×10^{-4}M) although decrease in rates in the range (1.00×10^{-3} - 1.00×10^{-2}M) were observed. These results render a quantitative analysis of the Fe(acac)$_2$/MMA system at 25°C meaningless. The only conclusion that can be drawn is that ferrous acetylacetonate alone can function as an initiator (although not efficiently) in the more polar methyl methacrylate at 25°C.

(b) Polymerization at 60°C:

It was decided to conduct the dilatometric runs at a higher temperature, this time at 60°C under conditions similar to those for styrene polymerizations (Part III, Chapter 2A). The results obtained are shown in figures III/3.1 and III/3.2. Sigmoidal curves were observed. The induction period was less than 3 minutes. The initial rates of polymerization were determined from the initial slope of the plot of % conversion against time (Figures III/3.1 and III/3.2), and these are cited in table III/3.1. As shown in table III/3.1, good reproducible results were obtained (as stated earlier in Part III, Chapter 1E) when used dilatometers were soaked in 50% warm nitric acid. The influence of ferrous acetylacetonate on the initial rate of polymerization of methyl methacrylate (and styrene) at 60°C is illustrated in figure III/3.3.

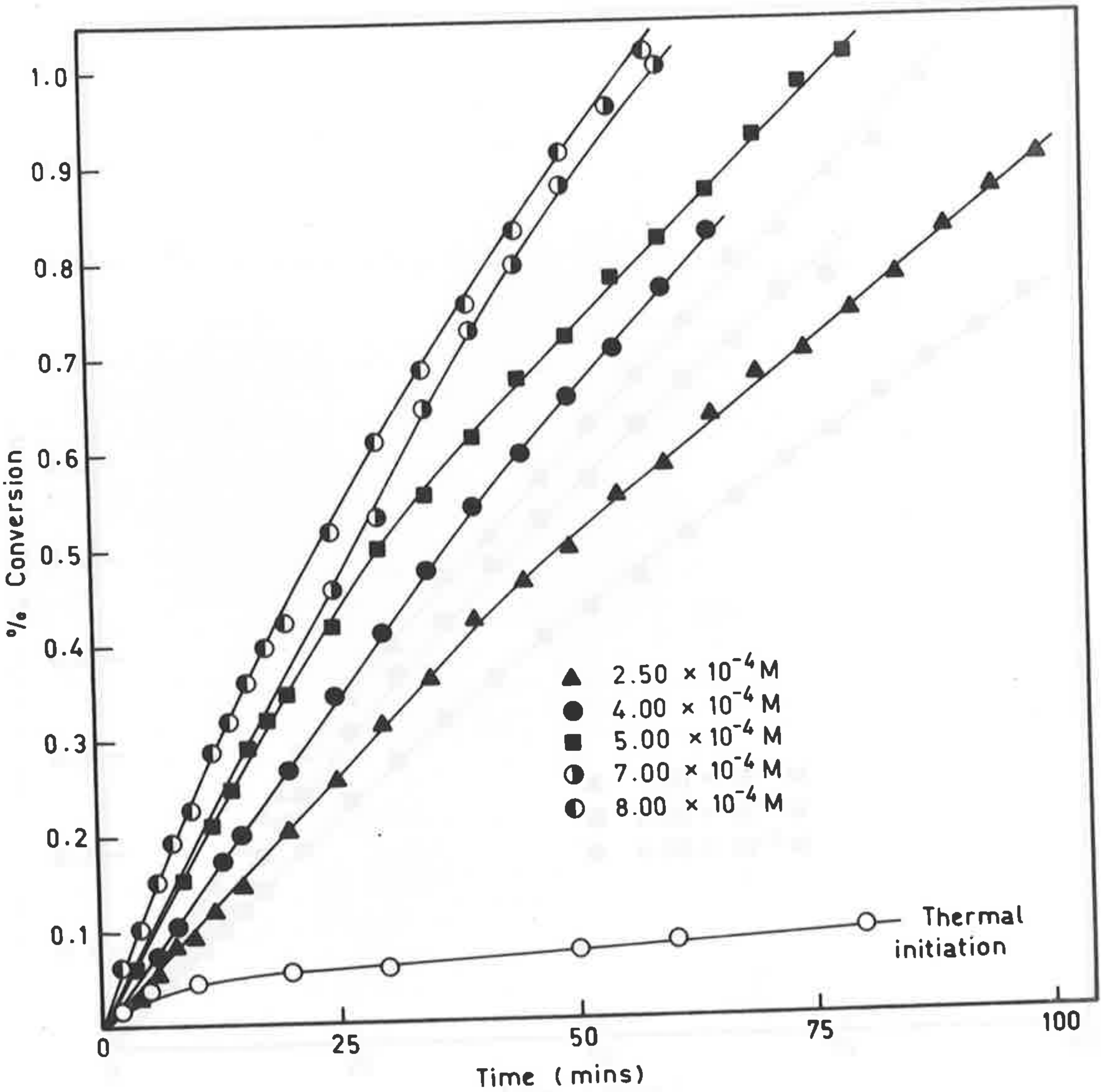


FIG. III/3·1 Monomer (MMA) conversion against time at 60°C with varying $[Fe(acac)_2]_0$.

Table III/3.1 Initial rates of polymerization of methyl methacrylate at various $[Fe(acac)_2]_0$ at 60°C

$10^4[Fe(acac)_2]_0$ mole l^{-1}	$10^5 \times Rp$ mole l^{-1} sec^{-1}	Cleaning technique for used dilatometers	$10^2[Fe(acac)_2]_0^{\frac{1}{2}}$ $mole^{\frac{1}{2}}$ $l^{-\frac{1}{2}}$
-	0.078	new dilatometer	-
1.67	1.50	50% warm NHO_3	1.29
2.50	1.70	chromic acid	1.58
2.50	1.58	50% warm HNO_3	1.58
4.00	2.04	chromic acid	2.00
4.00	1.65	chromic acid	-
5.00	1.56	RBS 25	-
5.00	2.46	50% warm HNO_3	2.24
5.00	2.49	50% warm HNO_3	2.24
5.00	2.40	50% warm HNO_3	2.24
7.00	2.49	50% warm HNO_3	2.65
7.00	2.44	50% warm HNO_3	2.65
7.00	2.67	50% warm HNO_3	2.65
8.00	2.79	50% warm HNO_3	2.83
8.00	2.50	chromic acid	-
8.00	3.06	50% warm HNO_3	2.83
10.00	1.96	RBS 25	
10.00	2.00	new dilatometer	-
10.00	1.85	50% warm HNO_3	-
10.00	1.98	50% warm HNO_3	-
20.00	1.86	new dilatometer	-
40.00	1.45	new dilatometer	-

Figure III/3.3 shows that $Fe(acac)_2$ is a more effective initiator with methyl methacrylate than with styrene. The thermal rate of methyl methacrylate at 60°C is slow. The initial rate increases with increasing concentration of $Fe(acac)_2$ to an optimum maximum at $[Fe(acac)_2]_o = 8 \times 10^{-4}M$ after which there is a sharp decrease in rate, almost a discontinuity until the rate is virtually independent of $[Fe(acac)_2]_o$. At low concentration ($1.00 \times 10^{-4} - 8.00 \times 10^{-4}M$) of $Fe(acac)_2$, the rate depends on $[Fe(acac)_2]^{\frac{1}{2}}$ as shown in figure III/3.4.

(c) Energy of Activation Experiments:

A series of polymerization experiments by dilatometry were performed to study the effect of temperature on the rate of polymerization of methyl methacrylate initiated by $Fe(acac)_2$. The concentration of $Fe(acac)_2$ was maintained at $5.00 \times 10^{-4}M$. The results are illustrated in figure III/3.5. The rates of polymerization are listed in table III/3.2. For the temperature range (40-80°C), the induction period was less than 5 minutes and the rates quoted are initial rates. At 25°C, the rates are steady-state rates as explained earlier. The Arrhenius plot of $-\ln R_p$ against $1/T°K$ over the range (25-80°C) was tested and is shown in figure III/3.6.

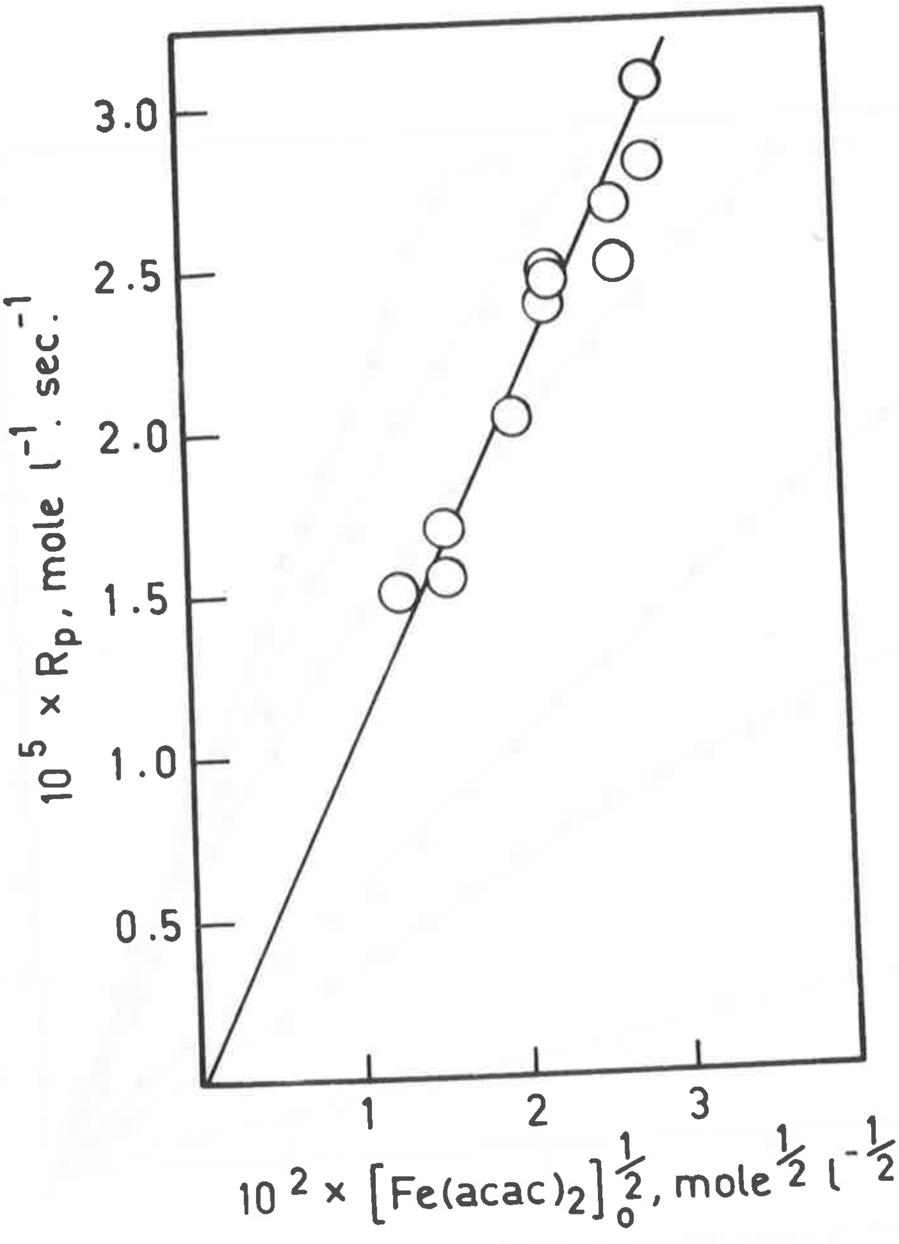


FIG. III/3·4 Dependence of initial rate of polymerisation of methyl methacrylate on $[Fe(acac)_2]_0^{\frac{1}{2}}$ at 60°C.

Table III/3.2 Effect of temperature on the rate of polymerization of methyl methacrylate at constant $[Fe(acac)_2]_o = 5.00 \times 10^{-4}$M

Temp. °C	Temp. °K	$10^5 \times$ Rp mole l^{-1} sec^{-1}	$-\log_{10}$Rp	-lnRp	$10^3 \times 1/T$
25	298	0.35	5.4559	12.57	3.356
25	298	0.37	5.4318	12.51	3.356
40	313	0.91	5.041	11.61	3.195
50	323	1.26	4.9031	11.29	3.096
60	333	2.49	4.6038	10.60	3.003
70	343	2.83	4.5482	10.47	2.915
70	343	2.92	4.5346	10.44	2.915
80	353	3.18	4.4979	10.36	2.833

The rates in the temperature range (25 - 60°C) obey the Arrhenius plot satisfactorily, the overall activation energy being 11 kcal.mole^{-1} which is unusually low for an initiation process and has the same value as the Fe(acac)/styrene system. Beyond 60°C, the rates do not conform to the Arrhenius equation. The deviation from Arrhenius plot above 60°C looks like the intervention of either a back reaction or a side reaction of high E. This could happen in a number of ways. One possible mechanism is to take the $Fe(acac)_2$ - MMA complex hypothesis and suppose that the scheme is

$$\begin{tikzcd}
Fe(acac)_2 + MMA \arrow[r, shift left, "k_1"] & MMA,\ Fe(acac)_2 \arrow[l, shift left, "k_{-1}"] \arrow[dl, "k_2"'] \arrow[dr, "k_3"] & K_1 \\
R + ? & & \text{Inactive products}
\end{tikzcd}$$

Stationary state concentration of complex $[C]$ is given by

$$k_1\ [Fe(acac)_2][M] = (k_2 + k_3)\ [C] + k_{-1}\ [C]$$

If $k_{-1} \gg k_2$ and k_3, only the last term on R.H.S. counts and the system tends to the 'equilibrium' case

$$R_i = d(R\cdot)/_{dt} = k_2 K_1\ [Fe(acac)_2][M]$$

This has an Arrhenius form

$$E_{obs} = E_2 + \Delta H_1$$

and $$A_{obs} = A_2 A_1 / A_{-1}$$

If $k_2 \gg k_{-1}$, $\mathrm{Lim}\ R_i = k_1 [Fe(acac)_2][M]$

which again is an Arrhenius form.

If k_3 is negligible, but k_{-1} and k_2 are comparable

$$R_i = \{k_1/(1 + k_{-1}/k_2)\}[Fe(acac)_2][M]$$

which is not an Arrhenius form. However it is not likely to differ much from an Arrhenius form unless there is a very great difference from E_{-1} and E_2. This is why it is preferable to add Reaction 3 a process with a high energy of activation which comes in at high temperatures.

$$R_i = \frac{k_2 k_1 [Fe(acac)_2][M]}{k_{-1} + k_2 + k_3}$$

$$\ln R_i = \underbrace{\ln A_1 A_2/A_{-1} - (E_2 + E_1 - E_{-1})/RT}_{\text{Arrhenius form}} - \underbrace{\ln\left(1 + \frac{k_2 + k_3}{k_{-1}}\right)}_{\substack{\text{deviation}\\ \text{from straight}\\ \text{line}}} + \ln [Fe(acac)_2][M]$$

When $(k_2+k_3)/k_{-1}$ is negligible, pure Arrhenius form arises. When it is small but not negligible, the deviation term is

$$- \frac{k_2 + k_3}{k_{-1}} = - \left\{ \left(\frac{A_2}{A_{-1}} e^{-(E_2 - E_{-1})/RT} \right) + \left(\frac{A_3}{A_{-1}} e^{-(E_3 - E_{-1})/RT} \right) \right\}$$

Thus, if $E_2 > E_{-1}$ and $E_3 > E_{-1}$ the deviation becomes important at high temperatures. To find out how important it would be necessary to differentiate the last equation with respect to 1/T.

This is only one possible mechanism that would give a non-Arrhenius form. It is possible that it could arise from competition in the later stages of the chain. Where you have to consider two competing reactions, and a term, such as $k + k'$ or $k - k'$ comes into the rate equation, will give a non-Arrhenius equation. The former case only deviates strongly when E and E' are very different.

2. Dilatometric Measurements of vinyl acetate at 60°C

The fact that ferrous acetylacetonate alone initiates the polymerization of styrene and methyl methacrylate led to further examination of the Fe(acac)$_2$ - vinyl acetate system. A preliminary dilatometric run on the pure vinyl acetate (purified as described in Part II, Chapter 1B) at 60°C using ferrous acetylacetonate (5.00×10^{-4}M) showed negligible contraction of the meniscus of the monomer/

$Fe(acac)_2$ solution over a period of 4 hours. The orange colour of the solution still persisted. To be absolutely certain about the purity of the monomer, the latter (purified as described in Part II, Chapter 1B) was distilled under vacuum into a reservoir vessel containing benzoyl peroxide, degassed twice and pre-polymerized by uv irradiation of the Bz_2O_2 / VA solution for about 2 hours, followed by warming the solution in warm water (60°C) for a further ½ hour. The pre-polymerized monomer was vacuum-distilled into another vessel containing a fresh lot of calcium hydride. Two further dilatometric runs were carried out on this new batch of very pure monomer at 60°C and at $[Fe(acac)_2]_0 = 2.00 \times 10^{-4}M$. In both instances, no polymerization was detected over a 3-hour period. Not satisfied with the monomer purified from local commerical vinyl acetate (C.S.R., Australia), another new fresh lot of commercial monomer (Fluka, Switzerland) was purified by the procedure described in Part II, Chapter 1B. Another kinetic run was performed on this new batch of pure monomer at $[Fe(acac)_2]_0 = 2.00 \times 10^{-4}M$. No polymerization was observed over 3 hours. Benzoyl peroxide did, however, polymerize the pure vinyl acetate. All the results showed that $Fe(acac)_2$ does not polymerize vinyl acetate. Two explanations for this phenomenon are possible.

(i) Vinyl acetate forms a stable adduct with $Fe(acac)_2$ preventing initiation.

$$Fe(acac)_2 + VA \rightleftharpoons \underset{\text{stable adduct}}{VA, Fe(acac)_2}$$

(ii) Ferrous acetylacetonate or the adduct inhibits polymerization by scavenging the propagating radicals.

$$P_n\cdot + Fe(acac)_2 \longrightarrow \text{inactive product}$$

$$P_n\cdot + \text{Adduct} \longrightarrow \text{inactive product}$$

B. DISCUSSION:

In the case of the $Fe(acac)_2$/MMA system, the kinetics are very complicated. Figure III/3.3 shows that 3 different mechanisms may operate, each within a certain concentration range of $Fe(acac)_2$.

1. Low Concentrations of $Fe(acac)_2$

In the low $Fe(acac)_2$ concentration range ($1.00 - 8.00 \times 10^{-4}$M), the polymerization rate depends on $[Fe(acac)_2]^{\frac{1}{2}}$ as shown in figure III/3.4. This is consistent with the postulated free-radical initiation mechanism and normal bimolecular termination. Methyl methacrylate is a more polar solvent than styrene. As such, it is postulated that the monomeric species i.e. the unassociated form, of $Fe(acac)_2$ prevails at the low concentration limit and initiates the polymerization.

The reaction scheme (I) is

Initiation: $$\text{Fe(acac)}_2 \longrightarrow \text{Radicals} \qquad k_d' \qquad \text{(III3.1)}$$

$$\text{Radicals} + \text{M} \longrightarrow \sim\!\sim \text{M}\cdot \qquad k_i \qquad \text{(III3.2)}$$

Propagation: $$\sim\!\sim \text{M}\cdot + \text{M} \longrightarrow \sim\!\sim \text{M}\cdot \qquad k_p \qquad \text{(III3.3)}$$

Termination: $$2 \sim\!\sim \cdot \longrightarrow \text{polymer} \qquad 2k_t \qquad \text{(III3.4)}$$

The above kinetic scheme gives the normal stationary state equation:

$$R_p = k_p \sqrt{\frac{k_d'}{2k_t}} \; [\text{M}] \; [\text{Fe(acac)}_2]_0^{\frac{1}{2}} \qquad \text{(III3.5)}$$

2. High Concentrations of Fe(acac)$_2$:

Buckingham and co-workers[73] have reported that the equilibrium

$$6\ \text{Fe(acac)}_2 \rightleftharpoons (\text{Fe(acac)}_2)_6$$

is involved in non-polar solvents, e.g. benzene. It was assumed earlier that at low concentrations of Fe(acac)$_2$ the unassociated form of the ferrous chelate prevails in methyl methacrylate which is highly polar. As the concentration of the iron increases the associated form takes over. At high concentrations ($> 3 \times 10^{-3}$M) the associated form (or its complex with monomer), which may be a hexamer, behaves as it does with styrene both initiating and terminating the chains. Mechanism II: is as follows:

Initiation: $$Fe_n(acac)_{2n} \longrightarrow \text{Radicals} \qquad k''_d \qquad \text{(III3.6)}$$

$$\text{Radicals} + M \longrightarrow \sim\!\sim\bullet \qquad k_i$$

Propagation: $$\sim\!\sim\bullet + M \longrightarrow \sim\!\sim\bullet \qquad k_p \qquad \text{(III3.7)}$$

Termination: $$\sim\!\sim\bullet + Fe_n(acac)_{2n} \longrightarrow \text{polymer} \qquad k''_t \qquad \text{(III3.8)}$$

Assuming stationary state approximation,

$$k''_d\,[Fe_n(acac)_{2n}] = k''_t\,[\sim\!\sim\bullet]\,[Fe_n(acac)_{2n}] \qquad \text{(III3.9)}$$

or $$[\sim\!\sim\bullet] = k''_d/k''_t \qquad \text{(III3.10)}$$

Substituting for $[\sim\!\sim\bullet]$ into equation

$$R_p = k_p\,[\sim\!\sim\bullet]\,[M] \qquad \text{(III3.11)}$$

gives

$$R_p = k_p k''_d\,[M]\,/\,k''_t \qquad \text{(III3.12)}$$

3. Intermediate Concentrations:

The sudden sharp change in kinetic behaviour in the intermediate concentration range ($8.00 \times 10^{-4} - 2.00 \times 10^{-3}M$) may be explained by a mixed mechanism of mechanism I and mechanism II. The mixed mechanism is governed by the equilibrium:

$$n\,Fe(acac)_2 \rightleftharpoons Fe_n(acac)_{2n}$$

where n may be 6.

(a) Equilibrium Equations :

Consider the equilibrium:

$$nC \overset{K}{\rightleftharpoons} C_n \qquad (III3.13)$$

where C is the unassociated form (i.e. monomer) and C_n the associated form (possibly a hexamer) of ferrous acetylacetonate.

The equilibrium constant is given by

$$[C_n] = K\,[C]^n \qquad (III3.14)$$

Total concentration C_o of ferrous acetylacetonate is

$$C_o = [C] + n[C_n] \qquad (III3.15)$$

Rearranging,

$$[C_n] = \frac{1}{n}(C_o - [C]\ ) = \frac{1}{n}(C_o - \frac{C_n^{1/n}}{K^{1/n}}) \qquad (III3.16)$$

If C_o is high,

$$\lim_{C_o \to \infty} [C_n] = \frac{1}{n} C_o \qquad (III3.17)$$

From equation (III3.14),

$$[C] = ([C_n]/\ K)^{1/n}$$

If C_o is high,

$$\lim_{C_o \to \infty} [C] = (\frac{C_o}{nK})^{1/n} \qquad (III3.18)$$

If C_o is low, equation (III3.15) becomes

$$\lim_{C_o \to 0} [C] = C_o \qquad (III3.19)$$

and equation (III3.14) is reduced to

$$\lim_{C_o \to 0} \left[C_n\right] = KC_o^{\,n} \qquad \text{(III3.20)}$$

(b) Mixed Mechanism

The 'Mixed' kinetic scheme is:

Initiation	$C \longrightarrow$	$R\cdot + ?$	k_d	(III3.21)
	$C_n \longrightarrow$	$R'\cdot + ?$	k'_d	(III3.22)
	$R\cdot + M \longrightarrow$	$P_1\cdot$	k_i	(III3.23)
	$R'\cdot + M \longrightarrow$	$P_1\cdot$	k'_i	(III3.24)
Propagation	$P_n\cdot + M \longrightarrow$	$P_{n}{\cdot}_{+1}$	k_p	(III3.25)
Termination	$P_n\cdot + P_n\cdot \longrightarrow$	polymer	$2k_t$	(III3.26)
	$P_n + C_n \longrightarrow$	polymer	k'_t	(III3.27)

Here $R\cdot$ and $R'\cdot$ are the primary radicals derived from the dissociation of the unassociated and associated species of ferrous acetylacetonate respectively, and $P_n\cdot$ are the propagating species.

Applying stationary-state assumption,

$$\left\{k_i[R] + k'_i\,[R']\right\}[M] = k_d[C] + k_n\,[C_n] \qquad \text{(III3.28)}$$

and therefore

$$R_i = k_d[C] + k'_d\,[C_n] = 2k_t[P]^2_{ss} + k'_t[P]_{ss}[C_n]$$

(III3.29)

or

$$[P\cdot]_{ss} = \frac{R_p}{k_p[M]} = \frac{-k_t'[C_n] \pm \{(k_t'[C_n])^2 + 8k_tR_i\}^{\frac{1}{2}}}{4k_t}$$

(III3.30)

The only real positive solution is

$$\frac{4k_t}{k_p[M]} R_p = \{(k_t'[C_n])^2 + \overset{+8k_tk_d[C]}{\wedge} 8k_tk_d'[C_n]\}^{\frac{1}{2}} - k_t'[C_n] \quad \text{(III3.31)}$$

or

$$\frac{4k_t}{k_p[M]} R_p = 2\sqrt{2k_tk_d[C]}\left\{1 + \frac{k_d'[C_n]}{k_d[C]} + \frac{(k_t'[C_n])^2}{k_d[C]}\right\}^{\frac{1}{2}} - k_t'[C_n]$$

(III3.32)

When C_o is small, $[C] \gg [C_n]$, $[C] \rightarrow [C_o]$ and $[C_n] \longrightarrow KC_o^n$ as derived earlier, Equation (III3.32) is reduced to

$$\frac{4k_t}{k_p[M]} R_p = 2(2k_tk_dC_o)^{\frac{1}{2}}\left\{\frac{1 + k_d'KC_o^{n-1}}{k_d} + \frac{(k_t'K)^2C_o^{2n-1}}{k_d}\right\}^{\frac{1}{2}} - k_t'KC_o^n$$

(III3.33)

$$= 2(2k_tk_dC_o)^{\frac{1}{2}}(1+AC_o^{n-1} + BC_o^{2n-1})^{\frac{1}{2}} - k_t'KC_o^n \quad \text{(III3.34)}$$

where $A = k_d'K/k_d$ and $B = k_t'K/k_d$

Applying the binomial expansion to equation (III3.34)

$$\frac{4k_t}{k_p[M]} R_p = 2(2k_tk_dC_o)^{\frac{1}{2}}\left\{1+\tfrac{1}{2}AC_o^{n-1} + \tfrac{1}{2}BC_o^{2n-1} - \frac{1}{8}(AC_o^{n-1} + BC_o^{2n-1})^2 + \frac{1}{16}(AC_o^{n-1} + BC_o^{2n-1})^3 - \ldots\right\} - k_t'KC_o^n$$

(III3.35)

or

$$\frac{4k_t}{k_p[M]} R_p = 2(2k_t k_d C_o)^{\frac{1}{2}} \Big\{ 1 + \tfrac{1}{2} AC_o^{n-1} + \tfrac{1}{2}BC_o^{2n-1} - \frac{1}{8} A^2C_o^{2n-2} - \tfrac{1}{4}ABC_o^{3n-2} - \frac{1}{8} B^2C_o^{4n-2} + \frac{1}{16} A^3D_o^{3n-3} + ---- \Big\} - k_t' KC_o^{n} \qquad (III3.36)$$

Two special cases are now considered

(i) Neglecting terms in C_o^{x} where $x \geqslant n - 1$, equation (III3.36) becomes

$$R_p = k_p \sqrt{\frac{k_d}{2k_t}} [M] C_o^{\frac{1}{2}} \qquad (III3.37)$$

which is similar to equation (III3.5). This is the stationary-state equation when C_o is in its lowest concentration range

(ii) Neglecting terms in C_o^{x} where $x \geqslant 2n-2$, i.e. C_o is increasing but still small, equation (III3.36) becomes

$$R_p = \frac{k_p [M]}{2k_t} \Big[2(2k_t k_d C_o)^{\frac{1}{2}} \Big\{ 1 + \tfrac{1}{2} \frac{k_d'K}{k_d} C_o^{n-1} \Big\} - k_t'KC_o^{n} \Big] \qquad (III3.38)$$

or

$$R_p = k_p \sqrt{\frac{k_d}{2k_t}} [M] C_o^{\frac{1}{2}} - \frac{k_p K}{2k_t} \Big(k_t' - \frac{k_d'(2k_t)^{\frac{1}{2}}}{(k_d C_o)^{\frac{1}{2}}} \Big) C_o^{n} [M] \qquad (III3.39)$$

Since $k_t' - k_d' \left(\frac{2k_t}{k_d C_o}\right)^{\frac{1}{2}}$ increases as C_o increases, equation

(III3.39) can be rewritten as

$$\frac{R_p}{k_p[M]} = \frac{k_d}{2k_t} \quad C_o^{\frac{1}{2}} - QC_o^{\,n} \qquad \text{(III3.40)}$$

where $Q = \frac{K}{2k_t} \left(k_t' - \frac{k_d'(2k_t)^{\frac{1}{2}}}{(k_dC_o)^{\frac{1}{2}}} \right) > 0$

The $C_o^{\frac{1}{2}}$ plot deviates downwards by a factor $QC_o^{\,n}$. The sharp change in kinetic behaviour beyond $[Fe(acac)_2]_o = 8.00 \times 10^{-4}M$ is very adequately explained by the 'mixed' kinetic scheme.

C. SUMMARY:

Ferrous acetylacetonate polymerizes styrene and methyl methacrylate, but not vinyl acetate. The mechanism of initiation of the vinyl monomers by the ferrous acetylacetonate is summarized in tabular form as illustrated in Table III/3.3.

Table III/3.3 Initiation by Fe(acac)$_2$ - Summary

Monomer	Form of Complex	Mechanism
Styrene	Probably associated	Complex initiates and terminates chain
MMA	Low Concentrations Probably monomeric	Complex initiates only
	High Concentrations Highly associated	Complex initiates and terminates chain
	Intermediate Concentrations Both forms	Mixed

PART IV INITIATION OF POLYMERIZATION OF METHYL METHACRYLATE BY FERROUS ACETYLACETONATE IN THE PRESENCE OF CUMENE HYDROPEROXIDE:

CHAPTER 1: EXPERIMENTAL

A. INTRODUCTION:

The essence of redox polymerization is that initiation occurs simultaneously with, and in consequence of, oxidation-reduction reactions between a system of catalyst components. The best-investigated type of redox initiator is a two-component system, comprised of a peroxidic oxidising agent and a reducing agent. The oxidant is hydrogen peroxide, persulphate, organic peroxide or organic hydroperoxide, and the reductant is a metal(II) ion, ferrous salts being normally preferred. However, this type of redox system is frequently carried out in aqueous media, but not in organic solvents or, in bulk monomers. Recently two groups of workers[52,53] have reported the low initiator efficiencies in styrene polymerization initiated by the reaction between acetylacetonato complexes and organic hydroperoxides in monomers as solvent. Their work is reviewed in Part I C3. The present work is an investigation of the kinetic consequences arising from the polymerization of the more polar methyl methacrylate initiated by the reaction between ferrous acetylacetonate and cumene hydroperoxide in monomer as solvent.

B. MATERIALS:

1. Methyl Methacrylate:

Methyl methacrylate was purified as described in Part II, Chapter 1B.

2. Anhydrous Ferrous Acetylacetonate, Fe(acac)$_2$

The anhydrous ferrous acetylacetonate, Fe(acac)$_2$ was prepared as described in Part III, Chapter 1B.

3. Cumene Hydroperoxide:

Cumene hydroperoxide (L.Light and Co. Ltd., Colnbrook, England) was used without further purification.

C. DILATOMETER AND FILLING OF DILATOMETER:

The dilatometer (10 ml. capacity) was of the type described in Part III, Chapter 1C. The dilatometer-filling assembly is shown in figure IV/1.1. This is almost similar to the apparatus illustrated in figure III/1.1, except that there is an additional open-neck with a

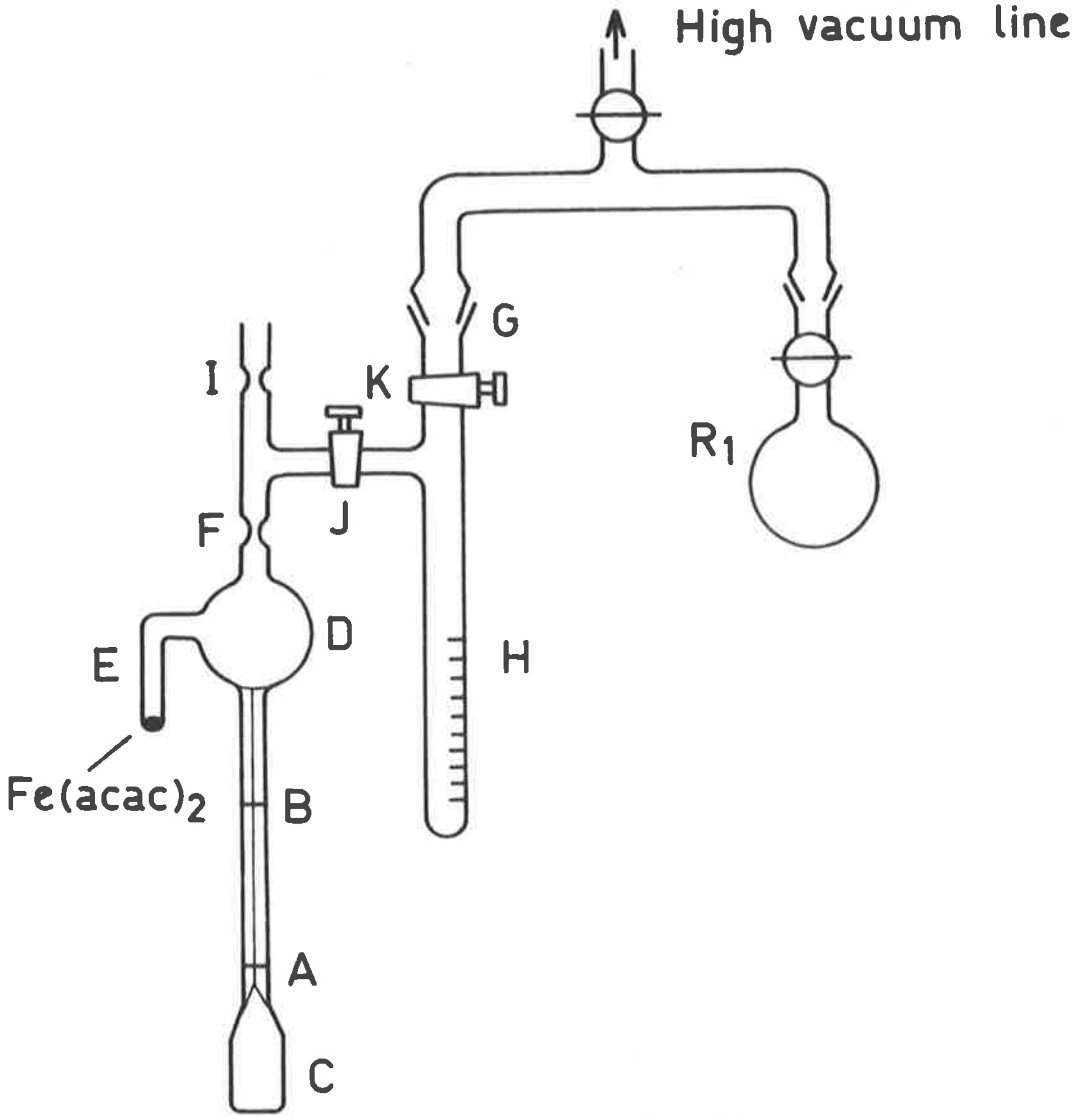


FIG. IV/1·1

thickened constriction I. A semi-micro pyrex tube containing a known weighed amount of ferrous acetylacetonate was sealed to the side-arm at E with the neck closed in a thick rubber teat. The whole apparatus was attached to the high vacuum line at G, evacuated and warmed with a smoky flame to get rid of any moisture that may be present. The apparatus was tested for leaks by means of a Tesla Coil. When no leaks were detected and the dilatometer had cooled down, the Springham tap J was closed, the rubber teat removed, and a known volume of cumene hydroperoxide was quickly introduced into the dilatometer by means of a syringe with a 30 cm. needle. The constriction at I was sealed off and the hydroperoxide was frozen by freezing the dilatometer bulb C and the capillary in liquid nitrogen. Tap J was opened and the whole apparatus was outgassed for about 3 hours. A known volume of monomer was then distilled under vacuum into the graduated burette with tap J closed. After a good degassing, Springham tap K was closed, and monomer was thawed and brought to room temperature. Tap J was opened and about 0.1 ml. of monomer was distilled into the capillary of the dilatometer. With tap J closed, the CmOOH/MMA solution was thawed and brought to room temperature by warming bulb C and the capillary with water at room temperature but not with warm temperature, and the solution was allowed to drain into bulb C by cooling the bulb. The dilatometer bulb and its contents were frozen in liquid nitrogen, tap J was opened and the remaining monomer was vacuum-distilled into the bulb. The frozen monomer solution was outgassed one more time and the dilatometer was sealed at F. The dilatometer was placed in a thermostat bath and contraction readings were noted, as explained in Part III Chapter I C up to about 1% conversion.

The polymerisation was carried out at 25°C by first varying the concentration range of ferrous acetylacetonate ($2.50 \times 10^{-4} - 5.00 \times 10^{-3}$M) at constant $[\mathrm{CmOOH}]_o = 3.32 \times 10^{-2}$M, and then varying the concentration range of cumene hydroperoxide ($6.00 \times 10^{-3} - 1.60 \times 10^{-1}$) at constant $[\mathrm{Fe(acac)_2}]_o = 1.25 \times 10^{-3}$M. Preliminary kinetic runs, using a 1 ml. syringe with a 30 cm. needle to maintain a constant $[\mathrm{CmOOH}]_o = 3.32 \times 10^{-2}$M, in a total 10 ml. solution, gave contradictory, confusing and irreproducible results. Subsequently, the 1 ml. syringe was replaced by a more precise Hamilton 0.1 ml. syringe with a 30 cm. needle which delivered 0.05 ± 0.001 ml. of cumene hydroperoxide each time into a constant total volume capacity of 10 ml., thereby maintaining a constant $[\mathrm{CmOOH}]_o = 3.32 \times 10^{-2}$M. Fairly good reproducible results were obtained

[Figure IV/2.2]. For the kinetic runs at constant $[Fe(acac)_2]_0$ = 1.25×10^{-3}M in the concentration range of cumene hydroperoxide (6.66×10^{-3} - 1.33×10^{-2}M), the Hamilton 0.025 ml. syringe was used; in the concentration range of hydroperoxide (2.00×10^{-2} - 3.32×10^{-2}M) the Hamilton 0.05 ml. syringe was used; and in the concentration range (5.90×10^{-2} - 1.53×10^{-1}M) the normal 1 ml. syringe was employed.

The thermostat baths were similar to the ones described in Part III, Chapter ID. The used dilatometers were cleaned in 50% warm nitric acid as described in Part III, Chapter IE.

CHAPTER 2: DISCUSSION AND RESULTS:

A. DISCUSSION:

1. Polymerization at 25°C

A comparison of the rates of polymerization of methyl methacrylate at 25°C using thermal initiation, cumene hydroperoxide alone (3.32×10^{-2}M), ferrous acetylacetonate alone (1.25×10^{-3}M), and a mixture of the ferrous complex (1.25×10^{-3}M) and the hydroperoxide (3.32×10^{-2}M) showed that the maximum rate of initiation was obtained using the mixture of the two initiator components as illustrated in figure IV/2.1. The rate of polymerization in the presence of ferrous acetylacetonate was higher than the thermal rate which was found to be thermally stable at 25°C. The selective initiation of free-radical polymerization by ferrous acetylacetonate was discussed earlier in Part III.

The kinetics were, therefore, studied at 25°C over a concentration range of ferrous acetylacetonate (2.50×10^{-4} - 5.00×10^{-3}M) at constant $[\mathrm{CmOOH}]_0 = 3.32 \times 10^{-2}$M, and also over a concentration range of cumene hydroperoxide (6.00×10^{-3} - 1.60×10^{-1}M) at constant $[\mathrm{Fe(acac)_2}]_0 = 1.25 \times 10^{-3}$M. The results are shown in figures IV/2.2, IV/2.3 and IV/2.4.

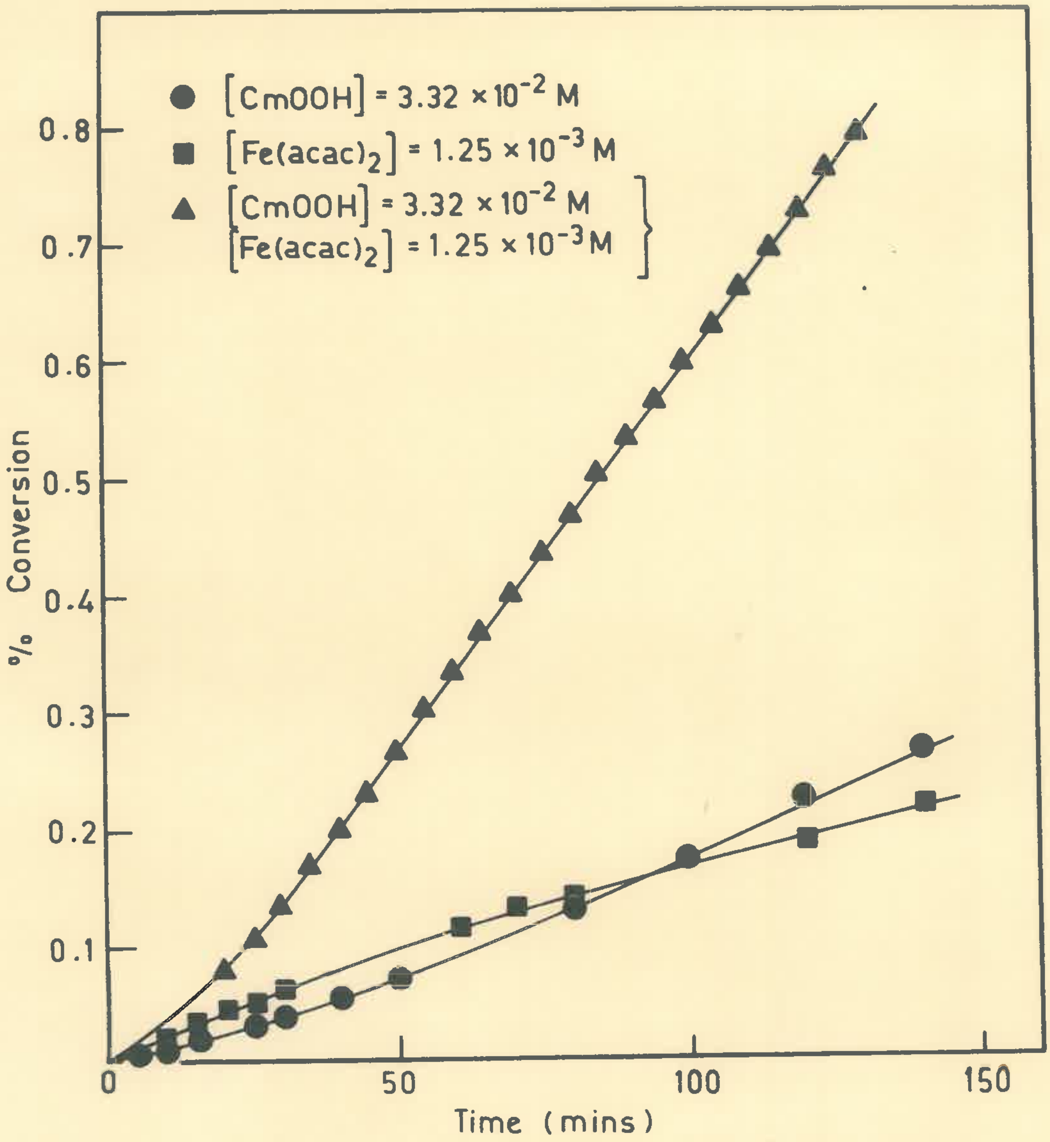


FIG. IV/2·1 Influence of $Fe(acac)_2$ and CmOOH on the rate of polymerisation of methyl methacrylate at 25°C.

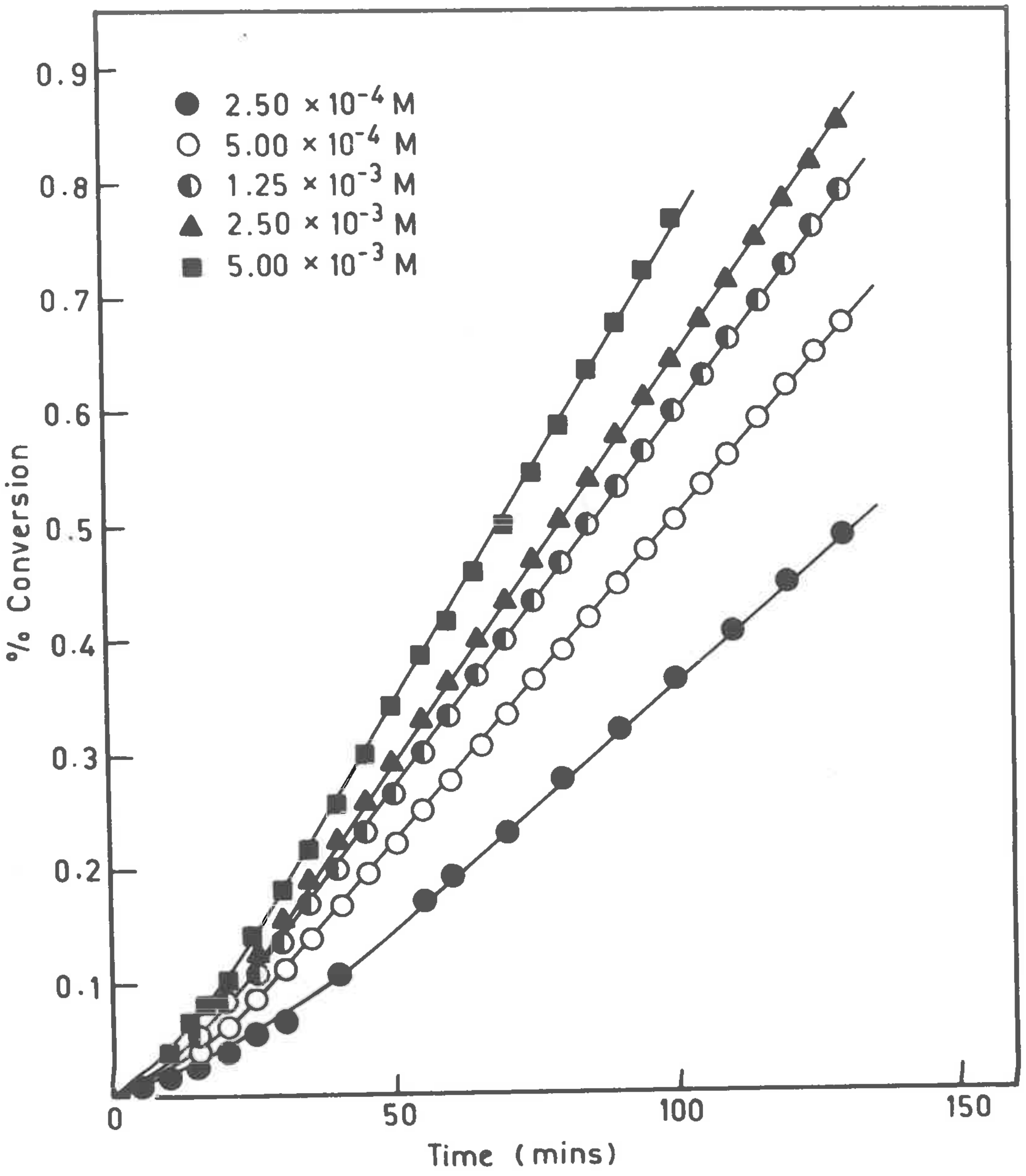


FIG. IV/2·2 Monomer (MMA) conversion against time at 25°C with varying $[Fe(acac)_2]_0$ and constant $[CmOOH]_0 = 3.32 \times 10^{-2}$ M.

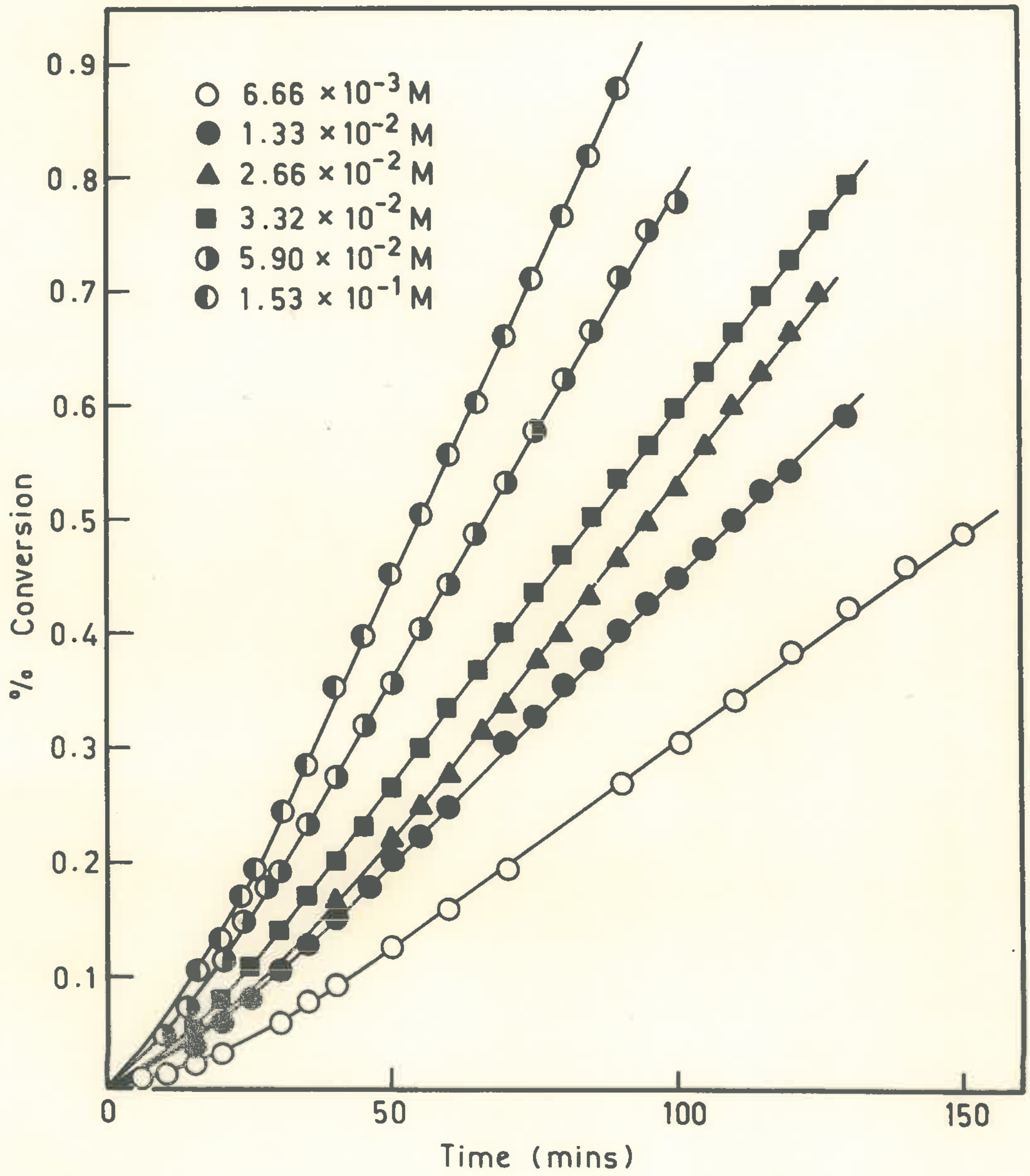


FIG. IV/2·3 Monomer (MMA) conversion against time at 25°C with varying $[\mathrm{CmOOH}]_0$ and constant $[\mathrm{Fe(acac)_2}]_0 = 1.25 \times 10^{-3}$ M.

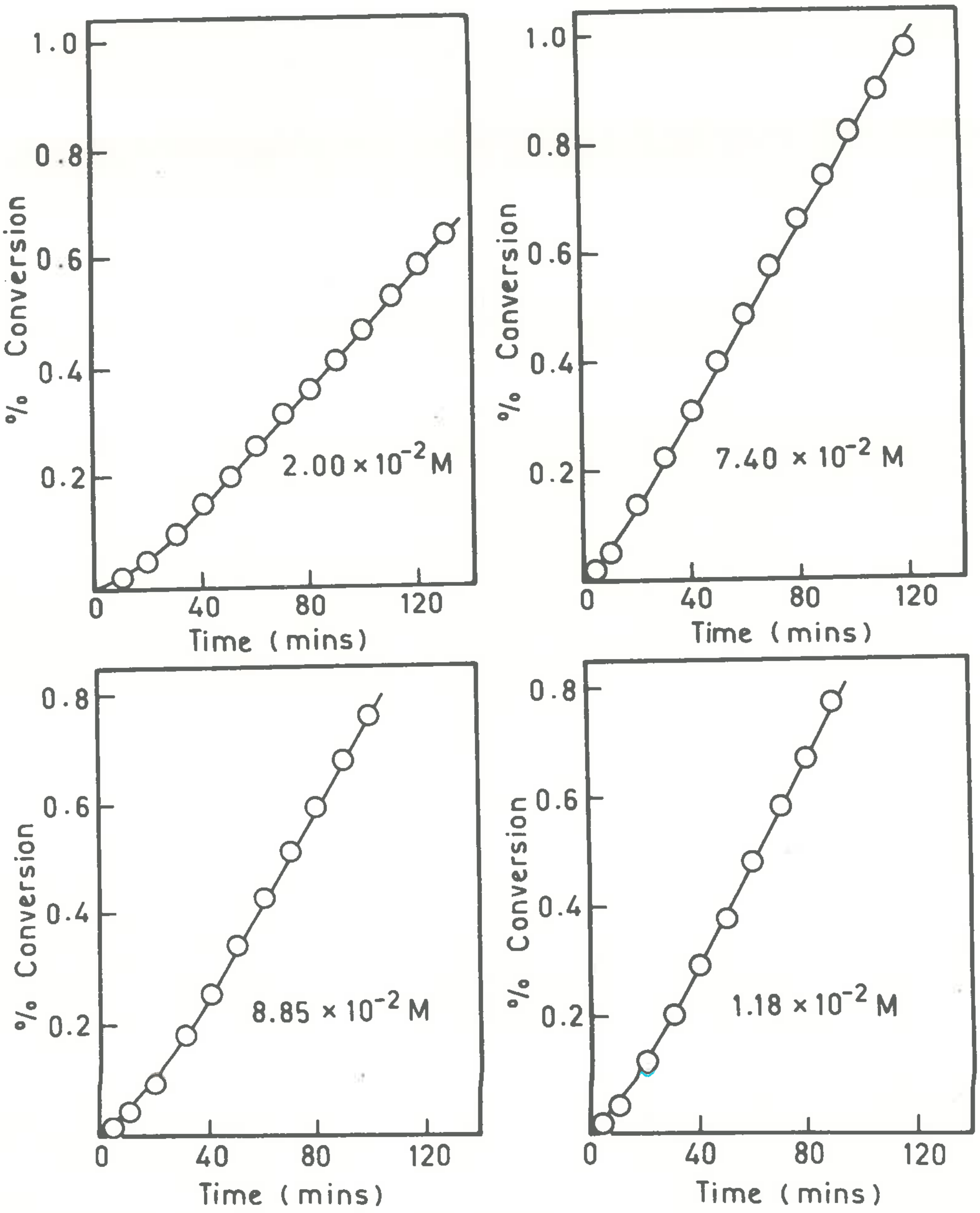


FIG. IV/2·4 Monomer (MMA) conversion against time at 25°C with varying $[\mathrm{CmOOH}]_0$ and constant $[\mathrm{Fe(acac)_2}]_0 = 1.25 \times 10^{-3}$ M.

The induction period was in the range 15-20 minutes, and the rates of polymerization are thus steady-state rates. The plots of monomer conversion against time were found to be fairly linear, in contrast to the sigmoidal curves observed by Burnett and North[52] for the polymerisation of styrene initiated by the reaction between ferrous acetylacetonate and cumene hydroperoxide. The steady-state rates obtained from the slope of the monomer, conversion against time are cited in tables IV/2.1 and IV/2.2. The variation in the rate of polymerization of methyl methacrylate as a function of ferrous acetylacetonate at constant cumene hydroperoxide concentration at 25°C is shown in figure IV/2.5, together with the variation in rate with ferrous acetylacetonate alone at 25°C. At constant ferrous acetylacetonate concentration, the variation in rate with concentration of the hydroperoxide is shown in figure IV/2.6, together the variation in rate with the hydroperoxide alone.

The polymerization rates were found to obey the rate law

$$R_p = K \left[Fe^{II}(acac)_2\right]_0^{0.18} \left[CmOOH\right]_0^{0{,}36} \qquad (IV/2.1)$$

at 25°C, as illustrated in figures IV/2.7, IV/2.8, IV/2.9 and IV/2.10.

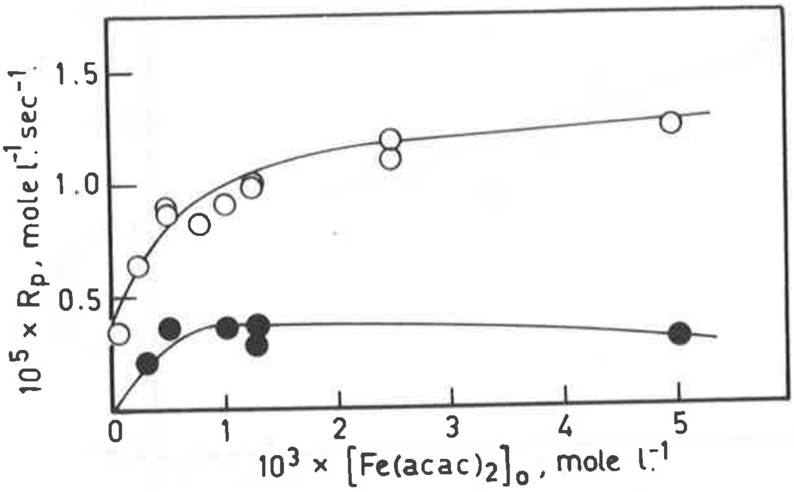


FIG. IV/2·5 Polymerisation of methyl methacrylate initiated by $Fe(acac)_2$ and CmOOH (○) at 25°C. $[CmOOH]_0 = 3.32 \times 10^{-2}$ M. ● $Fe(acac)_2$ alone.

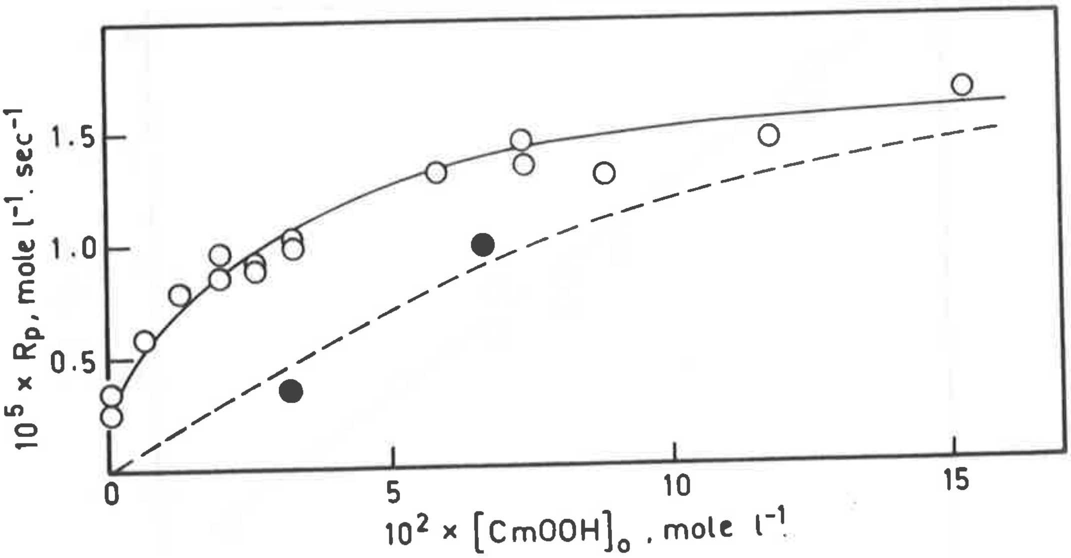


FIG. IV/2·6 Polymerisation of methyl methacrylate initiated by $Fe(acac)_2$ and CmOOH (○) at 25°C. $[Fe(acac)_2]_0 = 1.25 \times 10^{-3}$ M.

● CmOOH alone

--- Extrapolation assuming $R_p \propto [CmOOH]_0^{1/2}$

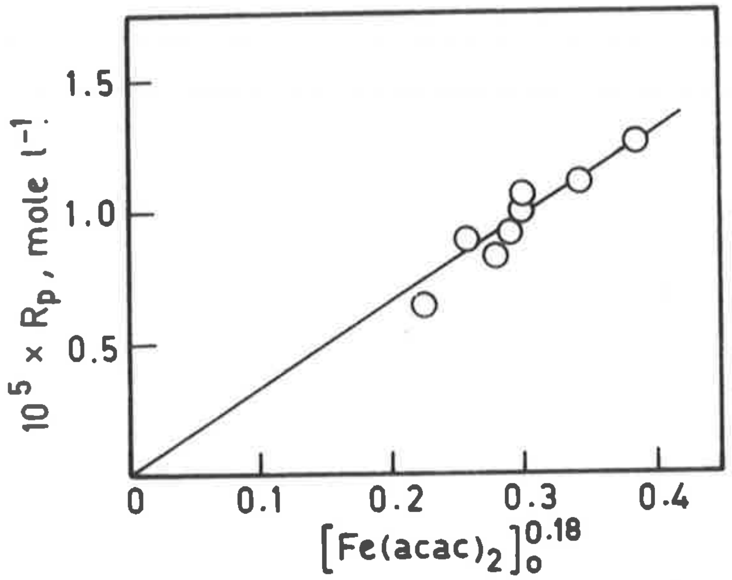


FIG. IV/2·9 A plot of R_p against $[Fe(acac)_2]_o^{0.18}$ at 25°C and constant $[CmOOH]_o = 3.32 \times 10^{-2}$ M.

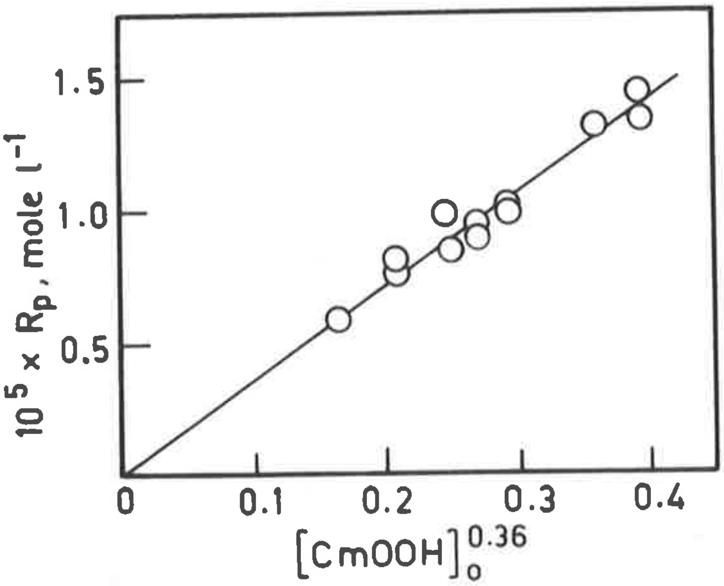


FIG. IV/2·10 A plot of R_p against $[CmOOH]_o^{0.36}$ at 25°C and constant $[Fe(acac)_2]_o = 1.25 \times 10^{-3}$ M.

Table IV/2.1 Steady-state rates of polymerization of methyl methacrylate at 25°C with varying $[Fe^{II}(acac)_2]_o$ and constant $[C_mOOH]_o = 3.32 \times 10^{-2}M$

$10^3 x [Fe^{II}(acac)_2]_o$ mole l^{-1}	$10^5 x R_p$ mole^{-1} sec.$^{-1}$	$\log[Fe(acac)_2]_o$	$\log R_p$	$[Fe(acac)_2]_o^{0.18}$ mole$^{0.18}$ $l^{-0.18}$ sec.$^{-0.18}$	$10^{-5} x 1/R_p$ mole^{-1} sec.	$10^2 x R_p/[Fe(acac)_2]_o$ sec^{-1}
-	0.35	-	-	-	-	-
0.25	0.65	-3.6021	-5.1871	0.2248	1.54	2.60
0.50	0.89	-3.3010	-5.0506	0.2570	1.12	1.78
0.50	0.88	-3.3010	-5.0555	0.2570	1.14	1.76
0.80	0.83	-3.0969	-5.0809	0.2771	1.21	1.04
1.00	0.92	-3.000	-5.0362	0.2884	1.09	0.92
1.25	1.00	-2.9031	-5.000	0.3003	1.00	0.80
1.25	1.02	-2.9031	-4.9914	0.3003	0.98	0.80
1.25	1.04	-2.9031	-4.9830	0.3003	0.96	0.80
2.50	1.11	-2.6021	-4.9547	0.3401	0.90	0.44
5.00	1.23	-2.3010	-4.9101	0.3854	0.81	0.25

Table IV/2.2 Steady-state rates of polymerization of methyl methacrylate at 25°C with varying $[\text{CmOOH}]_o$ and constant $[\text{Fe(acac)}_2]_o$ = 1.25×10^{-3}M.

$10^2 \times [\text{CmOOH}]_o$ mole l^{-1}	$10^5 \times R_p$ mole l^{-1} sec.$^{-1}$	$\log[\text{CmOOH}]_o$	$\log R_p$	$[\text{CmOOH}]_o^{0.36}$ mole$^{0.36}$ $l^{-0.36}$ sec.$^{-0.36}$
-	0.28	-	-	-
-	0.35	-	-	-
0.666	0.58	-2.1765	-5.2366	0.1646
1.33	0.77	-1.8761	-5.1135	0.2112
1.33	0.80	-1.8761	-5.0969	0.2112
2.00	0.97	-1.6990	-5.0332	0.2446
2.00	0.85	-1.6990	-5.0706	0.2446
2.65	0.90	-1.5768	-5.0458	0.2701
2.65	0.95	-1.5768	-5.0223	0.2701
3.32	1.00	-1.4789	-5.0000	0.2935
3.32	1.02	-1.4789	-4.9914	0.2935
3.32	1.04	-1.4789	-4.9830	0.2935
5.90	1.31	-1.2291	-4.8827	0.3611
7.40	1.33	-1.1308	-4.8761	0.3917
7.40	1.44	-1.1308	-4.8416	0.3917
8.85	1.28			
11.80	1.45			
15.30	1.68			

2. Energy of Activation Experiments:

The effect of temperature on the rate of polymerization of methyl methacrylate was investigated at constant $[Fe(acac)_2]_o = 1.25 \times 10^{-3}$M and constant $[CmOOH]_o = 3.32 \times 10^{-2}$M. Besides the three dilatometric measurements at 25°C, two more dilatometric runs were carried out at 40°C and 50°C. The results are shown in figure IV/2.11. Within the temperature range studied, the plots of monomer conversion against time were fairly linear, in contrast to the sigmoidal curves observed by Burnett and North[52] for the styrene system. The rates of polymerization at 25°C are, as explained earlier, steady-state rates. At higher temperatures in the range 40-50°C, the rates of polymerization are initial rates since the induction period was about 2 minutes. The rates are cited in table IV/2.3 and obey the Arrhenius plot (figure IV/2.12) over the temperature range 25-50°C. The overall energy of activation is 11 kcal.mole^{-1}.

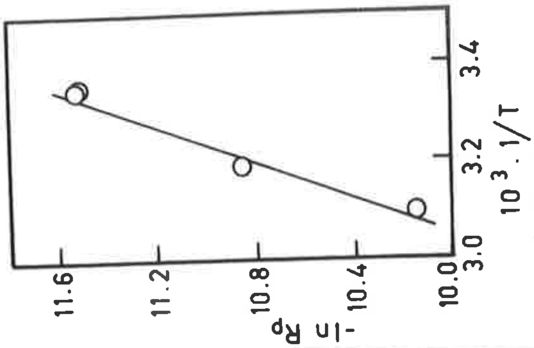


FIG. IV/2·12 Arrhenius plot of - ln R_p against 1/T

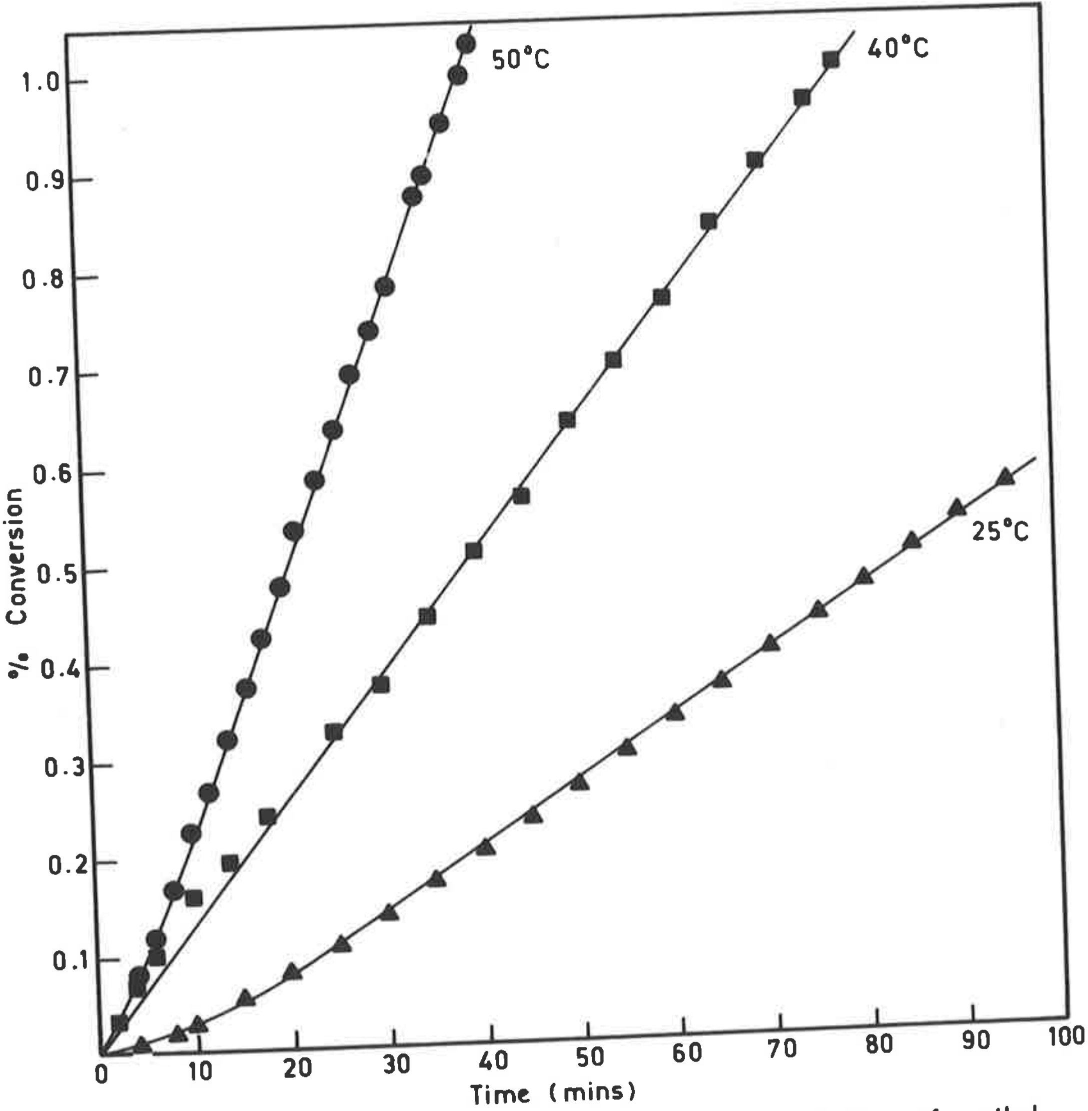


FIG IV/ 2·11 Effect of temperature on the rate of polymerisation of methyl methacrylate at constant $[Fe(acac)_2]_o = 1.25 \times 10^{-3}$ M and constant $[CmOOH]_o = 3.32 \times 10^{-2}$ M.

Table IV/2.3 Effect of temperature on the rate of polymerisation of methyl methacrylate at constant $[Fe(acac)_2]_o = 1.25 \times 10^{-3}M$ and constant $[CmOOH]_o = 3.32 \times 10^{-2}M$

Temp. °C	Temp. °K	$10^5 \times R_p$ mole l^{-1} sec^{-1}	$-\log_{10}R_p$	$-\ln R_p$	$10^3 \times 1/T$ °K^{-1}
25	298	1.00	5.0000	11.52	3.356
25	298	1.02	4.9914	11.49	3.356
25	298	1.04	4.9830	11.48	3.356
40	313	1.95	4.7100	10.85	3.195
50	323	3.93	4.4056	10.15	3.096

B. DISCUSSION:

The results obtained from dilatometric measurements of the ferrous acetylacetonate: cumene hydroperoxide: methyl methacrylate system differ considerably from those found by Burnett and North[52] for the styrene system initiated by a similar redox initiator. Burnett and North[52] have reported that the rates of polymerization obey the rate law

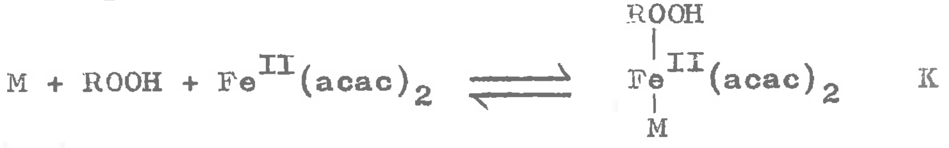
$$R_p = K\left[Fe(acac)_2\right]_o^{0.29}\left[CmOOH\right]_o^{0.32}$$

at 25°C and 40°C. Unfortunately, they failed to cite the concentration range of the ferrous chelate and the hydroperoxide. The main bulk of their work, however, was based on using stoichiometric mixture of the ferrous chelate and the hydroperoxide. Burnett and North[52] have reported that under their conditions, plots of monomer conversion against time were sigmoidal. This was, according to Burnett and North[52], attributed to the slow decomposition of the binuclear complex which was formed from the dimerization of the 1:1 adduct. The latter adduct was formed from the two initiator components.

In the present system under investigation, the experimental conditions were different. An excess of the hydroperoxide over the ferrous chelate was used in the presence of a more polar monomer, namely methyl methacrylate. No decrease in the rate of polymerization with time was observed. The kinetic order with respect to the ferrous acetylacetonate was low compared to that with respect to the cumene hydroperoxide (equation (IV2.1)). This could arise as a result of the termination occurring predominantly by reaction with ferrous acetylacetonate (ca. figure IV/2.5).

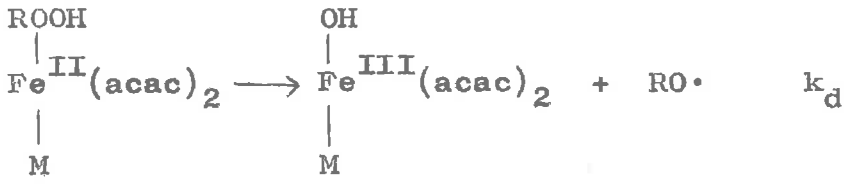
The significance of the termination of a growing radical by ferrous acetylacetonate on the kinetics of the polymerization of a vinyl monomer initiated by the ferrous chelate alone was discussed earlier in Part III. The higher kinetic order with respect to the hydroperoxide could be attributed concurrently with the decreasing importance of termination by the ferrous chelate and the increasing significance of the initiation of monomer by the hydroperoxide alone (ca. figure IV/2.6) which is in competition with initiation of monomer by the reaction between the ferrous chelate and the hydroperoxide. It was discussed earlier in Part III that a monomer: ferrous acetylacetonate complex may be involved in the initiation mechanism. Because of the larger size of the iron atom or ion, the ferrous acetylacetonate readily accepts two more donor ligands, probably one molecule of the hydroperoxide and one molecule of the polar monomer, to attain the octahedral configuration. This may explain the absence of the sigmoidal curves which were not observed in the present system because the complexing of the monomer to ferrous acetylacetonate precludes the formation of a binuclear complex.

The initiation mechanism must, therefore, consist of two concurrent initiation processes; initiation by reaction between the hydroperoxide and the ferrous chelate, together with initiation of monomer by the hydroperoxide alone. The first step in the initiation mechanism involving the two initiator components is the formation of a 1:1 adduct,



$$\mathrm{M} + \mathrm{ROOH} + \mathrm{Fe}^{\mathrm{II}}(\mathrm{acac})_2 \rightleftharpoons \underset{\mathrm{M}}{\overset{\mathrm{ROOH}}{\mathrm{Fe}}}{}^{\mathrm{II}}(\mathrm{acac})_2 \qquad K$$

which, by an electron transfer reaction, yields a cumyloxy radical:



$$\underset{\mathrm{M}}{\overset{\mathrm{ROOH}}{\mathrm{Fe}}}{}^{\mathrm{II}}(\mathrm{acac})_2 \longrightarrow \underset{\mathrm{M}}{\overset{\mathrm{OH}}{\mathrm{Fe}}}{}^{\mathrm{III}}(\mathrm{acac})_2 + \mathrm{RO}\cdot \qquad k_d$$

(C_I) (C_{II})

The overall kinetics of hydroperoxide-olefin systems are complex and to some extent contradictory.[74-78] However, the most extensive and reliable work was done by Walling and Chang,[77] and by Tobolsky and his associates.[76,78] The initiation mechanism of the cumene hydroperoxide - methyl methacrylate system, which will be discussed below, is based on the kinetic scheme postulated by these two groups of workers.[76-78] The initiation step probably involves the formation of a 1:1 adduct between monomer and hydroperoxide which decomposes to give two primary radicals:

$$\mathrm{ROOH} + \mathrm{M} \longrightarrow \mathrm{ROO\cdot} + \mathrm{HM\cdot} \qquad k_2$$

The overall kinetic scheme for the ferrous acetylacetonate: cumene hydroperoxide : methyl methacrylate system is thus:

Initiation:

$$\mathrm{M} + \mathrm{Fe(acac)_2} + \mathrm{ROOH} \overset{K}{\rightleftharpoons} \mathrm{C_I} \xrightarrow{k_d} \mathrm{R\cdot} + \mathrm{C_{II}} \qquad (IV2.1)$$

$$\mathrm{ROOH} + \mathrm{M} \longrightarrow 2\mathrm{R\cdot} \qquad k_2 \qquad (IV2.2)$$

$$\mathrm{R} + \mathrm{M} \longrightarrow \mathrm{P_1\cdot} \qquad k_i \qquad (IV2.3)$$

Propagation:

$$P_n\cdot + M \longrightarrow P_{n+1} \qquad k_p \qquad (IV2.4)$$

Termination:

$$P_n\cdot + P_m\cdot \longrightarrow \text{Polymer} \qquad 2k_t \qquad (IV2.5)$$

$$P_n\cdot + Fe^{II}(acac)_2 \longrightarrow \text{Polymer} \qquad k_t' \qquad (IV2.6)$$

Here R. is the unspecified primary radical, the equilibrium constant $K \gg 1$, and $[CmOOH]_o > [Fe(acac)_2]_o$. Under these conditions, $[C_I] = [Fe(acac)_2]_o$ and after time t, $[CmOOH]_t = [CmOOH]_o - [Fe(acac)_2]_o$.

Transfer reactions involving hydroperoxide are omitted as to a first approximation they are unlikely to affect the initial rate of polymerization.

Applying the stationary-state hypothesis,

$$\frac{d[R.]}{dt} = k_d[Fe(acac)_2]_o + k_2([CmOOH]_o - [Fe(acac)_2]_o)[M] - k_i[R.][M] = 0 \qquad (IV2.7)$$

$$\frac{d[P.]}{dt} = k_i[R\cdot][M] - 2k_t[P\cdot]^2 - k_t'[P\cdot][Fe(acac)_2]_o = 0 \qquad (IV2.8)$$

Substitution for k_i from equation (IV2.7) into equation (IV2.8) gives

$$k_2[\text{CmOOH}]_o[M] = \frac{2k_tR_p^2}{k_p^2[M]^2} + \frac{k_t'}{k_p[M]} R_p\,[\text{Fe(acac)}_2]_o + (k_2[M] - k_d)\,[\text{Fe(acac)}_2]_o \qquad \text{(IV2.9)}$$

At constant $[\text{CmOOH}]_o = 3.32 \times 10^{-2}M$ and over a concentration range of ferrous acetylacetonate ($2.50 \times 10^{4} - 5.00 \times 10^{-3}M$), equation (IV2.9) becomes

$$\frac{1}{R_p} = \frac{2k_t}{k_p^2\,[M]^2(k_d - k_2[M])}\;\frac{R_p}{[\text{Fe(acac)}_2]_o} + \frac{k_t'}{k_p[M]\;(k_d - k_2[M])} - \frac{1}{\left(\frac{k_d}{k_2[M]} - 1\right)}\;\frac{[\text{CmOOH}]_o}{R_p[\text{Fe(acac)}_2]_o} \qquad \text{(IV2.10)}$$

If the last term is small and may be neglected, equation (IV2.10) reduces to:

$$\frac{1}{R_p} = \frac{2k_t}{k_p^2[M]^2\;(k_d - k_2[M])}\;\frac{R_p}{[\text{Fe(acac)}_2]_o} + \frac{k_t'}{k_p[M](k_d - k_2[M])} \qquad \text{(IV2.11)}$$

Equation (IV2.11) predicts a linear relationship between $1/R_p$ and $R_p/[\text{Fe(acac)}_2]_o$. Figure IV/2.13 shows that the experimental rates fit this law for methyl methacrylate.

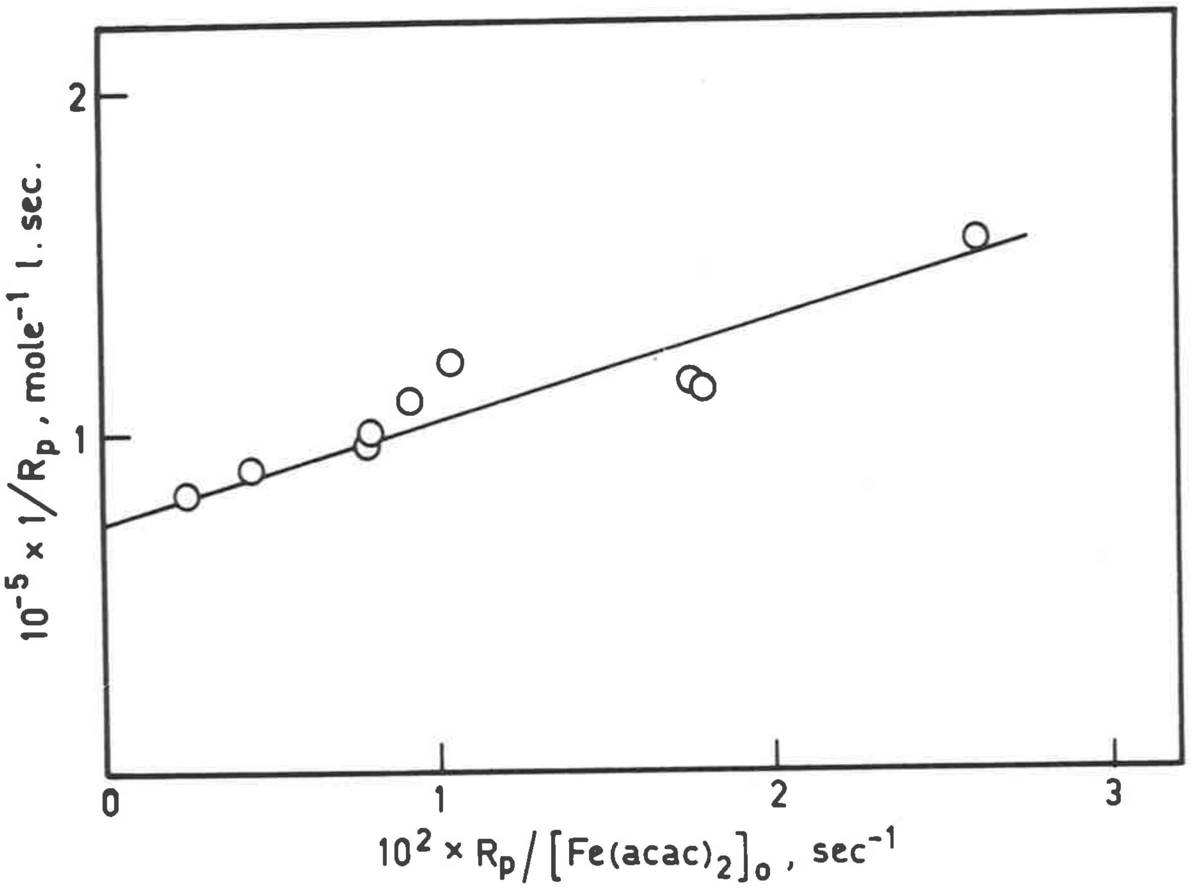


FIG. IV/2·13 Plot of $1/R_p$ against $R_p/[Fe(acac)_2]_o$ for the polymerisation of methyl methacrylate initiated by $Fe(acac)_2$ and CmOOH at 25°C.

The slope is a measure of the extent of bimolecular termination while the intercept shows the extent of termination by the ferrous chelate.

When the concentration of the cumene hydroperoxide is varied (6.00×10^{-3} - 1.60×10^{-1}M) at constant $[Fe(acac)_2]_o = 1.25 \times 10^{-3}$M, no simple plottable function of R_p against H_o is possible. Plots of H_o/R_p against R_p, H_o/R_p against $1/R_p$, and H_o against R_p^2 are all curved so that no term on the right hand side of equation (IV2.9) may be neglected. This is the general case in mixed mechanism of this type. However, it is puzzling that the proportionality of R_p and $[CmOOH]_o^{0.36}$ is observed over such a wide range of concentration (ca. figure IV/2.10). In a system showing mixed initiation, one process first order in CmOOH (ca. equation (IV2.2)) and the other effectively zero (ca. equation (IV2.1)), the order of reaction with respect to $[CmOOH]$ would be expected to lie between 0 and 0.5, but it is very surprising that this order would remain constant over a wide range of concentration. This would amount to the real positive solution of equation (IV2.9) approximating to the form:

$$R_p = \text{constant}\ [CmOOH]_o^{0.36} \qquad (IV2.12)$$

PART V:

A. GENERAL CONCLUSIONS:

The initiator efficiencies of the organometallic complexes so far studied are low. The mechanisms are complicated and monomer-initiator complexes may be involved. One of the most interesting aspects arising from this work is that two of the organometallic initiators are capable of selective initiation of free-radical polymerization. The redox initiator, which consists of cupric acetylacetonate and ammonium trichloracetate, initiates the polymerization of methyl methacrylate but not vinyl acetate. Ferrous acetylacetonate polymerizes styrene and methyl methacrylate, but not vinyl acetate.

In three systems, namely those of cupric acetylacetonate: ammonium trichloracetate : methyl methacrylate, ferrous acetylacetonate : styrene, and ferrous acetylacetonate : cumene hydroperoxide : methyl methacrylate, the polymerization rates obey the rate law

$$R_p = K[\text{initiator}]^n$$

where K is the proportionality constant and $n < 0.5$. n is independent of concentration in the case of the ferrous acetylacetonate: cumene hydroperoxide system, but is dependent on concentration in the other two systems. The low exponent of the initiator concentration $[I]$ can be adequately explained by a general linear relationship

$$\frac{1}{R_p} = AR_p/[I] + B$$

where the slope A is a measure of the extent of bimolecular macroradical termination, and the intercept B shows the extent of termination of a growing radical by the organometallic complex.

Although each system has its specific individuality, it has been found possible to explain the kinetic behaviour on similar mechanism. The basic rate equation appears to arise from the participation of the initiator, or component of the initiator, or complex in equilibrium with initiator or initiator component in termination. Alternatively a product of the initiation reaction may participate in termination. It is interesting that the same pattern of behaviour occurs in a series of systems having the presence of acetylacetonato transition complexes as a common factor, even though the actual molecular species involved are different. Unfortunately in no system is it possible to be confident that the proposed mechanism is unique. For this reason rate coefficients have not been evaluated.

B. SUGGESTIONS FOR FURTHER WORK:

1. The initiation mechanism of the cupric acetylacetonate : ammonium trichloracetate: methyl methacrylate system is not completely solved. The use of electron-spin resonance (e.s.r.) and nuclear magnetic resonance (n.m.r.) techniques may help to determine whether the intermediate formed is a 1:1 adduct between the cupric chelate and the salt, or whether the monomer is involved with the 1:1 adduct, or whether the intermediate is different from either of these two.

2. The kinetic data for the ferrous acetylacetonate : styrene system, the ferrous acetylacetonate : methyl methacrylate system, and the ferrous acetylacetonate: cumene hydroperoxide : methyl methacrylate system, suggest that monomer may be

involved in the initiation process. Spectrophotometric measurements can be carried out for these systems in the visible region 550-900 mμ. using 5 cm. or 10 cm. silica or quartz cells. These measurements can give information not only about complexing of monomer to the ferrous chelate, but also about the type of adduct formed. Furthermore, if a monomer-initiator complex is involved, the shifts of the vinyl hydrogen atoms can be observed in the n.m.r. runs.

3. Molecular weight measurements of the polymers obtained from these systems can be determined. These yield values of the degree of polymerization which can lead to better understanding of the termination reactions as well as transfer reactions.

4. A tracer technique can be utilised for the present work on the ferrous acetylacetonate:cumene hydroperoxide:methyl methacrylate system. This will indicate the extent of the RO- and ROO- groups attached to the polymer, and give further insight into the reaction mechanism.

5. Further dilatometric work can be carried out on the ferrous acetylacetonate:cumene hydroperoxide: methyl methacrylate system by using an excess of the ferrous chelate over the hydroperoxide, and also by using stoichiometric mixture of the ferrous chelate and the hydroperoxide.

PART VI, APPENDIX:

DETERMINATION OF NUMBER-AVERAGE MOLECULAR WEIGHT OF POLYMERS FROM OSMOTIC PRESSURE - AN EXTENSION OF PART II:

The kinetics of the polymerization of methyl methacrylate initiated by mixtures of cupric acetylacetonate and ammonium trichloracetate at 65°C were discussed earlier in Part II. To understand more about the kinetics, it is most essential to determine the number-average molecular weight of the polymers and hence calculate the average degree of polymerization $\overline{DP}$.

The polymers were obtained by precipitation in methanol at about 1% conversion. The polymers were dissolved in benzene, reprecipitated in excess methanol, and freeze-dried.

Number-average molecular weights of the polymers were determined by measuring the osmotic pressure of toluene solutions of the polymers at 30°C with the Hewlett-Packard/ Mecrolab Model 501 high-speed Standard Membrane Osmometer. The number-average molecular weight $\bar{M}_n$ was calculated from van't Hoff's limiting law for osmotic pressure:

$$\bar{M}_n = \frac{RT}{(\pi/C)_{c \longrightarrow o}}$$

Values of $\bar{M}_n$ and $\overline{DP}$ are shown in table VI/1.1.

At constant $[Cu(acac)_2]_o = 1.98 \times 10^{-3}M$ and low ammonium trichloracetate concentration ($< 5.00 \times 10^{-4}M$), the degree of polymerization first decreases with increasing salt concentration ($1.33 \times 10^{-5} - 3.55 \times 10^{-5}M$) and then increases with further increasing salt concentration ($3.55 \times 10^{-5} - 5.00 \times 10^{-4}M$). The latter trend is most unusual, since in free-radical polymerization the degree of polymerization, as a general rule, decreases with increasing initiator concentration. This was found to be the case for the present system when the temperature was raised from 65°C to 80°C.[55]

The only known case so far reported in the literature where $\overline{DP}$ increases with increasing initiator concentration for a system involving a free-radical mechanism, is the methyl methacrylate:ferric laurate system.[79]

Table VI/1.1 Rates and degrees of polymerization of methyl methacrylate at low ammonium trichloracetate at 65°C

$10^4\ [\mathrm{Cu(acac)_2}]_o$ $= 10^4 \times C_o$ mole l^{-1}	$10^4[\mathrm{CCl_3COONH_4}]_o$ $10^4 \times S_o$ mole l^{-1}	$10^4\ [\mathrm{Cu(acac)_2}]_{excess}$ $10^4\ (C_o - S_o)$ mole l^{-1}	$10^4 \times R_p$ mole l^{-1} $\mathrm{sec.}^{-1}$	$10^6 \times \bar{M}_n$	$10^{-4} \times \overline{DP}$	$10^4 \times (1/\overline{DP})$
19.8	0.133	19.67	0.313	2.86	2.86	0.3497
19.8	0.355	19.45	0.373	0.695	0.695	1.439
19.8	0.909	18.81	0.425	0.801	0.801	1.248
19.8	0.921	18.88	0.418	0.988	0.988	1.012
19.8	2.16	17.64	0.440	1.29	1.29	0.7752
19.8	4.53	15.27	0.452	6.76	6.76	0.1479
19.8	6.20	13.60	0.403	1.08	1.08	0.9259

For the modified mechanism set out in Part II, Chapter 2C, the average degree of polymerization is given by

$$\overline{DP} = \frac{k_p[P\cdot][M]}{2k_t[P\cdot]^2 + k_I[P\cdot][I]}$$

Which on inversion becomes

$$\frac{1}{\overline{DP}} = \frac{2k_t[P\cdot]}{k_p[M]} + \frac{k_I S_o}{k_p[M]} \qquad (VI1.1)$$

where $[I] = S_o$.

Substituting for $S_o = \dfrac{2k_t[P\cdot]^2}{k_d - k_I[P\cdot]}$ into equation (VI1.1) gives

$$\frac{1}{\overline{DP}} = \frac{2k_t[P\cdot]}{k_p[M]} + \frac{2k_I k_t[P\cdot]^2}{k_p[M]\,(k_d - k_I[P\cdot])}$$

which may be written as

$$\frac{1}{\overline{DP}} = \frac{2k_t[P\cdot]}{k_p[M]}\left(\frac{1}{1 - \frac{k_I[P\cdot]}{k_d}}\right) \qquad (VI1.2)$$

Thus as long as $\overline{DP}$ is positive, $1/\overline{DP}$ increases as $[P\cdot]$ and R_p increase. The modified mechanism cannot, therefore explain the peculiar trend of $1/\overline{DP}$ with increasing R_p and S_o as shown in tableVI/1.1 and figure VI/1.1. In order to explain this trend, an additional non-terminating transfer

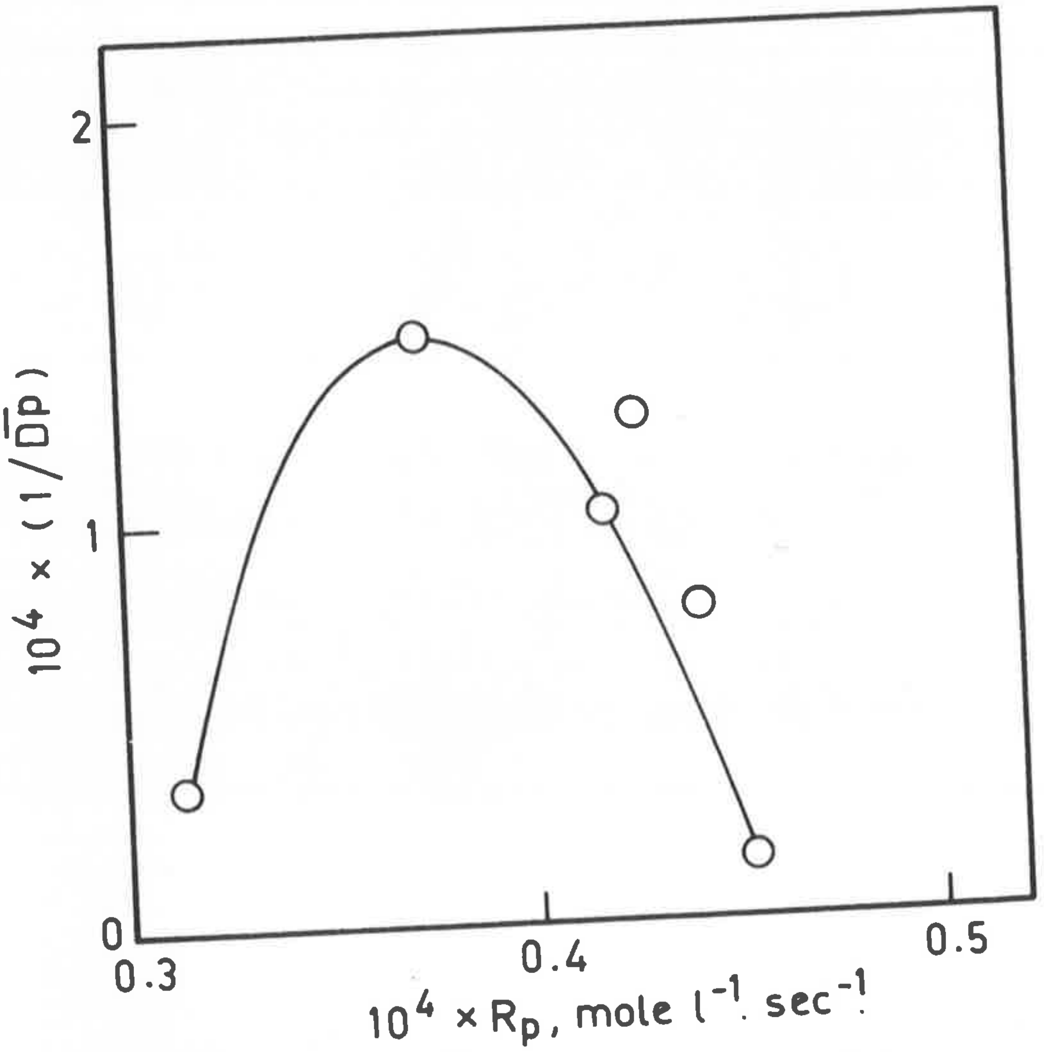


FIG. ~~IV~~ VI/1·1 $1/\overline{Dp}$ against R_p for the polymerisation of methyl methacrylate initiated by Cu(acac)$_2$ and CCl_3COONH_4 at 65°C. [Cu(acac)$_2$]$_0$ = 1.98×10^{-3} M.

reaction term, $k_c[P\cdot][C_o - S_o]$, which is the transfer of the growing radical to the excess, uncomplexed cupric acetylacetonate, must be added to the modified mechanism. This transfer reaction has no effect on the overall rate of polymerization. Equation (VI1.1) thus becomes:

$$\frac{1}{\overline{DP}} = \frac{2k_t[P\cdot]}{k_p[M]} + \frac{k_I S_o}{k_p[M]} + \frac{k_c[C_o - S_o]}{k_p[M]} \qquad (VI1.3)$$

which may be rearranged in the form

$$\frac{1}{\overline{DP}} = \frac{2k_t[P\cdot]}{k_p[M]} - \frac{(k_c - k_I)S_o}{k_p[M]} + \frac{k_c C_o}{k_p[M]} \qquad (VI1.4)$$

If $k_c < k_I$, $1/\overline{DP}$ increases with increasing $[P\cdot]$ and R_p, and S_o.
If $k_c > k_I$, $1/\overline{DP}$ decreases with increasing $[P\cdot]$ and R_p, and S_o.
A more rigid mathematical treatment of the dependence on R_p of the maximum or/and minimum values of $1/\overline{DP}$ is as follows:
Substitution for $S_o = \frac{2k_t[P\cdot]^2}{k_d - k_I[P\cdot]}$ into equation (VI1.4) gives

$$\frac{1}{\overline{DP}} = \frac{2k_t[P\cdot]}{k_p[M]} - \frac{k_o - k_I}{k_p[M]} \cdot \frac{2k_t[P\cdot]^2}{k_d - k_I[P\cdot]} + \frac{k_c C_o}{k_p[M]} \qquad (VI1.5)$$

which may be written as

$$Y = AR_p - \frac{BR_p^2}{C - R_p} + D \qquad (VI1.6)$$

where $Y = 1/\sqrt{DP}$, $A = \frac{2k_t}{k_p{}^2[M]}2$, $B = \frac{(k_c - k_I)2k_t}{k_I k_p{}^2[M]^2}$

$C = \frac{k_d k_p[M]}{k_I}$, $D = \frac{k_c C_o}{k_p[M]}$

Taking the first differential of Y w.r.t. R_p gives

$$\frac{dY}{dR_p} = A - \frac{2BR_p}{C-R_p} - \frac{BR_p^2}{(C-R_p)^2} \qquad \text{(VI1.7)}$$

For maximum and minimum values of Y, put $\frac{dY}{dR_p} = o$ into equation (VI1.7). This becomes

$$(A+B)\ R_p^2 - 2C\ (A+B)R_p + AC^2 = 0 \qquad \text{(VI1.8)}$$

The two roots of R_p are, therefore, given by

$$R_p = C\ \left(1 \pm \sqrt{1-\frac{A}{A+B}}\right) \qquad \text{(VI1.9)}$$

Since R_p must be real and positive, the term $\frac{A}{A+B}$ must be positive and less than 1 i.e.

$(1-\frac{A}{A+B}) < 1$ and positive

There are, therefore, two real roots of R_p. To differentiate which root of R_p gives a maximum or a minimum value of Y, the second differential of Y w.r.t. R_p is taken. This is of the form

$$\frac{d'Y}{dR'_p} = -\frac{2BC}{(C-R_p)^3} \qquad \text{(VI1.10)}$$

When $R_p = C\left(1 + \sqrt{1 - \frac{A}{A+B}}\right)$, $\frac{d'Y}{dR'_p}$ is positive. The minimum value of Y i.e. $1/\overline{DP}$ corresponds to $R_p = C\left(1 + \sqrt{1 - \frac{A}{A+B}}\right)$. When $R_p = C\left(1 - \sqrt{1 - \frac{A}{A+B}}\right)$, $\frac{d'Y}{dR'_p}$ is negative. The maximum value of $1/\overline{DP}$ is at $R_p = C\left(1 - \sqrt{1 - \frac{A}{A+B}}\right)$. The maximum value of $1/\overline{DP}$ is at $R_p = 3.73 \times 10^{-5}$ mole 1^{-1}. sec.$^{-1}$, as clearly shown in figure VI/1.1. There is no evidence for a minimum in the range studied. However, $1/\overline{DP}$ versus S_o (table VI/1.1) shows both maximum and minimum values of $1/\overline{DP}$.

The reciprocal of the degree of polymerization can thus be adequately expressed by equation (VI1.3). In terms of R_p, equation (VI1.3) becomes

$$\frac{1}{\overline{DP}} = \frac{2k_t R_p}{k_p^2 [M]^2} + \frac{k_I S_o}{k_p [M]} + \frac{k_c (C_o - S_o)}{k_p [M]} \qquad \text{(VI1.11)}$$

which may be written in the form

$$\frac{1}{\overline{DP}} = \frac{(k_{tc} + 2k_{td}) R_p}{k_p^2 [M]^2} + \frac{k_I S_o}{k_p [M]} + \frac{k_c (C_o - S_o)}{k_p [M]} \qquad \text{(VI1.12)}$$

The total second-order termination rate is defined here as

$$-\frac{d\,P.}{dt} = 2k_t [P.]^2 \qquad \text{(VI1.13)}$$

If mutual termination occurs exclusively by combination

$$-\frac{d[P\cdot]}{dt} = 2\frac{d[\text{Polymer}]}{dt} = 2k_{tc}[P\cdot]^2 \qquad (\text{VI1.14})$$

However, if mutual termination occurs exclusively by disproportionation,

$$-\frac{d[P\cdot]}{dt} = \frac{d[\text{Polymer}]}{dt} = 2k_{td}[P\cdot]^2 \qquad (\text{VI1.15})$$

The total second-order termination rate constant is defined by

$$k_t = k_{tc} + k_{td} \qquad (\text{VI1.16})$$

The first term in equation (VI1.12) involves bimolecular macroradical termination, the second term termination of a growing radical by complex I and the third term transfer of a growing radical to the uncomplexed cupric acetylacetonate.

At 80°C, $\overline{DP}$ decreases with S_o at constant C_o, as shown by Bamford et.al.[55] This would be explained if $k_I > k_c$.

The results of molecular weight of polymers are thus consistent with the mechanism proposed with the addition of a transfer reaction.

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