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THE KINETICS OF FREE RADICAL
BULK POLYMERISATION AT
HIGH CONVERSION

By

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Submitted in partial fulfilment
of the requirements for the degree
of Doctor of Philosophy of
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1991

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DEDICATION

This work is dedicated to

Philip, Nadia, Peter and Jenny,

- my brothers and sisters.
ACKNOWLEDGEMENTS

My first and greatest thanks go to my Supervisor, Professor Brooks, for his unfailing support and encouragement during the execution of this work. I should like to record my gratitude for his ideas and patience.

Many friends have helped "along the way"; to Jeff, Margaret, Helen and John in particular I owe a debt of gratitude.

Thanks to my typist - Karen - for tolerating my handwriting!

Lastly, Messrs A Milne and H Clayton, by their high skill with laboratory equipment, made possible several aspects of this work. My thanks go to them.
An investigation was carried out to discover the effects of high conversion on the kinetic rate coefficients for the polymerisation of styrene. In such regimes, the reaction medium is of such high viscosity that these coefficients ($k_\text{r}$ and $k_\text{t}$) exhibit profound changes. The changes were investigated with respect to the viscosity of and volume fraction of polymer present in the reaction medium. To circumvent the need to polymerise the monomer from the zero conversion, pre-formed polystyrene of known molecular weight was dissolved in purified styrene monomer. The resulting viscous solutions were then polymerised with AIBN as initiator.

Effects on $k_\text{r}$, $k_\text{t}$ and a reduction in $f$, initiator efficiency, were noted. Volume-fraction based models of termination kinetics were shown to be less applicable than one based on viscosity.
Abstract

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1.1 Free Radical Polymerisation - Ideal Kinetic Scheme

Many vinyl monomers can be polymerised by anionic, cationic or free radical means. Free-radical polymerisation proceeds via the chain reaction mechanism outlined below, in ideal conditions:

Initiation
Dissociation of the initiator, I, yields two reactive primary radicals, R.

The rate coefficient for the process is \( k_0 \):

\[
I \rightarrow 2R^* \quad (1.1)
\]

The second stage of initiation is attack of a monomer molecule by one of these reactive primary radicals. The rate coefficient is \( k_1 \):

\[
\begin{align*}
R^* + M &\rightarrow MR^* \\
\text{or:} &
\end{align*}
\]

\[
R^* + M \rightarrow M_1 \quad (1.2)
\]

The foregoing only applies in organic media. Other routes of initiation, eg redox systems, can be used in aqueous or other non-organic media.

Propagation
This occurs when \( M_1 \) grows by successive addition of monomer molecules with rate coefficient \( k_p \):

\[
\begin{align*}
M_1 + M &\rightarrow M_2 \\
\end{align*}
\]
Termination

This reaction "finishes off" a growing chain and involves the conjunction of two growing polymer radicals. In styrene polymerisation, termination is wholly by combination, yielding one polymer molecule; a straightforward pairing of the electrons on two radicals leads to a "dead" polymer molecule. The rate of coefficient is $k_t$:

$$k_t, M_n + M_n \rightarrow M_{n+1} \quad (1.3)$$

Combination by disproportionation, wherein a hydrogen atom is lost by one radical to the other, results in one saturated and one partially unsaturated "dead" molecule:

$$k_t, M_n + M_n \rightarrow M_n + M_n \quad (1.4)$$

Such a mode of termination occurs in the polymerisation of methyl methacrylate; it is present with combination. Consider the ends of each radical:

\[
\begin{align*}
\text{HHH} & \quad \text{IIII} \\
\text{C} & \quad \text{C} \\
\text{C} & \quad \text{C} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}
\end{align*}
\]
Termination by disproportion is not observed in styrene polymerisation (1). This is because the bulky pendant phenyl group obstructs movement of the hydrogen atom.

The scheme described is an ideal one, and makes the following assumptions:

a) **Radical reactivity is independent of chain length**, so unique values of $k_p$ and $k_t$ prevail throughout the lifetime of a polymer radical. This assumption is valid at low conversion; at high conversions such as those simulated in this study, the chain length may become important by introducing diffusion rather than activation control into the reaction system. It is likely that, because of the sizes of the participating radical molecules, $k_t$ is influenced before $k_p$ and this approach will be adopted.

b) **The Long-chain Assumption**

Consumption of monomer in the initiation step is assumed to be negligible in comparison with that consumed during propagation. This seems to be reasonable; initiation involves just one monomer molecule whereas propagation involves a vastly greater number.

c) **The Steady-State Hypothesis**

It is assumed that the concentration of free radicals is at a stationary value during polymerisation. This is equivalent to stating that the rate of production of free radicals equals their rate of consumption, and is found to be valid in many polymerisations, even at high viscosities.

d) **Primary Radical Termination (PRT)**

Primary radical termination is ignored. PRT involves the addition to a growing polymer radical of an initiator fragment, $R$. As so few of these
are present compared with the number of growing radicals, PRT will make an insignificant contribution. This would not be the case in other work where the initiation concentration is much higher than the relatively low ones employed here.

e) Chain Transfer is insignificant
This is valid in the present work, concerned only with styrene. With many monomers, however, this is not true and results from this study would therefore need to be applied with caution. An example is vinyl acetate in the polymerisation of which chain transfer plays a significant role in determining the molecular weight distribution.

f) Radical Indistinguishability
In deriving the rate equation, terminating radicals above a certain length are indistinguishable.

1.2 Free-Radical Polymerisation-Derivation of the Rate Equation

Dissociation of the initiator is by thermal homolysis, and its rate is given by:

\[ R_i = 2f k_d [I] \quad (1.5) \]

Where \( f \), the initiator efficiency, is the fraction of radicals which do not instantly recombine and thus go on to initiate kinetic chains.

The factor 2 appears as two primary radicals are generated per molecule undergoing homolysis. As subsequent initiation by addition of primary radicals to monomer is much faster than \( R_o \), initiator dissociation is the rate determining step in initiation. Hence the rate of initiation, \( R_i \), is given by:
The rate of polymerisation is identical with the rate of monomer consumption:

$$R_t = 2fk_d[I] \quad (1.6)$$

This only holds true in a constant-volume batch reactor; the dilatometers used in this study are such, so equation (1.7) is valid.

The long-chain assumption justifies excluding $R_t$ from this equation; so the rate of polymerisation is the sum of the rates of all the propagating steps:

$$R_p = k_p [M] [M^+] \quad (1.8)$$

Where $[M^+] = \sum_{n=1}^{\infty} [M_n] \quad (1.9)$

The rate of termination is given by:

$$R_t = k_t[M_n]^2 \quad (1.10)$$

- invoking assumption (f)

Applying the steady-state hypothesis:

$$d [M^+] = 0 \Rightarrow R_t = R_t \quad (1.11) \text{ and } (1.12)$$

Hence we obtain:

$$2fk_d[I] = k_t[M^+] \quad (1.13)$$

Rearranging:

$$[M^+] = \left( \frac{2fk_d[I]}{k_t} \right)^{1/2}$$
Substituting for \([M^*]\) in equation (1.8) gives:

\[
R_\varphi = k_\varphi[M] \left( \frac{2f_kd[I]}{k_t} \right)^{1/2}
\]

(1.14)

This shows that the reaction is first-order with respect to monomer, and the course of a vinyl polymerisation (in a batch reactor) would be expected to proceed as follows:

![Graph showing the decrease of monomer concentration over time.](Image)

\[\text{Fig. 1}\]

In practice, however, the rate does not decrease as shown but decreases more slowly implying an acceleration in rate and an apparent departure from first-order kinetics. This increase in rate is termed AUTOACCELERATION. An increase in the viscosity of the reaction mixture is noted (3) and its temperature increases dramatically.

This so called GEL EFFECT has obvious industrial and practical implications - the heat build-up may, if not efficiently liberated, be sufficient to cause an explosion. Transport of the increasingly viscous medium becomes difficult too.
1.3.1 Diffusion Control of Termination and Propagation

In a free-radical polymerisation, the kinetic chains are held to terminate when combination or disproportionation take place:

\[ k_t \xrightarrow{M_n + M_m} M_{n+m} \text{ (or } M_n + M_m) \]  \hspace{1cm} (1.4)

Equation 1.14 shows the inverse dependence of \( R_p \) on the square root of \( k_t \); so a decrease in the value of \( k_t \), all other parameters remaining fixed, will lead to autoacceleration. Such a decrease in \( k_t \) would be signalled by a decrease in the rate of the termination reaction. A decrease in rate of reaction of two polymer radical molecules could be caused by an increase in the viscosity of the reaction medium and the decrease in \( k_t \) may be three or four orders of magnitude. (4). Both Trommsdorff (3) and Robertson (5) attributed the gel effect therefore to the decrease in rate at which polymer radicals react with one another. In 1960, Hayden and Melville developed a thermal non-stationary state method of measuring \( k_p \) and \( k_t \) in situ thus making it possible to analyse the effect of decrease in radical reaction rate and to study the effect of the environment on them. Hayden and Melville studied the kinetics of bulk polymerisation of methyl methacrylate (MMA) and also the cross-linked and heterogeneous reactions; previous work had been done on vinyl acetate (7) and the first 35% conversion of MMA (8). The paper (6) dealt with the whole range of conversion of MMA; the situation when a cross-linking agent (glycol dimethacrylate - GDMA) was introduced; and when precipitation of polymer occurs in a solvent for the monomer only. They found, in bulk, that after 10% conversion, \( R_p \) increases with conversion as does kinetic chain lifetime. Beyond 40% conversion, the activation energy for chain
propagation increased with a consequent decrease in $k_\text{p}$. This was due, possibly, to the monomer molecules having difficulty in diffusing to a growing polymer radical through the increasingly viscous reaction medium. Such an eventuality is referred to as diffusion control of the propagation reaction, the normal Arrhenius dependence being deviated from. Work by Atherton et al in 1959 (9) on the trapping of radicals in polymeric gels was the inspiration for the second part of Hayden and Melville's paper. These radicals can be studied by electron spin resonance techniques and Atherton and his co-workers hoped to extend work by Bamford and Jenkins (10) who proposed that the kinetic features of polymerisation by free-radical mechanisms could be explained by occlusion of the radicals in a gel network. Hayden and Melville expected that, by studying the polymerisation of MMA under conditions that give rise to a cross-linked network, kinetic features caused by radical occlusion in linear media should be enhanced. Accordingly, they polymerised MMA in the presence of GDMA, a divinyl monomer. Such vinyl/divinyl systems exhibit an abrupt transition from a liquid to a gelled solid. Walling (11) had observed such gel points in the systems vinyl acetate/divinyl adipate and MMA/GDMA in his work on trapped radicals in such gelled networks - radicals were still detectable some months later. Using their thermocouple method for non-stationary state reactions, Hayden and Melville confirmed the enhanced degree of diffusion control of termination and propagation in crosslinked gels. Conversion was noted to cease prematurely due to occlusion of monomer within the cross-linked reaction medium. It was also noted that polymerisation of MMA in cyclohexanone solution (50%) had the kinetic characteristics of a unimolecular process. This was attributed to concurrent homogeneous and heterogeneous processes. At volume fractions of around 50%, the
polymerisation is thought to be in two parts. Homogeneous polymerisation akin to the bulk process occurs whilst a heterogeneous polymerisation takes place of monomer adsorbed onto flocculated particles of polymer. In the latter situation, bimolecular termination is restricted.

Other work on the effect of diluents was carried out by Norrish and Smith (12) and Thomas and Pellon (13). Norrish and Smith investigated the polymerisation of MMA, and discovered the profound effect of diluents on the onset of autoacceleration. Monomer solvents which were also good polymer solvents delayed or prevented the phenomenon. Conversely, polymer precipitants induced early and marked auto-acceleration. Bamford and Jenkins (10) reported a similar autoacceleration in the thermal and photosensitised polymerisations of bulk acrylonitrile. In this case the polymer is insoluble in its own monomer. They and Thomas and Pellon (13) noted large deviations from the normal dependence of $R_p$ on $[I]^{1/2}$. These kinetic characteristics were explained on the basis of radical occlusion by flocculated polymer. Under extreme conditions, these radicals are inaccessible to all but the smallest molecules. These occluded radicals, whose presence was inferred by kinetic reasoning, were discovered by ESR (14) when Bamford et al determined the concentration of occluded radicals as functions of the degree of swelling of the polymer, rate of initiation and temperature of polymerisation. By this time, work by Murphy and Wassermann (15), Benson and North (16) and Oster, Oster and Prati (18) was also adding to the evidence that the termination reaction is diffusion controlled even at zero conversion.
1.3.2 *Viscosity Effects on Diffusion Control*

North and Reed (19) performed experiments in MMA polymerisation using various esters as solvents. They showed the inverse dependence of $k_t$ on the viscosity of the medium. Examination of the intrinsic viscosities of the solvent-polymer systems showed that the effect was not due to any difference in solvent power or to the shape of the solvent molecule. Consequently, the termination reaction is diffusion-controlled under all normal conditions. They explained the initial decrease in $R_c$ (noted by Hayden and Melville (6)) and the onset of auto-acceleration after a certain conversion in terms of a two-stage diffusion process:

\[ A^* + B^* \rightarrow A' \text{---- B'} \text{ TRANSLATIONAL DIFFUSION (1.15)} \]

\[ A' \text{---- B'} \rightarrow A' : B' \text{ SEGMENTAL DIFFUSION (1.16)} \]

\[ A' : B' \rightarrow AB \text{ TERMINATION (1.17)} \]

In order for two radicals to undergo termination, they must first diffuse to form a proximate pair (translation of the centres of mass of the two radicals typifies this stage). The active chain ends must then move into a favourable position for reaction (this stage, involving a small number of repeat units in the radical, is entitled segmental diffusion). Only now may termination occur. Comparison of the diffusion-controlled $k_t$ with the self-diffusion and mutual diffusion coefficients of PMMA as a function of polymer concentration indicated that the rate-determining step of the termination process is segmental diffusion of the radical chain ends out of the coiled polymer chain, not translational diffusion. As the chain ends' diffusional rate is directly proportional to the concentration of polymer
segments in the coil it will be affected by the concentration of the polymer in solution and its molecular weight. This work was continued in 1962 by Benson and North (20), who worked out a kinetic scheme for chain polymerisation with diffusion-controlled termination. They proposed two models, applying in cases where the polymer content of the reaction medium is low:

i) 'Ball and Chain'

In this model the segmental diffusion constant is proportional to the chain diffusion constant, given by the Smoluchowski equation (21):

\[ F_a = 8\pi r D_A c_A \]  

where \( F_a \) = the flux of A along its concentration gradient;  
\( D_A \) = diffusion coefficient of A  
\( c_A \) = concentration gradient of A along its direction of diffusion  
and \( r \) = distance for encounter to occur.

This model provided reasonable values for \( k_n \), but predicts that:

\[ R_{r,} \propto M^{1/3} \]  
\[ R_{r,} \propto R_{i,}^{1/3} \]

where \( R_{r,} \) = rate of initiation.

ii) As the ball and chain model was not in accord with experimental observation, the second model was proposed which assumes that segmental diffusion is characterised by chain-length dependence equivalent to the ball and chain model for small chain lengths \( n \) but becomes independent of chain length for \( n \geq N_L \) where \( N_L \) is a characteristic chain length associated with segmental diffusion. For values of \( N_L \), the kinetic chain length, the
rate equation is very nearly conventional, with very reasonable values of mean termination coefficients, given by:

\[ K_t = 4P_{AD}kT \frac{R_E}{3\gamma} \frac{x_0N_l^{1/2}}{x_{\alpha}} \]  

(1.21)

where \( P_{AD} \) = A factor to correct the segmental diffusion constant to entanglement and direction of approach;

\( \gamma \) = the viscosity of the medium;

\( R_E \) = the transition-state end separation;

\( x_0 \) = the hydrodynamic radius divided by the square root of the chain length.

At low degrees of polymerisation (\( \mathcal{D} < N_L \)), Benson and North showed that \( R_E \) varied with \( [M]^x \) where \( x \) was just greater than 1 and with \( R^y \) where \( y \) was just less than 0.5. They also developed techniques for obtaining rate laws for polymerising systems with chain-length dependent termination constants in systems where chain transfer was a factor.

Subsequent to this work, North and Reed (22) studied values of \( k_t \) for the free-radical polymerisation of monomers in a homologous series. A change is usually noted; such change hitherto attributed to the inductive effect of groups around the reactive carbon atom or shielding of the centre by bulky substituents. One investigated series was the alkyl methacrylates (23). The decrease in \( k_t \) as the alkyl group increased in size was ascribed to steric interactions of the ester groups on the radicals. Further work was necessary as there was evidence that MMA terminates by disproportionation (24) which is not dependent on bulky end groups and termination was shown to be diffusion-controlled (20). North and Reed
showed in this paper (22) that $k_t$ was diffusion-controlled over the entire range of viscosity studied which was up to 5.72 centipoise for the system comprising sucrose acetate isobutyrate, ethyl acetate, and monomer, either methylmethacrylate or butyl methacrylate. Moreover, by calculating $k_t$ on the bases of translational or segmental diffusion being rate-determining, they were able to demonstrate that segmental diffusion was the rate-determining step. As the alkyl group becomes larger, it diffused more slowly leading to a decrease in $k_t$. The viscosities of the systems investigated in the present work go beyond those of North and Reed. Their maximum was 5.92 centipoise, compared with 93 PaS here. The maximum volume fraction (North and Reed studied conversion from zero percent by mixing monomer with the viscogens) they could have obtained, assuming 100% conversion was 25%. The present study looks at systems with an initial volume fraction of polymer of 50% maximum.

1.3.3 The Free Volume Approach

In 1968, Horie et al (25) determined $R_p$, for the bulk polymerisation of MMA and that of styrene over the whole range of conversion using differential-scanning calorimetry. At the later stages of the accelerated polymerisation of MMA, a previously unremarked inflection or peak in the rate of polymerisation was observed. The variation in rate after the onset of the gel effect, including this inflection, was interpreted in terms of the diffusion behaviour of monomer molecules and polymeric radicals in the polymer-monomer system. The diffusion rates were predicted from a consideration of the free volume available to them. The final conversion at which no further polymerisation occurred was determined for both
monomers. It was affirmed quantitatively that the final conversion has a close relation with the transition of the polymer-monomer system from a viscous liquid to a glassy state, lending credence to an idea that free volume may be important as a system parameter in the study of diffusion-controlled termination. Balke and Hamielec (26) in 1973 investigated the bulk polymerisation of MMA using AIBN as initiator. They continued their experiments to limiting conversion at temperatures of 50°C, 70°C and 90°C. Using a gel-permeation chromatographic method, they studied the molecular weight distribution of the polymer formed. By differentiating the cumulative differential molecular weight distribution (CDMW) the instantaneous version (IDMW) was obtained. The IDMW's were found to fit well to those predicted by classical free-radical kinetics over the entire conversion range and where diffusion control of the termination reaction was pronounced. They proposed a correlation of the dimensionless group $\alpha$ with free volume, $\alpha$ being given by equation 1.22:

$$\alpha = \frac{k_t R_o}{k_o R (M)^2}$$  \hspace{1cm} (1.22)

This was found to account for diffusion control of the termination reaction quite adequately. Balke and Hamielec also developed a good - though complex - model for the bulk polymerisation of MMA. They concluded that classical free-radical kinetics are applicable during auto-acceleration. Additionally, they demonstrated the close connection of free volume with the onset and magnitude of $k_t$. The increase in $R_o$ at the onset of the gel effect has consequences as follow. The IDMW broadens, and if no chain transfer is present, the IDMW goes to higher molecular weights. Hence $M_w$ increases with conversion. When auto-acceleration was pronounced, the IDMW was even found to become bimodel. When chain-transfer reactions are
significant, as when they are used to control chain length, IDKWD was not affected by auto-acceleration and only the overall $R_o$ displayed anomalous behaviour (27). In this paper, Abdel-Alin and Hamielec polymerised vinyl chloride with AIBN. Further progress was made in 1982 when Marten and Hamielec published a paper outlining a kinetic model for the polymerisation of styrene (27). Based on the free-volume theory, it was capable of describing the course of polymerisation in bulk and in solution it accounted for the diffusion. Control of termination and propagation and predicted a limiting conversion. Previous work of theirs (28) on MMA gave rise to a semi-empirical model which could describe the polymerisation under a wide range of experimental conditions. Their paper of 1982 tested the applicability to the case of styrene polymerisation at temperatures below 80°C. Assuming that the termination reaction becomes diffusion-controlled when the diffusion coefficient $D_p$ for a polymer radical becomes equal to less than a critical diffusion coefficient $D_{p,c}$ and that $D_p$ then becomes proportional to $D_{p,c}$:

$$k_t = k_1D_{p,c} \quad (1.23)$$

According to Bueche (47) the diffusion coefficient can be related to the free volume and the molecular weight by:

$$D_p = \frac{\phi_0 \delta^2 \exp \left(\frac{-A}{k_2M \frac{1}{V_f}}\right)}{k_1 k_2 A} \quad (1.24)$$

where $\phi_0$ = the jump frequency;

$\delta$ = the jump distance;

$k_1, k_2, A$ = constants;

$V_f$ = free volume of polymer

$M$ = molecular weight of polymer
Free volume fraction in a partially converted bulk system is given by the following expression:

\[
V_f = \left\{ \begin{array}{c}
\frac{0.025 + \alpha_p (T - T_{g,p})}{V_T} V_p \\
\frac{0.025 + \alpha_m (T - T_{g,m})}{V_T} V_m \\
\frac{0.025 + \alpha_s (T - T_{g,s})}{V_T} V_s
\end{array} \right\} 
\]  \hspace{1cm} (1.25)

Where subscripts m, p and s denote monomer, polymer and solvent respectively;

- \( T \) = polymerisation temperature
- \( V \) = volume of component;
- \( V_T \) = total volume
- \( T_g \) = glass transition temperature;
- \( \alpha = \alpha_m - \alpha_s \)

where \( \alpha_m \) = expansion coefficient liquid phase

and \( \alpha_s \) = expansion coefficient, glassy state

\( T_g \) of the polymer is given by:

\[
T_g = T_{g,m} - Q \frac{1}{\langle M_r \rangle} 
\]  \hspace{1cm} (1.26)

where \( T_{g,m} = T_g \) at infinite molecular weight

- \( Q \) = a constant,
- \( \langle M_r \rangle \) = number-average molecular weight.

It was shown (28) that the best correlation with experimental data was obtained when \( M \) in equation 1.24 was replaced with \( \langle M_w \rangle^{1/2} \). Combining equations 1.23 and 1.24 gives \( k_e \) as a function of conversion, molecular weight and temperature. For unentangled polymer solutions:
\[ k_t = k_0 \frac{\delta^2}{k_2 \bar{M}_w^{1/2}} \exp \left( -\frac{A}{V_r} \right) \quad (1.27) \]

and for entangled polymer solutions:

\[ k_t = k_1 \frac{\delta^2}{k_2 \bar{M}_w^{1.76}} \exp \left( -\frac{A}{V_r} \right) \quad (1.28) \]

If it is assumed that the termination reaction becomes diffusion-controlled before the occurrence of entanglement at the onset of the gel effect, a constant \( K_\alpha \) may be defined:

\[ K_\alpha = \frac{k_1 \delta^2}{k_2} \quad (1.29) \]

Hence for a given \( \bar{M}_w \), at constant temperature, there will only be one conversion that satisfies equn 1.29. As \( \bar{M}_w \) varies with the concentration of initiator, chain transfer effects and the nature of the solvent, the conversion at which the gel effect starts is predicted to be dependent on these factors which is precisely what is observed in practice. Thus, the concept of volume fraction may help in predicting the onset of the gel effect and thus the inference according to Marten and Hamielec is that the diffusion effect on \( k_t \) is related to the volume fraction of polymer present in the system.

The work of Benson and North (20) developed the idea of the chain-length dependence of \( k_t \). They did not solve the mathematical kinetic scheme as it was too complex, but Ito (29,30) showed in 1969 that segmental diffusion was rate-controlling for termination. He modified Smoluchowski's theory of the kinetics of colloidal reactions and applied it to polymerisation. Using the collision theory of chemical reaction, he derived an expression for segmental-diffusion controlled \( k_t \) which explained why \( k_t \propto \gamma^{-1} \) in the
radical polymerisation of alkyl methacrylates and is independent of the molecular weight of the polymeric free radical. The key was that Ito's $k_t$ was dependent on conversion which in turn alters the viscosity of the medium.

1.3.4 Chain Entanglement

In 1976 Cardenas and O'Driscoll reviewed the current situation and concluded that none of the proposed developments at that stage adequately described free-radical polymerisation completely. They objected to models which contained parameters which were difficult to determine experimentally and the fact that some effects (e.g. relative magnitudes of segmental and translational diffusion) were difficult to assess. They noted that in an infinitely dilute solution, viscosity was due to polymer/solvent interactions but as the concentration was increased, a point was reached where the viscosity contribution from polymer/polymer interactions became appreciable. For a given molecular weight, the point at which the transition occurs between these two mechanisms of viscosity is designated the critical concentration. Beyond this point, viscosity is very strongly influenced by polymer/polymer interactions. Bueche (32,22) attributed this to entanglement of polymer chains, as did Graessley. The nature of entanglements and their formation is complex but theories and experimental practice correlate well (32,33,34). The relationship between the polymer concentration and its molecular weight at the critical concentration is given by:

$$K_c = \bar{X}_c \varphi_p$$

(1.30)
Where \( X_e \) = average chain length
\( \alpha_p \) = volume fraction of polymer;
\( K_c \) = a "critical constant".

Weight-average of viscosity-average degrees of polymerisation may also be used instead of \( X_e \). The value of the parameter \( \beta \) depends on the model of polymer in solution under consideration. Onogi used a packed-sphere model in his studies of non-Newtonian flow of concentration solutions of high polymers, giving \( \beta = 0.5 \) (33,35). Bueche's entanglement theory gives \( \beta = 1.0 \) (32,33). There is experimental data to support both theories. The value of \( K_c \) depends on the polymer being studied and the thermodynamic quality of the solvent (which may, of course, be the monomer). With these ideas, Cardenas and O'Driscoll described high-conversion polymerisation (31), developing a model based on the assumption that two populations of radicals exist in a highly-converted system:

i) Those whose chains are long enough to become entangled with neighbouring molecules and thus have restricted mobility;

ii) Shorter radicals whose mobility is not affected by diffusional effects.

They also assumed that \( k_{\tau,\tau} \propto E^{-1} \)

Where \( k_{\tau,\tau} \) is \( k \) between entangled radicals
and \( E \) is the entanglement density.

Their model contains two parameters in addition to the kinetic constants at low conversion: \( K_c \) from equation 1.30 and \( \alpha_o \) which is a measure of reduced chain mobility due to entanglement. \( K_c \) was estimated by measuring zero-
shear viscosities of polymer/monomer solutions at different polymer concentrations for a given molecular weight. The critical concentration is then determined from the break in a log-log plot of viscosity vs. concentration:

\[ \log \eta \text{ vs. } \log [\text{polymer}] \]

Kc then follows from equation 1.30. The parameter \( a \) is obtained by fitting known experimental data to the model. Using literature data on the bulk polymerisation of MMA, satisfactory agreement was found between predicted and experimental conversions and average molecular weights. Their assumptions, therefore, seem valid, and the idea that entanglement phenomena govern the basic aspects of high conversion polymerisation of MMA in bulk is supported. It also seemed unlikely that non-entangled radicals are subject to strong diffusion effects, at least to conversions of 80%-90%. They assumed that:

1) Chain transfer is negligible;
2) Initiation and propagation, involving small molecules, are not affected by the gel effect;
3) Termination is by disproportionation;
4) The average mobility of an entangled radical is constant.
1.4.1 Viscosity Effects on Initiator Efficiency

It was suggested in 1960 by Hayden and Melville (6) that increased viscosity of the reaction medium may have effects on elementary reactions involving smaller species than the polymeric macro-radicals. They postulated that $k_n$ may be affected at high conversion. Such a hypothesis begged the question of similar effects occurring with the initiation reaction. After all, initiator fragments are often larger than monomer molecules and so may reasonably be expected to be hindered when the viscosity of the medium is high.

In 1977, Brooks (37) presented the results of work carried out investigating the polymerisation of MMA in the presence of calculated amounts of PMMA. By dissolving pre-determined mass fractions of the polymer in its monomer, it was possible to simulate a highly-converted system without recourse to polymerising a monomer from zero conversion and stopping the reaction at the desired stage - a process fraught with practical difficulties. Azobisisobutyronitrile was used as the initiator. It was found that the initiator efficiency, $f$, was not a function of the reaction medium within the viscosity range investigated during the work ($5.07 \times 10^{-4} - 13.33 \text{ Pas}$). In other words the viscosity of the medium was found not to affect the number of initiator fragments available to initiate kinetic chains. In the higher viscosity regimes investigated, Brooks found that the chain termination step was influenced by the rate of translational diffusion of the polymeric radicals. In addition, the simple kinetic scheme, particularly the final elementary reaction, (e.g. 1.4) was unable
to account for the dependence of $k_n$ on the solution viscosity. The ideas of North and Reed (19) were recalled by a finding that only those macro-radicals above a certain size were significantly hindered. That is, a critical size of macroradical existed, above which the mutual termination rate coefficient $k_t$ was determined by the viscosity of the solution and below which no viscosity effect was apparent. Moreover, in a termination reaction between a radical of smaller than the critical size and one of larger than the critical size, some amount of diffusion-related change to $k_t$ was apparent. The critical, or limiting, size decreased as the solution viscosity increased.

Further work on the effects of viscosity on initiator decomposition was carried out by Kulkarni and Mashelkar (38). They investigated the decomposition of AIBN and p-nitrophenylazotriphenylmethane (NAT) in solutions of polyacrylonitrile and dimethylformamide, glycerol and dimethylformamide and polyethylene glycols. Their findings led to the proposal of a kinetic model for decomposition of the initiator, the diffusive separation of the fragments, and subsequent recombination when it occurred. The rate coefficients for diffusion separation were calculated using the Smoluchowski equation (21). The diffusional resistance imposed by different environments on the various processes was accounted for by the concept of microviscosity, $\gamma^*$. This is related to individual polymer chain segment/solvent molecule interactions, rather than chain entanglement. Three methods were proposed which enabled calculation of $\gamma^*$ for low viscosity and medium viscosity solvents and polymer solutions. All the methods involve a knowledge of the diffusion coefficient of the initiator fragment.
Diffusion in low-viscosity systems

For fragments diffusing in low-viscosity systems, such as NAT in DMF, the Stokes-Einstein equation may be invoked:

\[ \frac{D}{T} = \text{Constant} \quad (1.31) \]

Diffusion in Polymer solutions

For initiator fragments in polymer solutions, Kulkarni and Mashelkar proposed that:

\[ D = D_0 \gamma^\# \quad (1.32) \]

Where \( \gamma^\# \) = solvent viscosity;
\( D_0 \) = diffusivity of solute in polymer solution;
\( D \) = Diffusivity of solute in pure solvent

Evaluation of \( \gamma^\# \) in this case requires a knowledge of \( \gamma \) which is easily measured, and the ratio \( D/D_0 \). The latter quantity, they assume, will be the same as the ratio of any other pertinent transport parameters such as electrical conductivities in pure solvent and polymer solution. Alternatively, \( D/D_0 \) may be calculated according to the model proposed by Li and Gainer in 1968:

\[ \frac{D_3}{D} = \left( \frac{M}{M_0} \right)^{1/2} \left( \frac{V_0}{V} \right) \left( \frac{1 - \Delta H_m}{\Delta H_{m,p}} \right) \quad (1.33) \]

Where \( M \) = molecular weight;
\( V \) = molar volume;
\( \Delta H_m \) = enthalpy of mixing of polymer and solvent
and \( \Delta H_{m,p} \) = enthalpy of vaporization of solvent.
Hence the microviscosity can be calculated from a knowledge of solution properties.

**Diffusion in Medium Viscosity systems**

By arguments deduced from the Eyring Rate Theory the microviscosity of a medium-viscosity system is given by:

$$
\gamma^* = \left( \frac{\gamma^a}{\gamma} \right)^{2/3} \gamma
$$

(1.34)

By application of the Smoluchowski equation (39) to initiator decomposition, the rate coefficient for decomposition may be obtained as:

$$
k_{da} = \frac{N \cdot 4\pi DR}{1000}
$$

(1.35)

Where

- $N$ = Avogadro's number;
- $D$ = the diffusivity;
- $R$ = the radius of the reacting molecule.

Given equation 1.32, it follows that:

$$
k_{da} \gamma^* = \text{constant}
$$

(1.36)

If the following mechanism be assumed for the decomposition of the initiator:

Initiator $\xrightarrow{k_1, k_{-1}}$ (Cage I) $\xrightarrow{k_{da}}$ free radicals $\xrightarrow{k_{\beta}}$ (Cage II) + small molecules

(1.37)
then the overall rate constant may be deduced to be:

\[ k = \frac{k_1 (k_d + k_B)}{k_{-1} + k_d + k_B} \]  

(1.38)

For AIBN, a multi-bond initiator, there is no recombination in cage I as nitrogen gas is evolved on decomposition; \( k_{-1} = 0 \). Hence, as the gas is released instantaneously, \( k_B \approx k_d \) and thus:

\[ k = k_1 \]

It follows therefore that for an initiator like AIBN where more than one bond is broken during decomposition, the observed rate coefficient is independent of the viscosity of the medium.

In contrast to AIBN, decomposition of which involves the simultaneous scission of two C-N bonds, initiators such as NAT decompose by scission of a single C-N bond. Thus recombination may occur in cage I and \( k_{-1} \neq 0 \). Also, \( k_d \approx k_B \), giving:

\[ \frac{1}{k} = \frac{1}{k_1} + \frac{1}{k_d} \]  

(1.39)

From (1.39) and (1.35),

\[ \frac{1}{k} = \frac{1}{k_1} + \frac{1}{\alpha D} \]  

(1.40)

Where

\[ \alpha = \frac{k_1 N}{4\pi R} \frac{1}{k_{-1}} \frac{1}{1000} \]

As

\[ D \propto \frac{1}{\eta^*} \]

\[ \frac{1}{k} = \frac{1}{k_1} + \frac{\eta^*}{\alpha} \]  

(1.41)
Plotting $1 \frac{\text{measured}}{k}$ against $\gamma^* \frac{\text{calculated}}{\alpha}$

therefore gives a straight line from which $1 \frac{\text{intercept}}{k}$ and $1 \frac{\text{gradient}}{\alpha}$ may be obtained.

The foregoing discussion and careful experimental work by Kulkarni and Mashelkar yielded these results:

i) For AIBN, the rate coefficient for decomposition is independent of viscosity;

ii) For NAT, the rate coefficient is dependent on the viscosity;

iii) For NAT in polyethylene glycol solutions, increasing the chain length of the viscogen has no effect on the diffusion of radicals from the cages. This indicates that segmental motion, rather than translational, is the controlling factor in the diffusion process.

1.4.2 Limiting Conversion for a Decrease in $f$

More recent work by Russell, Napper and Gilbert in 1988 (40) highlights the well-documented cessation of polymerisation, or at least, an appreciable slowing-down of the reaction at certain high levels of conversion. Previously, this phenomenon had been attributed to the decrease in $k_r$ as the medium becomes sufficiently viscous to preclude rapid movement of even a single monomer molecule through a tangled network of polymeric radicals (Flory, (41); Hayden and Kelville 1961 (6)) It is obvious, certainly, that $k_r$ cannot suddenly increase again. Russel et al (40) cited three
refutations of the argument that $k_\alpha$ may decrease to cause cessation of the reaction:

i) Studies of the variation of $k_\alpha$ with the weight fraction of polymer in the system (Ballard et al 1986, Lau et al 1987) reveal that $k_\alpha$ is many orders of magnitude higher than values predicted by free-volume theories such as that of Marten and Hamielec (28). In these studies, measurement of rate of polymerisation was coupled with the concentration of free radicals as measured by electron-spin resonance spectroscopy. The system under investigation was the emulsion polymerisation of methyl methacrylate. This method of polymerisation is often used to furnish values of $k_\alpha$ applicable to bulk systems, by utilising the ideas of Smith-Ewart kinetics (44).

ii) Complete conversions, given only moderate initiator concentrations and sufficient time, can be obtained (in 10 days or so for bulk systems) (Stickler, 1982; Vunderlich et al 1985). Thus the proposition that propagation of kinetic chains ceases at the glass transition point, is seen to be false.

iii) Direct measurement of diffusion coefficients (Lee et al 1986) revealed them to be relatively insensitive to the "glassiness" of the system. Thus, $k_\alpha$ cannot be diffusion-controlled as it is directly proportional to the diffusion coefficient of the monomer. The study by Lee et al was based on forced Rayleigh Scattering by probe organic penetrant diffusion in polymer solutions at high concentration.

Russell et al (40) propose that the large observed decrease in $R_\alpha$ is due to a fall in $f$, the initiator efficiency, rather than $k_\alpha$. They give as the reason the comparability of times of diffusion apart of the two initiator
moieties formed by decomposition of the molecule, and that of propagation. When propagation has started, the radicals produced by decomposition are less mobile than before. At a certain critical conversion, the two radicals are likely to be trapped close to each other and it is very likely that they will undergo geminate recombination. Thus, when diffusion and propagation times are comparable, the efficiency of the initiator would, according to Russell et al., decrease dramatically. Using the relation:

\[
f = \frac{dx}{dt} \left( k_p (1-x) \right)^{\frac{1}{2}} = k_t/k_d \] (1.42)

Where \( f \) = initiator efficiency

and \( x \) = fractional conversion of monomer to polymer

They plot graphs of \( f \) against the weight fraction of polymer (related to \( x \)) and show that \( f \) falls dramatically at weight fractions of about 0.8 for methyl methacrylate polymerisation with AIBN as the initiator. The values to which \( f \) falls are as low as six orders of magnitude lower than the value appertaining in the lower-conversion regimes. In addition, the decline in \( f \) as far as the critical weight fraction of polymer (\( W_p \)) is slow, barely changing at all until the critical point is reached, when the fall, as remarked above, becomes dramatic. Russell et al. assumed that \( k_t \) also varies with conversion, so the value of \( k_t \) for a given \( x \) in equation (1.42) was calculated from the following equations:

\[
\ln k_t/\text{dm}^3\text{mol}^{-1}\text{sec}^{-1} = 17.7 - 14.2 W_p; W_p < 0.75 \] (1.43)

and \( k_t = 4 \pi k_p [M] a^2 v; W_p > 0.75 \) (1.44)

Where \([M] = \) monomer concentration

\( a = \) r.m.s. end-to-end distance per square root of the chain length;
\[ W_p = \text{weight-fraction of polymer}; \]
and \[ \sigma = \text{Lennard-Jones diameter of the MMA monomer molecule}. \]

Both equations (1.43) and (1.44) derive from previous work of theirs (48), 1.43 being obtained from plots of the free-radical concentration as a function of \( W_p \) in emulsion polymerisations. Equation 1.44 is the mathematical expression of the rigid-chain residual termination limit.

### 1.5 Further Characterisation of the Gel Effect

In 1979, Dionisio et al. (49) redefined the onset of the gel effect on the grounds that a fundamental definition was preferable to a phenomenological one, and that this would enable comprehensive and more precise theories to be applied. Recognising the work of previous years as attributing the onset of auto-acceleration to the rate of radical diffusion, they proposed that:

\[ \frac{1}{k_t} + \frac{1}{k_s} + \frac{1}{k_T} < \frac{1}{k_R} \quad (1.45) \]

Where \( k_t \) = termination rate coefficient;
\( k_s \) = segmental diffusion rate coefficient;
\( k_T \) = translational diffusion rate coefficient;
\( k_R \) = rate coefficient for radical reaction

As it is reasonable to assume that the rate of chemical reaction of the radicals is too fast to be rate-controlling, viz. \( k_R \gg k_T, k_s \), it follows that:
Given that the onset of the gel effect is caused by a change from segmental diffusion to translational diffusion being rate-controlling (16), the onset of the gel effect corresponds with the point at which $k_T = k_o$ increases linearly with conversion according to equation 1.47:

$$k_o = k_{o,0} (1 + \delta x)$$  \hspace{1cm} (1.47)

Where  

- $\delta$ = a function of solvent power, polymer molecular weight and chain stiffness;
- $x$ = conversion;
- $k_o$ = as above for eq. 1.45;
- $k_{o,0}$ = $k_o$ at zero conversion.

The reason for this linearity is that the increasing amounts of polymer in the system make the medium a poorer solvent in the thermodynamic sense; thus the polymer chains coil up more tightly and this creates a higher concentration gradient across the coil for reaction of its active end.

In contrast, increasing the polymer concentration causes $k_T$ to decrease. Thus a graph can be drawn:
The dotted curve in Fig. 4, representing the sum of the curves for $k_r$ and $k_g$, shows the variation of $k_t$ with conversion:

$$k_t = \frac{k_g + k_r}{k_g k_r}$$

(1.48)

$x_g$ is the gel-point conversion.

In consequence of this definition, it can be shown that $R_\infty$ and $\bar{P}$ (the degree of polymerisation) should pass through a minimum at the gel point; the former by equation 1.14 and the latter by equation 1.49:

$$\frac{\bar{P}}{P} = \frac{R_\infty}{R_t}$$

(1.49)

where $R_t = \text{rate of termination}$.

Careful experimental work showed the small decrease in $R_\infty$ prior to auto-acceleration; evidence that equation 1.46 is valid when monomer and
initiator consumption are accounted for. Account needs to be taken of these as otherwise the graph of $R_f$ versus $x$ obscures the small dip:

$$R_f[M] = 2.29 \times 10^{-6} t^2 - 2.62 \times 10^{-6} t + 7.6 \times 10^{-4}$$

Now, $dR_f/dx$ will decrease with any factor that reduces the effect of other polymer chains on the radical-containing ones (e.g. smaller chains or a poorer solvent). $k_r$ decreases slowly with conversion because of increasing viscosity, then suddenly at the onset of entanglement. Hence the higher the molecular weight of the polymer or the better the quality of the solvent, the faster the rate of decrease and the earlier is the sharp change in gradient. This definition and its construction may be used qualitatively to predict experimentally verifiable facts. An example given by Dionisio et al. is the effect of increasing initiator concentration. This causes a decrease in $dR_f/dx$ hence the onset of the gel effect is delayed.
Another method of distinguishing the onset of the gel effect was provided by Tulig and Tirrell in 1982 (50). They devised a time-scaling procedure to enable superposition of data obtained at differing temperatures and concentrations of initiator at low conversion. Auto-acceleration is then signified by deviations from the master-curve:

\[
R_t \propto \frac{R_0}{I} \exp(-k_t \cdot t)
\]

From kinetic arguments,

\[
\frac{dx}{dt} = \frac{2f_k d \lll}{k_t \cdot c} \left( \frac{I \cdot k_p (1-x)}{k_t \cdot c} \right)^{1/2}
\]

(1.50)

making these assumptions:

1. Steady state applies;
2. Zero monomer consumption by initiator;
3. Invariant rate coefficients;
4. No volume change on polymerisation;
5. Invariant initiator concentration with time.
By scaling 'real time' Tulig and Tirrell suggest a dimensionless time for free-radical polymerisation:

\[
\tau = \left( \frac{2fk_{d}I_{0}}{k_{t,0}} \right)^{1/2} k_{d}t \tag{1.51}
\]

which, on using equation (1.50), gives:

\[
\tau = \frac{t}{dx} \frac{1-x}{dt} \tag{1.52}
\]

Fig 5, above, shows the course of MMA polymerisation initiated by AIBN at three different temperatures. Correlation of the gel point with conversion is indistinct, and direct comparisons of the data so obtained at the different temperatures is difficult. Fig 6 shows the fractional conversion \( x \) plotted against the dimensionless time \( \tau \) obtained from equation (1.52). Deviations from the master curve \( x = 1-e^{-\tau} \) (on which all the points lie prior to auto-acceleration) are much more obvious, facilitating comparison of polymerisations at different temperatures. It was shown that, in scaled time, the onset of auto-acceleration is dependent only on the molecular weight of the polymer formed in the reaction mixture up to that conversion. Use of data from the literature, especially that of Balke and Hamielec (26), shows that the transition from normal to accelerated behaviour is sharp for a polymer of high molecular weight and more diffuse when one of lower molecular weight is being formed. Tulig and Tirrel also reported parallels between this observation and studies of the concentration dependence of solution viscosity and mutual diffusion coefficients at various molecular weights. From several sets of scaled data they extracted the molecular weight dependence of the critical concentration, \( c^{**} \), for onset of auto-acceleration:

\[
c^{**} \approx N^{-0.24} \tag{1.53}
\]
Compared with:

\[ c* \approx N^{-0.5} - N^{-0.6} \]  \hspace{1cm} (1.54)

which expresses the molecular weight dependence of molecular overlap, and

\[ c* \approx N^{-1.0} \]  \hspace{1cm} (1.55)

expressing the molecular weight dependence of entanglement. In equations 1.53 and 1.55, \( N \) represents molecular weight and \( c* \) and \( c** \) are critical concentrations. Tulig and Tirrell suggest that the difference arises from the method of measurement; rheological experiments give an exponent of 0.5-1.0 whereas kinetic experiments lead to an exponent of 0.24 implying a different fundamental sensitivity to chain length in the two methods.

Further work on the point of onset to auto-acceleration was carried out in 1980 by Dionisio and O'Driscoll. They defined a region of conversion as the "explosive region" using a quantitative but arbitrary process. Their explosive region is a window of conversion beginning at the point where commences the deviation from first-order kinetics. They constructed a table of conversion range in the explosive region using solution data from the literature at different temperatures and initial concentrations of monomer. When considering the free-volume fraction range during the explosive region they investigated the use of the product:

\[ \phi_p \bar{X}_n^{1/2} \]  \hspace{1cm} (1.56)

Where \( \phi_p \) = volume fraction of polymer in the reaction
\( \bar{X}_n \) = critical value of the number-average chain length required to cause the chain-entanglement phenomenon at a given volume fraction of polymer.
The value of the product (1.56) was roughly the same at any given temperature. This showed the explosive region to be coincidental with the transition in the slope of the straight lines on a plot log log $\eta_0$ versus log $X_n$ ($\eta_0$ is the zero-shear viscosity of the reaction mixture). Using their own model from reference 31, they described the bulk polymerisations they carried out, investigating the explosion limits as they had defined them. The value of their model's adjustable parameter $K_c$ compared well with the range of $\sigma X_n^{1/2}$ found in the explosive regions of these polymerisations. Thus support was lent to the idea that, in bulk, the explosive region of kinetics corresponds to the chain entanglement phenomenon of solution behaviour. However, the region was not defined at a constant value of free volume; but free volume does play a role in determining the rate of termination at a given level of chain entanglement.

1.6 **Kinetics and Reactor Design**

For the design of polymerisation reactors to be efficient and successful, quantitative relationships between reactor conditions and reaction kinetics need to be established. Thus, via conceptual models of the molecular basis of reaction, measurable quantities such as rate of reaction; molecular weight and concentration of polymer; and solution viscosity may be related to values of $k_0$ and $k_\tau$, fundamental quantities used in the design of polymerisation reactors.

Work by Hui and Hamielec (1) led to empirical relationships between reactor contents' conditions (conversion and molecular weight) and a computer model of operating conditions. The work of Cardenas and O'Driscoll
(relationships between $k_c$ and $\varphi, \lambda$) is of value in this exercise. In 1977, Brooks (37) investigated the relationship between solution viscosity and kinetic parameters in a well-characterised environment and in an extension to the technique developed in that work, Brooks and Bogunjoko (42) in 1983 sought to clarify relationships between chain termination processes and physical properties of the reaction solutions. The essence was polymerisation of various vinyl monomers in the presence of preformed polymer of known molecular weight using AIBN as the initiator. In each experiment, $[I]$ and the zero-shear solution viscosity were calculated from measured values. The value of this technique is that $\varphi$ and $\lambda$ can be varied independently. As it is not easy to distinguish between polymer formed in solution and preformed polymer, different vinyl preforms were used as viscosity modifiers in the reaction medium; e.g. polymerisation of MMA in PS solution. Bogunjoko and Brooks found that, with a reasonable kinetic scheme, correlations between radical mobility and solution viscosity were more consistent than those between radical mobility and volume fraction of dissolved polymer. As an attempt to improve current kinetic schemes, the possibility of primary radical termination was investigated and found to be unimportant at low viscosity. This work and that of 1977 (37) showed that the free-radical polymerisation of MMA was strongly influenced by the presence of PMMA preformed and dissolved in the monomer prior to polymerisation. The rate data obtained were found to be compatible with more than one mechanism. In order to decide which mechanism was the more likely, the molecular weight and molecular weight distribution of the polymer formed, were required. As work had been done on the relationships between solution viscosity and molecular weight parameters (26), comparison of molecular weight distributions both
calculated and determined experimentally could differentiate between the mechanisms. In a subsequent paper (53) Bogunjoko and Brooks confirmed that primary radical termination, when included in the scheme, did not explain all the results. It was postulated that when radicals above a certain size are terminating, the termination step they experienced differed as their mobilities are more restricted than those of the radicals below the critical size. Subsequent to this paper, Brooks in 1985 (54) published a paper outlining a kinetic scheme which was consistent, for styrene polymerisation in a batch and in a back-mixed continuous flow reactor, with this idea. By taking the classical kinetic scheme and adding two extra chain termination steps, a scheme was obtained which fitted kinetic data. The extra steps comprised reaction of hindered radicals (above a critical size for restriction to occur) with hindered and non-hindered ones. The restricted radicals conform to a diffusion equation for plasticised polymer (37) and it was shown that relationships between the kinetic coefficients predicted a molecular weight distribution which was, in fact, obtained.

1.7.1 Polymerisation of Styrene by Anionic Initiation: Mechanism

The anionic polymerisations carried out in this study to prepare host polymer samples took place under circumstances where termination did not occur. Namely, chain-terminating agents such as OH\(^-\) were not present until purposely introduced. Therefore, propagation was assumed to occur with complete consumption of monomer, and so the molecular weight required could be forecast in advance and achieved in practice. The mechanism for the mode of polymerisation is as follows:

1) Addition of the initiator to styrene monomer:
i) Successive additions of styrene monomer constitute propagation

\[
\begin{align*}
\text{C}_4\text{H}_9\text{Li} + (\text{CH} = \text{CH}_2) & \rightarrow \text{C}_4\text{H}_9-\text{CH}_2-\text{CH Li} \\
\text{C}_4\text{H}_9-\text{CH} & \rightarrow \text{CH Li} + n (\text{CH} = \text{CH}_2)
\end{align*}
\]

As remarked above, termination does not occur until introduction of OH\(^-\); in the present study, methanol and distilled water were added to the reaction mixture to induce termination and precipitate the newly-formed host polymer.

The propagating anions were coloured deep orange, so impurities in the system were easily detectable by the said colour disappearing during the course of the reaction or not presenting in the first place. Such anions were designated "living polymers" by Szwarc (55) as they can be preserved indefinitely and further chain growth may be induced by merely adding further amounts of monomer. As the number of polymer molecules remains the same, no further initiation taking place after the first initiation has occurred, this results in an increase in molecular weight. L'Abbe and Smets (56) showed this effect in the polymerisation of methyl methacrylate initiated by a complex of butyllithium and diethylzinc; the initiating species is \(\text{C}_4\text{H}_9\text{LiZn}(\text{C}_2\text{H}_4)^{n}\).
The graph of Fig. 7 represents the outcome of adding further monomer to the "living" poly(methylmethacrylate). The full circular points show that the average molecular weight increases with conversion; at 100% conversion the reaction stops and the viscosity average molecular weight is at a maximum, temporarily. Addition of fresh monomer increases $\overline{M}_v$ to a higher maximum; further polymer chains do not form.
1.7.2 Molecular Weight Distributions in Anionic Polymerisations

Flory in 1940 (57) showed that in a polymer formed by addition of monomer units to a fixed number of polymer molecules, the numbers of species of each size are represented by a Poisson's Law type of distribution. The paper dealt with polyethylene oxides formed by reaction of polyethylene oxide with ethylene glycol; the results, however, are applicable in anionic polymerisations where similar addition of monomer to anion occurs. In such polymers, the polydispersity ratio approaches unity (provided that the process is carried out in a batch reactor.) Thus anionic polymerisation is the method of choice for preparing polymer to a known molecular weight and with a narrow distribution of molecular weight.

In his treatment, Flory made the following assumptions:

i) The total number of molecules with propagating functional groups is constant throughout the reaction;

ii) Chains must be built up by a sequence of kinetically identical additions of monomer.

These assumptions hold equally well in the polymerisation of styrene by butyllithium.

Let $N_1, N_2, N_3$ etc be the numbers of species $M_1, M_2, M_3$ etc. possessing zero, one, two, etc added ethylene oxide molecules.

\[
\frac{d}{dt} (N_i) = -f (N_i) \quad (1.57)
\]
where \( f \) is some function dependent only on the reaction kinetics and the manner of polymerisation, and is identical for each addition (assumption (ii) above).

\( f \) will be a function of monomer concentration, time and the number of propagating molecules, and will thus include all rate constants appearing in the rate equation for the reaction. As long as the assumptions made above are satisfied, the solution of the problem does not depend on the actual nature of \( f \).

By assumption (ii), the rate of conversion of \( \text{H}_2 \rightarrow \text{M}_3 \) must be \( fN_2 \). Hence:

\[
\frac{dN_2}{dt} = fN_1 - fN_2 \tag{1.58}
\]

and

\[
\frac{dN_\alpha}{dt} = fN_{\alpha-1} - fN_\alpha \tag{1.58}
\]

The rate of disappearance of monomer is:

\[
\frac{dm}{dt} = fN^m \tag{1.59}
\]

where \( N^m \) = the number of propagating molecules.

Then the ratio at time \( t \) of monomer consumed to \( N^m \) is given by:

\[
v = \frac{\Delta m}{N^m} = \int_0^t f \, dt \tag{1.60}
\]

By the same reasoning,

\[
dv = fdt \tag{1.61}
\]
By substituting (1.61) in (1.57) and (1.58),

\[ dN_1 = -N_1 dv \]  \hspace{1cm} (1.62)  

\[ dN_x = (N_{x-1} - N_x) dv \]  \hspace{1cm} (1.63)  

Integrating (1.62) yields:

\[ N_1 = N_0 e^{-y} \]

Substituting in (1.63) with \( x=0 \), then integrating, we obtain:

\[ N_2 = N_0 v_2 e^{-y} \]

Substitution of this equation in (1.63) with \( x = 3 \) and then integrating,

\[ N_3 = N_2 \frac{v_2}{2} e^{-y} \]

Continuation yields:

\[ N_x = \frac{v^{x-1}}{N_0 (x-1)!} e^{-y} \]  \hspace{1cm} (1.64)  

This is a general expression for the mole fraction of \( x \)-mer in the wholly-formed polymer (excluding unreacted monomer) and is the formula describing a distribution of the Poisson type.

In real systems, monomer is consumed in an initiation step and polymer chains are generated at different times. Thus Flory's treatment is an approximation which becomes good if \( k_2/k_4 \) is very small, and the relationship

\[ X_n = \frac{[M]}{[I]} \]  \hspace{1cm} (1.65)  

may be used in determining the relative amounts of monomer and initiator required to form polymer with the requisite molecular weight.
Odian (58) quotes:

\[ X_{V} = 1 + X_{n} \quad (1.66) \]

\[ \frac{X_{V}}{X_{n}} = (X_{n} + 1)^{2} \]

As an alternative description of the Poisson distribution, it may be approximated by:

\[ \frac{X_{W}}{X_{n}} \approx \frac{1 + 1}{X_{n}} \quad (1.67) \]

Equation (1.67) indicates that the higher the degree of polymerisation that is pursued, the more nearly monodisperse is the distribution of the chain lengths. The G.P.C. curves in Appendix II show how well this relationship was borne out.

1.8.1 Radical Scavenging Experiments-Introduction

The process of initiation in a free-radical polymerisation is in two stages: decomposition of the initiator to furnish primary radicals, and attack of monomer molecules by these radicals, equations (1.1) and (1.2). As the decomposition stage is the slower of the two, it is rate determining, so rate of initiation equals the rate of decomposition:

\[ R_{d} = 2f k_{d}[I] = R_{i} \quad (1.5) \]

The factor \( f \) takes account of the fact that each initiator molecule undergoing homolysis is surrounded by a 'cage' of solvent molecules which prevents, to a greater or lesser degree, subsequent movement apart of the fragments. Hence some may recombine, nullifying the effect of the decomposition and leading to efficiency of initiation of less than 100%. The cage factor is then the fraction of fragments which subsequently go
onto initiate kinetic chains. In normal media, \( f \) is usually between 0.6 and 0.7. In viscous media, however, it is conceivable that egress of primary radicals from the solvent cage will be more hindered with a consequent decrease in \( f \). As the reaction media studied in this work where of extremely high viscosity, it was thought advisable to check on the value of \( f \). The method used was the radical-scavenging technique adopted by Brooks (37) with minor adaptations to the equipment (detailed in 2.4.7).

1.8.2 Radical Scavenging Experiments—Theory

The initiator decomposes with rate given by:

\[
\frac{d [I]}{dt} = k_d [I] \tag{1.68}
\]

Where \( k_d \) = rate coefficient for dissociation;

and \( [I] \) = the instantaneous concentration of the initiator.

The decomposition gives rise to free radicals which are reacted as soon as they leave the solvent cage with the material diphenylpicrylhydrazyl, dpph. This substance is an extremely efficient reactor with other free radicals; 100% reaction may be assumed. Moreover, dpph is very highly coloured; as it reacts the colour disappears so the concentration of dpph is easily monitored.

As one dpph molecule can react with two initiator fragments, the proportion of primary radicals leaving the solvent cage is given by:

\[
f = \frac{1}{2} \left( \frac{d [I]}{dt} \right) \left( \frac{d [dpph]}{dt} \right)^{-1} \tag{1.69}
\]
Hence by plotting the decrease in \( [dpph] \) and drawing a tangent to the graph at \( t = 0 \), when \( [I] \) is known with certainty, the instantaneous value of \( f \) may be calculated.
2.1 Introduction

The experiments carried out in this work were to investigate:

i) Relationships between the density and viscosity of solutions of polystyrene of different molecular weights and concentrations in styrene;
ii) The effects of pre-formed and dissolved polystyrene on the kinetics of polymerisation;
iii) Relationships amongst these effects in terms of either the absolute viscosity of the reaction medium or the volume fraction of polymer already present; and the molecular weight of the 'host' polymer;
iv) Possible models for the mechanisms of the termination step and the propagation step in free-radical polymerisation of styrene at high levels of conversion.

In order to achieve these objectives, styrene polymerised by anionic initiation ('host polymer') was dissolved to the required level in pure styrene monomer (the anionic method was used as it enables polymer of a required Mn to be prepared easily and quickly, with a narrow molecular weight distribution). Such solutions (experimental material) were made up in duplicate with inhibited and non-inhibited styrene. The former solutions were used in density and viscosity measurements at 50°C, the reaction temperature. At this temperature, it is possible that thermal polymerisation could have a significant effect on the solution's
composition before measurement of the property was completed. The presence of inhibitor would prevent this and therefore its effects on solution density and viscosity were considered negligible. Of course, kinetic experiments ('runs') were carried out using solutions made with uninhibited styrene.

The samples of anionically-polymerised styrene were not assumed to have the molecular weight calculated beforehand and targeted. For a variety of reasons (impurities on the inner surfaces of the reactor vessels, initiator loss by spray as it was introduced, errors in measurement) it was considered sensible to determine the molecular weight of each sample after preparation. The method used for this determination was solution viscometry measurement; although not an absolute method, it has the advantages of speed and straightforwardness.

By these means, analogues were produced which correspond to well characterised, highly-polymerised bulk systems.

Accurate and precise volumes of about 20cm³ were polymerised in a specially designed dilatometer using azobisisobutyronitrile (AIBN) as the initiator. The volume change with time was converted, using the previously-determined density measurements, to a change in monomer concentration with time. Monomer depletion curves were drawn up and the tangent at zero time then furnished a figure for the initial rate of polymerisation. This figure represents an instantaneous rate at a moment when the environment of the reaction is well-characterised - the solution viscosity, volume fraction of polymer present, concentrations of initiator and monomer are all known and
complications due to the formation of uncharacterised polymer may safely be ignored.

2.2 Materials

2.2.1 Monomer

Styrene supplied by Fisons (Loughborough) was inhibited for storage purposes with p-tertiarylutylcatechol (10-15ppm):

\[
\begin{array}{c}
\text{OH} \\
\text{C(CH₃)₃} \\
\end{array}
\]

Destabilisation of the monomer was achieved by distillation under reduced pressure. At a pressure of 125 mm Hg (obtained by use of a filter-pump) the styrene evaporated at an appreciable rate at around 40°C. The alternative method of destabilisation whereby the inhibitor is removed by reaction with sodium hydroxide solution and the monomer then subjected to vacuum distillation, was not employed. The danger here is that water, of lower boiling point than that of styrene (426.2K), may collect in the distillate. Although this may only have conferred an induction period in subsequent free-radical polymerisation, it would have been disastrous in anionic polymerisation used to prepare host polymer. This polymer, of course, had also to be free of inhibitor so as to allow polymerisation of the experimental material.

At the temperature and vacuum level specified, it took about 2 hours to collect 1dm³ of destabilised monomer in batches of ca 200cm³. The first
few cm³ of each distillate were discarded in order to 'flush out' the glassware and get rid of any impurities borne with the styrene vapour such as low boiling point liquids.

The destabilised styrene was subsequently purged and saturated with nitrogen gas (oxygen-free) and stored in 250cm³ reagent bottles. The headspace was filled with nitrogen gas and they were stored in sealed polythene bags at -35°C until required. The bags were used to prevent ingress of condensed water vapour from the atmosphere into the bottle/stopper joint when the styrene was removed from the freezer.

2.2.2 **Anionic Initiator**
n- butyllithium was selected to initiate the polymerisation in preparation of host polymer. It was supplied by the Chemistry Department at Loughborough University as a solution in hexane (15% M/v). Standardisation was carried out by titration according to the method of Gilman and Haubein (61).

2.2.3 **Free-Radical Initiator**
Azobisisobutyronitrile (AIBN) (ex. B.D.H.) was recrystallised from methanol at low temperature and stored under nitrogen at the same low temperature as the purified monomer (-35°C). A saturated solution of AIBN was made up at room temperature then left overnight at -35°C. The supernatant was then decanted off, and the needle-shaped crystals of AIBN filtered at the pump and washed with small portions of cold ethanol.

2.2.4 **Solvents and Precipitant**
Toluene (Fison's) SLR grade used as received.
Benzene (Fison's) SLR grade - stored over sodium wire.
Methanol (Fison's) SLR grade - used as received.
Methanol was added to a sample of destabilised styrene each time the latter was used to see if any polystyrene could be precipitated. Such an eventuality would imply that slow reaction had occurred in the freezer. If a precipitate was induced, the batch of styrene was discarded and a further quantity destabilised.

Ethylbenzene (Fison's) SLR grade - distilled under reduced pressure and purged with nitrogen.

2.2.5 Miscellaneous

Nitrogen, used for purging, filling headspaces, and flushing the dilatometer prior to use, was B.O.C. high-purity gas.

Chloroform and acetone, used for general cleaning purposes, were S.L.R. grade. In the case of obstinate deposits in capillaries or glassware, chromic acid was deployed. It was prepared from SLR sulphuric acid and SLR potassium dichromate.

Diphenylpicrylhydrazyl - DPPH - used in the radical scavenging experiments, was supplied by B.D.H. and used as supplied.

2.3 Apparatus

2.3.1 Thermostat Bath

Measurements of the density and viscosity of the experimental material were made at the temperature selected for the kinetic experiments, viz 50°C.
Measurements of the intrinsic viscosities of the host polymers were made at 25°C, for which temperature the correct Mark-Houwink constants for the type of polymer and method of polymerisation were available. All these measurements were carried out in a Townson and Mercer "Bridge Control Series III" thermostatted water bath, accurate to ± 0.01°C.

2.3.2 Density Measurement

In order to interpret the data from dilatometry and as an essential parameter in the calculation of viscosity, the densities of the various experimental materials were required. A density bottle was designed and made for this study:

![Diagram of density bottle](image)

**Fig 2.1**

The capillaries of the standard type of specific gravity bottle or pycnometer were too narrow-bore for even the least viscous solution to flow through. Moreover, the necks of the standard apparatus were too narrow to pour the experimental material through. Figure 2.1 shows how these problems were overcome. The stopper comprises a through-cone ("Quickfit") in which a length of glass tubing (4mm bore), with flared ends, has been inserted and fixed. The flared ends were joined to the ends of the cone, as shown in fig 2.1.
The "bottle" part of the instrument was a test-tube with its base flattened. A "Quickfit" socket of the appropriate size was attached to the tube, ensuring a tight seal with the stopper through which no material could leak.

2.3.3 Viscosity Measurement

It was essential to determine the viscosity of each solution of host polymer in styrene at the reaction temperature, 50°C, over the range of concentrations studied. The Haake "Rotovisco" Rotary Viscometer was tried originally, but all the solutions were very pseudoplastic and temperature control with the cone and plate (the only sensing head appropriate for the high viscosities) was very poor. Hence two other methods were used:

i) A falling-ball in conjunction with Stokes' Law, giving zero-shear values for the viscosity;

ii) Capillary viscometry for solutions through which the ball fell too quickly for accurate timings to be recorded. This method also gives a zero-shear value.

2.3.3.1 Falling-ball Viscometry

A test-tube was used for this, with a scale fixed to it on which were two marks 8.19mm apart (measured by travelling microscope), 3cm below the level to which the tube was filled. To it was attached a "Quickfit" cone in which would fit the stopper of the density bottle. This then became the "aimer" for the ball-bearing. The ball-bearings used were of 0.992mm diameter; they were all measured individually with a micrometer and were washed with toluene, chloroform and methanol before and after use.
2.3.3.2 Capillary Viscometry

Capillary viscometers of the suspended-level or Ubbelohde type were used in determination of the absolute viscosities of some of the experimental materials and also for determination of the intrinsic viscosities of the host polymers. The latter ones were narrow-bored with nominal constants of 0.001 cS sec\(^{-1}\) and the former had wider bores, from 3 cS sec\(^{-1}\) to 30 cS sec\(^{-1}\).

2.3.4 Dilatometers

Measurement of volume contraction during polymerisation was carried out with a specially designed dilatometer (2.4.6). The apparatus was all-glass with the exception of the stainless steel insert.

2.3.5 Rotary Evaporator

The Buchi model Rotavapor-R was used for reduced-pressure distillation of monomer and ethylbenzene. A small water-bath equipped with a Julabo “Paratherm II” impeller-heater was used to control the temperature of the material to be distilled.

2.3.6 Grinder

The Waring “Industrial Blender” was used to pulverise the host polymer after drying.

2.3.7 Vacuum Oven

The oven used to dry the host polymer was made by Townson and Mercer.
2.3.8 **Spectrophotometer**

Used in radical scavenging experiments; Pye Unicam model.

2.4 **Procedures**

2.4.1 **Preparation of Host Polymer**

This was carried out in the apparatus shown in Figure 2.2:

![Diagram](image)

The five necked reaction vessel (Capacity: 1dm³) was charged with a mixture of styrene (100g) and benzene (140cm³). The styrene was taken from the freezer at least three hours prior to use so that no water vapour contaminated it by condensation. The mixture of liquids was stirred for 20 minutes with a nitrogen bleed to purge any oxygen in the benzene. Initiator was drawn up into a syringe in the quantity I calculated by:

\[
M_n = S : I = S \\
- I M_n
\]  

(2.1)

Where \(M_n\) = desired number-average molecular weight
S = amount of styrene present
I = amount of initiator required
(both quantities in moles).

The theory of the molecular weight distribution obtained in the reaction is
dealt with above (1.7.1 and 1.7.2). The initiator was stored in a dark
bottle equipped with a self-sealing rubber stopper. To ease withdrawal of
the aliquot, the same volume of nitrogen was first injected. The initiator
solution was then injected speedily into the reaction mixture via the self-
sealing rubber septum, to ensure that initiation was as nearly
instantaneous as possible. During the injection period the speed of the
stirrer was increased from 300 rpm to 800 rpm to induce turbulence and thus
enhance the mixing process. The rapid appearance of the dark orange colour
of the polystyryl anion signified successful initiation; if this did not
appear, the preparation was abandoned as impurity, probably water, would
have been present. To avoid this happening as far as possible, all the
glassware was flamed and flushed with nitrogen to desorb as many water
molecules as possible. As the reaction proceeded, the temperature rose and
the viscosity increased until at about 45°C, rapid heat build-up threatened
thermal runaway. At this stage, ice was placed in the water in the
dessicator bowl. Even so, the benzene would still boil; but the reaction
mixture would then cool. Its viscosity was lowered by the addition of more
benzene, thus making it easier to stir in water (distilled, 10cm³) to
terminate the kinetic chains followed by methanol (150cm³) to precipitate
the polymer. The excess liquid was then poured away and the remaining soft
mass of polystyrene, with its occluded liquid, was transferred to a large
everating basin. The mass was dried out at 90°C in a vacuum oven
working at 150 mmHg pressure during which period the mass foamed up to
resemble meringue or expanded polystyrene ceiling-tiles depending on the molecular weight of the polystyrene. The blocks were broken up roughly by hand and dried further, then ground to powder with an industrial blender and further dried until benzene and monomer were no longer detectable.

The molecular weight of each sample was determined as outlined in the next section, and production runs whose molecular weights were within 2% of the value required were mixed. Equal masses of the components were mixed, and the weight average of their molecular weights taken to be the molecular weight of the resulting host polymer.

2.4.2 Solution Viscometry for $M_w$ determination

Assuming that the densities are equal, the ratio of flowtimes for a polymer solution and that of the pure solvent in the same capillary is equal to the ratio of their viscosities. In dilute solution, the assumption is justified, and so:

$$\eta = \frac{t}{\eta_0}$$

Where $t = \text{flow-time}$

$\eta = \text{viscosity}$

subscript 0 implies a value for pure solvent and no subscript implies a value for the solution.

Hence solutions of between 0.7%v/v and 1.2%v/v were prepared, made up of host polymer dissolved in toluene. Their flow-times were measured in an Ubbelohde viscometer with nominal constant equal to 0.001 cS sec^-1; this viscometer exhibited a flow-time for pure toluene of about 62-69 seconds. This was considered sufficiently accurate as the timing was done with a
digital stopwatch reading to 1/100 sec. The calculations were carried out as follows:

Relative Viscosity \[ \eta_{\infty} = \frac{t}{t_0} \] (2.3)

Specific Viscosity \[ \eta_{sp} = \eta_{\infty} - 1 \] (2.4)

This quantity represents the contribution of the polymer molecules to the solution viscosity. To assess the contribution of one molecule, the reduced quantity \[ \eta_{sp}/C \] is calculated for each concentration. A plot of \[ \eta_{sp}/C \] vs. \[ C \] then yields, by extrapolation to \[ C = 0 \], the intrinsic viscosity \[ [\eta] \]:

\[ \eta_{sp}/C \]

\[ \ln (\eta_{\infty}) \]

\[ \ln (\eta_{\infty}) \]

\[ \frac{\eta_{sp}}{C} \]

\[ C \]

From equation 2.4,

\[ \eta_{sp} + 1 = \eta_{\infty} \]

\[ \therefore \ln \eta_{\infty} = \ln (\eta_{sp} + 1) \]

\[ = \eta_{sp} - \eta_{sp}^2/2 + \ldots \] (neglecting higher terms)

Hence the intrinsic viscosity is also given by:

\[ [\eta] = \frac{(\ln \eta_{\infty})}{C} \] (2.5)

\[ C=0 \]
providing a method of checking on the value of \([\gamma]\) deduced by the previous method, based on equation (2.4). The intrinsic viscosity is related to the viscosity-average molecular weight, \(M_v\) by the Mark-Houwink equation:

\[
[\gamma] = K M_v^\alpha
\]

where \(K\) and \(\alpha\) are the Mark-Houwink constants.

For solutions of anionically-polymerised styrene in toluene at 25°C, (viz, narrow molecular weight distribution samples),

\[
\begin{align*}
K &= 34.5 \times 10^{-6} \text{ dl g}^{-1} \\
\alpha &= 0.62 \quad \text{Ref 63}
\end{align*}
\]

giving the molecular weight as:

\[
\bar{M}_v = \left( \frac{[\gamma]}{34.5 \times 10^{-6}} \right)^{1/0.62}
\]

2.4.3 Production of Host Polymer Solutions

This was extremely time-consuming. As much polystyrene as possible was dissolved in styrene, consistent with the resulting solution being pourable. In practice, this placed an upper limit on the polystyrene concentration of between 55% and 60% by mass, depending on the molecular weight of the host polymer. Although it is possible to produce a solution whose concentration tends to 100% – polymers and their corresponding monomers are thermodynamically compatible to this level – it became progressively more difficult to incorporate polymer as the concentration rose. Thus nature set an effective upper limit on the conversion level up to which the present study applies. There were two other major problems involved in manipulation of solutions of this type:
1) The 'pouring stream' of about 1.5cm thickness, from which the solvent flashed away, leaving a 'skin' on the outside and practically immobilising the stream. The solutions were therefore handled in a polyethylene bag with a few drops of styrene therein. By this means, the space in the bag was filled with styrene vapour and the tendency for the skin to form was substantially reduced.

ii) Solution of the initiator to produce uniformly distributed solutions was not easy. The difficulty involved was overcome by pre-dissolving the calculated amount of AIBN in a little of the monomer used in the anionic polymerisations. This solution was then incorporated in the experimental material by the device of a spinning glass rod. An ordinary glass stirring rod was secured in the chuck of a stirrer motor, and this was lowered into the beaker containing the experimental material on which, due to the vastly differing viscosities, floated the initiator/styrene solution. The resulting vortex gradually caused dispersion of the one liquid in the other, but slowly. It was felt that slow mixing, although inefficient in time, was preferable to turbulent, which would have entailed degassing of entrained air with consequent problems of compositional inexactitude.

The solutions of host polymer were prepared by addition of polystyrene in small amounts (Ca 20g) to styrene (prepared specially as detailed above) in a flask shaker initially. When the solution became too viscous for the shaker to be effective, the bottle (250cm³ size) was transferred to a ball-mill running at low speed. In this way it took between 4 and 7 days to produce a solution free of gel and bubbles of gas. The 'stock' solution thus formed was diluted down with stabilised or destabilised styrene as
necessary to provide solutions for density and viscosity measurement or for kinetic runs.

2.4.4 Measurement of Density

The bottle shown in Figure 2.1 was calibrated for volume with distilled water, boiled and cooled to eliminate dissolved gases. The shape of the meniscus at the top of the 'capillary' was found to be the same as that of the host polymer solutions at 50°C. Density tables for water (Ref 64) furnished the volume of the bottle and a simple calculation based on the masses of the bottle when empty and when full of host polymer solution at 50°C gave the solution's density.

2.4.5.1 Falling-ball Viscometry

For a sphere falling through an infinite medium, Stoke's law gives the terminal velocity as:

\[ V = \frac{2 g r^2 (\rho_1 - \rho_2)}{9 \eta} \]  

(2.8)

Where

- \( V \) = terminal velocity,
- \( g \) = acceleration due to gravity,
- \( \eta \) = viscosity of the medium,
- \( \rho_1 \) = density of the sphere,
- \( \rho_2 \) = density of the medium

Rearranging equation (2.8) gives:

\[ \eta = \frac{2 g r^2 (\rho_1 - \rho_2)}{9 V} \]  

(2.9)

The apparatus described in 2.3.3.1 was clamped perpendicular in the thermostat bath using two plumb-lines. Twenty minutes temperature
equilibration was allowed with the aiming-hole bunged to prevent evaporation. A ball-bearing was dropped into the viscosity solution via the aimer. It would probably have attained terminal velocity immediately after breaking the surface of the solution, but the fall of 3cm before passing the marks ensured that this speed was attained. Ten balls were dropped to provide a good mean figure for time elapsed on passage between the marks. Inserting the following values into equation 2.9, we obtain for the viscosity:

$$\eta = 2.620 \times 10^{-4} t \left(7.990 \times 10^{3} - \rho^2\right)$$

with

- $g = 9.813 \text{ ms}^{-2}$
- $r = 0.992 \times 10^{-2} \text{m}$
- $\rho_i = 7.990 \times 10^{3} \text{kgm}^{-3}$
- $t =$ mean timing to pass between the marks, whence $V$ can be eliminated from 2.9 using

$$V = \frac{8.190 \times 10^{-3}}{t} \text{ ms}^{-1}$$

The value of viscosity so obtained is in the SI. unit of pascal seconds, and was the zero shear value. This method of determining viscosity eliminates the need for extrapolation to zero-shear of a viscosity/shear rate graph, were such a graph obtainable. It wasn't, for the reasons outlined in 2.3.3. No corrections to Stoke's law were required as the sphere diameter was less than 1/10 that of the viscometer tube.

2.4.5.2 Capillary Viscometry

Where necessary, because of very short fall-times, the viscosities of lower-concentration solutions were measured in a wide-bore Ubbelohde
viscometer. Various ones were used; the manufacturer's own calibration
certificates were available for some of them. Others, used to give a
reasonable flow-time, had to be calibrated. Solutions of sucrose (dried in
the vacuum oven to constant mass) were used immediately after preparation
as sucrose solutions are hygroscopic. There is a table of viscosities of
sucrose solutions in the "Handbook of Chemistry and Physics" (66).

2.4.6.1 Dilatometry

A dilatometer was designed and constructed especially for this study.
Dilatometry was selected as the technique for following the reaction rather
than the withdrawal of aliquots followed by precipitation and subsequent
gravimetric analysis. The latter technique is not truly differential and
suffers from the disadvantage that aliquots of very viscous media would
have been difficult to withdraw, cool quickly, dilute and precipitate. It
was intended to use dilatometers designed by Brooks (figs 2.3 and 2.4):

![Fig 2.3](Spiral Dilatometer)
![Fig 2.4](Annular Dilatometer)

These were originally designed to be filled with the aid of a vacuum or by
gravity but the highest vacuum available in the laboratory would not pull
the experimental material of this study into the tubing. With the
relatively low polystyrene concentrations used originally in these
dilatometers, the fluid could be allowed into the capillary in which it
would flow and could be washed out easily. The solutions in the present
investigation however would not flow in a capillary and it proved
impossible to wash out a capillary once it was contaminated. Thus, the new
design had to fulfil the following criteria:

1) It must be amenable to introduction of high viscosity solutions;
2) It must effect good heat transfer from the water in the thermostat
bath to the centre of the reaction material;
3) Polymerising fluid must not enter the capillary.

With these goals in mind, the new dilatometer was constructed as shown in
Fig 2.5. In this dilatometer, the polymerising fluid floats on the
mercury. As the reaction progresses, the fluid decreases in volume and
pulls the mercury with it. Hence the mercury meniscus travels down the
capillary which is fitted with a half-millimetre scale, and there is no
danger of polymer solution entering the capillary. The large mass of
mercury aids heat transfer. The stainless steel insert causes the
thickness of polymer solution to be just 0.375mm, so heat transfer from the
outside inwards is very good. The fluid is warmed from the inside, too, by
the insert which is in thermal equilibrium with the water in the thermostat
bath. Stainless steel was chosen for the insert instead of the more
obvious brass, copper or aluminium; this was so because the latter-named
metals may have contributed reducible ions (Cu²⁺, Al³⁺) as would iron (Fe²⁺,
Fe³⁺) or any iron-containing steel.
2.4.6.2 Filling the dilatometer

The dilatometer had a wide neck ('Quickfit' 14/23 size) to enable it to be filled by pouring. The filling procedure was as follows:

a) A small beaker (25cm³) was weighed;
b) Stock experimental medium was introduced to the 20cm³ mark;
c) The beaker was reweighed to find the mass of experimental medium;
d) The amount of destabilised styrene required to give the appropriate percentage of host polymer was calculated;
e) The density graph then gave the volume of the system to be produced in step (g);
f) The initiator was dissolved in the styrene;
g) The initiator solution was incorporated into the stock solution by a rapidly spinning glass rod (see 2.4.3). Mixing was complete when striations (called Schlieren figures) were no longer visible in the material.
h) Mercury was poured into the dilatometer to the pre-determined mercury level;
i) Nitrogen was introduced into the space above the mercury;
j) The experimental material, with initiator now incorporated, was poured on top of the mercury to the pre-determined level.
k) The insert was positioned, the polymer solution being at such a level that displacement of it filled the headspace by displacing the nitrogen. This action also pushed the mercury up the capillary to near the top.
l) The scale was attached and the apparatus clamped vertically, with the aid of two plumb lines, in the thermostat bath.
Thermal expansion caused the mercury to exude from the end of the capillary. Such care was taken to exclude oxygen that any inhibition period was subsumed in this initial expansion time. Small inhibition periods of up to three minutes were noted occasionally but as inhibition to small degrees does not affect kinetics these were ignored. The stopwatch, reading to 1/5 second (analogue) was started as soon as thermal expansion was over and readings of meniscus weight were taken every half-minute initially and then more infrequently as the reaction slowed down. The monomer depletion curve was plotted roughly as the experiment proceeded to check that all was going well. The experiment was stopped when sufficient points had been obtained to give a good curve.

2.4.7 Radical Scavenging Experiments—Procedure

A series of standard solutions of dpph in ethylbenzene was made up and used to calibrate the spectrophotometer. Ethylbenzene was used as literature values of $\lambda_{\text{max}}$ of dpph in this solvent were easily available and the molecule bears a basic similarity to that of styrene. The calibration solutions were placed in the same soda-glass test-tube (1cm x 6cm) that was to serve as the reaction vessel; this tube was so marked that it could always be placed in the spectrophotometer in the same orientation. A solution of the highest molecular weight host polymer was made up in ethylbenzene, with a slightly higher viscosity than the most viscous solution used in the kinetic runs.

The correct amount of solvent required to lower the viscosity was calculated and the appropriate amounts of AIBN and dpph were dissolved in this. It was then incorporated into the host polymer/ethylbenzene solution.
by the spinning rod technique. The reaction mixture was then introduced into the soda-glass tube in a nitrogen atmosphere in order to exclude oxygen. A bung fitted with a small gas syringe was then inserted. This arrangement allowed expansion and contraction of the contents with the temperature differential. (see Fig 2.5)

The reactor was then immersed in the thermostat bath at 50°C for five minutes to allow the contents to heat up. After this time, the stopwatch was started and the reactor cooled by immersion in a salt/water/ice mixture for 20 seconds. The concentration of dpph was measured in the spectrophotometer as quickly as possible and the reactor returned to the thermostat bath for another five minutes. This procedure was repeated until the concentration of dpph was zero. A graph was then plotted (Graph 30) of dpph versus time which proved to be a smooth curve. The technique detailed in §2 was then applied to determine the initiator efficiency, f.

Fig 2.6
CHAPTER 3: RESULTS TABLES

This section contains all derived results: experimental data for each kinetic run are to be found in Appendix III. Sample calculations for initial rates and the parameters derived therefrom are in Appendix IV. The contents are:

Table 3.1. : $k_p$ and $k_t$ for all polymerisations derived from initial tangent slopes of graphs 1 - 16;

Table 3.2.1: Spectrophotometer calibration data from which graph 29 was plotted;

Table 3.2.2: Radical scavenging data from which graph 30 was plotted;

Tables 3.3.1: Solution viscosity data leading to graphs 23 - 26a;

Tables 3.3.2: Tables of kinetic parameters: initial rate of polymerisation, $R_p$; and reduced kinetic ratio, $\gamma$, equal to $k_p \cdot k_t^{-1}/k_{p}^{2} k_{t}^{2}$.

N.B. i) Repeat trials were carried out if any factor (such as extended induction period) led to doubt in validity of an experiment;

ii) The same results were obtained when any trial was repeated.
## Results Table: derived $k_\alpha$ and $k_\beta$ for all Polymerisations

<table>
<thead>
<tr>
<th>Ref</th>
<th>$\log\eta/\text{PaS}$</th>
<th>$\phi$</th>
<th>$\psi$</th>
<th>$k_{\beta}X$</th>
<th>$k_{\alpha}X/10^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
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<td>1.4</td>
<td>-0.590</td>
<td>0.365</td>
<td>3.82</td>
<td>357.08</td>
<td>16.68</td>
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<td>0.412</td>
<td>22.23</td>
<td>861.41</td>
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<td>0.461</td>
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<td>1.96</td>
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<td>0.516</td>
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<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
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<td>1.12</td>
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<td>78.89</td>
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<td>0.670</td>
<td>0.455</td>
<td>776.25</td>
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<td>3.6</td>
<td>0.960</td>
<td>0.505</td>
<td>1081.43</td>
<td>6008.11</td>
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* $X = 1 \text{ mol dm}^{-3} \text{sec}^{-1}$
3.2.1 Experimental Data: Spectrophotometer Calibration

<table>
<thead>
<tr>
<th>[d.p.p.h.l] $10^{-4}$mol dm$^{-3}$</th>
<th>absorbance arbitrary units</th>
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<tr>
<td>0.17</td>
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<td>0.43</td>
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<td>0.86</td>
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<td>1.29</td>
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<td>1.72</td>
<td>0.70</td>
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<td>2.15</td>
<td>0.88</td>
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<tr>
<td>2.58</td>
<td>1.04</td>
</tr>
<tr>
<td>3.03</td>
<td>1.21</td>
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<tr>
<td>3.44</td>
<td>1.35</td>
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</table>
3.2.2 Experimental Data: Radical Scavenging Experiment

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<th>time (minutes)</th>
<th>absorbance (arbitrary units)</th>
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</tr>
<tr>
<td>90</td>
<td>0.14</td>
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</table>
3.3.1 Results Table: Solution Viscosity Data for all Host Polymers

<table>
<thead>
<tr>
<th></th>
<th>PS 1</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[PS]/%</td>
<td>log[PS]</td>
<td>η/PaS</td>
<td>logη/PaS</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.20</td>
<td>1.547</td>
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<td>45.09</td>
<td>1.654</td>
<td>0.467</td>
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<td>1.701</td>
<td>0.877</td>
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<td>54.76</td>
<td>1.738</td>
<td>1.654</td>
<td>0.219</td>
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<tr>
<td>59.60</td>
<td>1.775</td>
<td>3.395</td>
<td>0.531</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>PS 2</th>
<th></th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>[PS]/%</td>
<td>log[PS]</td>
<td>η/PaS</td>
<td>logη/PaS</td>
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</tr>
<tr>
<td>20.8</td>
<td>1.317</td>
<td>0.103</td>
<td>-0.987</td>
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</tr>
<tr>
<td>29.73</td>
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<tr>
<td>34.88</td>
<td>1.543</td>
<td>0.623</td>
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<td>38.02</td>
<td>1.580</td>
<td>0.896</td>
<td>-0.048</td>
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</tr>
<tr>
<td>47.40</td>
<td>1.656</td>
<td>3.388</td>
<td>0.53</td>
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3.3.2 Results Table: Kinetic Parameters for Host Polymer PS1 
($M_w=15,100$)

<table>
<thead>
<tr>
<th>Ref</th>
<th>[PS]/%</th>
<th>$\phi$</th>
<th>log$\gamma$/PaS</th>
<th>$R_p/10^{-4}$</th>
<th>log$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-5</td>
<td>35.0</td>
<td>0.318</td>
<td>-0.820</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1-4</td>
<td>40.0</td>
<td>0.365</td>
<td>-0.590</td>
<td>0.667</td>
<td>0.582</td>
</tr>
<tr>
<td>1-3</td>
<td>45.0</td>
<td>0.412</td>
<td>-0.345</td>
<td>1.500</td>
<td>1.347</td>
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<tr>
<td>1-2</td>
<td>50.0</td>
<td>0.461</td>
<td>-0.070</td>
<td>1.667</td>
<td>1.512</td>
</tr>
<tr>
<td>1-1</td>
<td>55.0</td>
<td>0.516</td>
<td>0.230</td>
<td>5.000</td>
<td>2.546</td>
</tr>
<tr>
<td>1-6</td>
<td>59.5</td>
<td>0.556</td>
<td>0.530</td>
<td>6.667</td>
<td>2.891</td>
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</table>

$M = 1 \text{ mol dm}^{-3}\text{sec}^{-1}$

$\gamma = k_0^*k_1/\gamma_0^*k_1^*$ ...

Data for PS4 are omitted because

(i) PS3 and PS4 are indistinguishable from a density/volume fraction point of view (graph 26)

(ii) It became apparent as the work progressed that results with PS4 did not conform easily with results from the other host polymers.
### Results Table: Kinetic Parameters for Host Polymer PS2

\( M = 1 \text{ mol dm}^{-3}\text{sec}^{-1} \)

\[ \gamma = \frac{k_p}{k_t} \frac{k}{k_{p,t}} \]

<table>
<thead>
<tr>
<th>Ref</th>
<th>[PS]%</th>
<th>( \phi )</th>
<th>( \log \eta /PaS )</th>
<th>( Rp /10^{-4}M )</th>
<th>( \log \gamma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>37.4</td>
<td>0.334</td>
<td>0.635</td>
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<td>2-2</td>
<td>40.1</td>
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<td>0.820</td>
<td>0.833</td>
<td>0.762</td>
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<tr>
<td>2-3</td>
<td>44.9</td>
<td>0.405</td>
<td>1.190</td>
<td>1.884</td>
<td>1.434</td>
</tr>
<tr>
<td>2-4</td>
<td>49.8</td>
<td>0.453</td>
<td>1.545</td>
<td>5.000</td>
<td>2.453</td>
</tr>
<tr>
<td>2-5</td>
<td>54.6</td>
<td>0.500</td>
<td>1.895</td>
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</table>

### Results Table: Kinetic Parameters for Host Polymer PS3

\( M = 38,500 \)

\[ \gamma = \frac{k_p}{k_t} \frac{k}{k_{p,t}} \]

<table>
<thead>
<tr>
<th>Ref</th>
<th>[PS]%</th>
<th>( \phi )</th>
<th>( \log \eta /PaS )</th>
<th>( Rp /10^{-4}M )</th>
<th>( \log \gamma )</th>
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</thead>
<tbody>
<tr>
<td>3-5</td>
<td>30.0</td>
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<td>0.417</td>
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<td>34.2</td>
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<td>3-6</td>
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<td>9.167</td>
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</table>

\[ \gamma = \frac{k_p^2}{k_t} \frac{k}{k_{p,t}} \]

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4.1.2.1 Solution Viscosity/Molecular Weight

Graph number 26 shows the relationship between solution viscosity and molecular weight on a log - log plot. Three features are immediately apparent:

1. The viscosity/concentration dependence is anomalous for host polymer PS4 in relation to that of the other three;
2. For PS1, PS2 and PS3, log (viscosity) is strongly dependent on log (concentration); all the lines having very steep, positive gradients;
3. A solution of given log (concentration) is more viscous the higher the molecular weight of the host polymer concerned, remembering the following:

<table>
<thead>
<tr>
<th>Host Polymer</th>
<th>Molecular Weight</th>
</tr>
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<tbody>
<tr>
<td>PS1</td>
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</tr>
<tr>
<td>PS2</td>
<td>126,000</td>
</tr>
<tr>
<td>PS3</td>
<td>38,500</td>
</tr>
<tr>
<td>PS4</td>
<td>60,000</td>
</tr>
</tbody>
</table>

4.1.2.2 Anomalous Behaviour of PS4

If this particular host polymer followed the general trend, its graph of log (viscosity) versus log (concentration) would lie somewhere (possibly midway) between those of PS1 and PS2. In addition to demonstrating that
PS4 solutions are apparently more viscous than those of PS2, with double the molecular weight, the co-efficient $d\gamma/d[\text{PS}]$ is also lower. Had not the point (1.741, 1.971) been measured, it would be tempting to surmise that the lines follow this pattern:

![Graph showing viscosity vs concentration for PS1, PS2, PS3, and PS4](Image)

Fig 4.1

(the dotted line represents the concentration beyond which the graphs are extrapolated.)

Such a variation of viscosity with concentration at such high regimes of viscosity is not dealt with in the literature, although there have been reports of $log \gamma$ vs $log$ (concentration) for a number of polymers at lower concentrations (31). Such relationships generally show a smooth increase linearly with an increase in gradient at the critical concentration (if reached).
4.1.2.3 Concentration/Viscosity Relationships

The curves are of a shape which may be treated in the following manner to yield a value for critical concentration of polymer, the parameter used by Cardenas and O'Driscoll (31) to which they assigned the symbol c*. Either side of the approximate C*, tangents are drawn to the curve. The points at which the tangents are drawn are those where the curve appears to become linear. Informed judgement on tangents is frequently used. Precision is difficult but work of others suggests that the current work is carried out in regions of entanglement where Kc and c* have significance.

\[ \log \eta \]

\[ \log [\text{PS}] \]

The following values of critical concentration for each host polymer are obtained:

<table>
<thead>
<tr>
<th>PS</th>
<th>M_ν</th>
<th>C*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15,100</td>
<td>1.68</td>
</tr>
<tr>
<td>3</td>
<td>38,500</td>
<td>1.57</td>
</tr>
<tr>
<td>4</td>
<td>60,000</td>
<td>1.65</td>
</tr>
<tr>
<td>2</td>
<td>120,000</td>
<td>1.55</td>
</tr>
</tbody>
</table>
With the exception of PS4 whose graph seems anomalous anyway, these values of \( C^* \) show the expected variation. Namely, the critical concentration exhibits a monotonic decrease as polymer chain length increases. If, as Cardenas and O'Driscoll have claimed, this is due to chain entanglements and polymer-polymer interactions becoming significant, the result is sensible. Naturally, the longer is the molecule the greater is the number of ways in which it may interact with its nearest neighbours. Hence these interactions become entropically favoured and \( C^* \) decreases.

4.2.1.1 Diffusion Effects on Propagation and Termination - Introduction

Using equation 1.14 and re-arranging it, an expression linking the rate coefficients for propagation and termination may be obtained:

\[
Rp = kp \left[ N \left( \frac{2fk_d[I]}{k_t} \right)^{1/2} \right]
\]

\[
\frac{k_p^2}{k_t} = \frac{n_p^2}{2[M]^{2fk_d[I]}}
\]

As it is necessary to execute non-stationary-state experiments in order to separate \( k_t \) and \( k_p \), and such trials were not carried out in this study, the ratio \( k_p^2/k_t \) has the status of being the only kinetic parameter which can be discussed here. In order to assess diffusion control in terms of this ratio, it is important to have a value with which it may be compared. The obvious choice for this standard parameter is the ratio \( k_p^2/k_t \) in the absence of diffusion control. The Polymer Handbook (49) includes an Arrhenius plot from which \( kp \) and \( k_t \) can be determined: a regression line is
drawn on the plot. This was felt to give the "best values" as the scatter of data on \( k_\alpha \) and \( k_\beta \) in the literature is so wide. Using the values of the coefficients at 50°C:

\[
k_\alpha = 6.37 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}
\]

and

\[
k_\beta = 182 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}
\]
gives value of \( k_\alpha^2/k_\beta = 5.2 \times 10^{-4} \). This is written \( k_\alpha^2/\alpha k_\beta \) and leads directly to the REDUCED KINETIC RATIO, psi, which is a dimensionless quantity:

\[
y = \frac{k_\alpha^2}{k_\beta^2} \frac{k_\beta}{\alpha k_\alpha^2} (4.2)
\]

Values of this parameter are tabulated and plotted in Chapter 3.

With the proviso above, that this study is carried out on the kinetics during the stationary state, it is possible nevertheless to assess viscosity effects on \( k_\alpha \) and \( k_\beta \). For:

\[
y = \frac{k_\alpha^2}{k_\beta^2} = \frac{k_\alpha}{\alpha k_\beta^2} (4.3)
\]

\[\therefore k_\alpha = (\alpha y k_\beta)^{-1/2}
\]

with \( \alpha = k_\alpha^2/\alpha k_\beta \).

Assigning numerical values to the quantities in this equation we obtain:

\[
k_\alpha = 182.7 \ y^{1/2} (4.4)
\]

with \( \alpha = 5.2 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \)

\[k_\beta = 6.37 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1}\]
This assumes that \( k_t \) is not viscosity dependent and thus remains unchanged at \( 6.37 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \) throughout the polymerisation.

To obtain an equivalent formula for \( k_t \), \( k_p \) is assumed to be invariant:

\[
k_t = k_p \alpha \psi
\]

Assigning the invariate value of \( 182 \text{ dm}^3 \text{ mol}^{-1} \text{ sec}^{-1} \) to \( k_p \) and letting \( \alpha = 5.2 \times 10^{-4} \). As before, we obtain:

\[
k_t = \frac{(182)}{5.2 \times 10^{-4}} \cdot 1 = 63.7 \times 10^5
\]

(4.5)

Tables and graphs of these data are also to be found in Chapter 3.

4.2.1.2 Relationship between Rate Coefficient for Propagation and Solution Viscosity

This section assumes that \( k_t \) is invariant (and remains constant throughout the polymerisation) in order to bear out all past work showing this to be not the case.

Graph 33 shows the relationship between these two parameters for each of the three molecular weights of polymer under consideration. It will be noted that \( k_p \), without exception, appears to increase with solution viscosity. This, however, contradicts intuitive and soundly based knowledge. The migration of monomer radicals through a viscous medium will be hindered as the radicals encounter an ever-more crowded environment.
Thus it may quite reasonably be argued that the rate coefficient for propagation will decrease with increasing system viscosity. Work by Hayden and Melville (6) on the bulk polymerisation of methyl methacrylate provided evidence for the correctness of this argument. Beyond 40% conversion, the activation energy for propagation was found to increase, causing $k_p$ to reduce. Indeed, in crosslinked gels (7,8,9,10) polymerisation was found to cease prematurely due to monomer occlusion. The present results, therefore, could be regarded as anomalous. The likeliest explanation is that the assumption made in deriving equation 4.4 is incorrect. Namely, $k_t$ does not remain constant over the range of viscosities here studied. This conclusion accords with current thought and supports the basis of this work - that the rate coefficient for termination changes throughout a polymerisation.

4.2.1.3 Relationship between Rate Coefficient for Propagation and Volume Fraction of Host Polymer

Graph 34, relating $k_p$ with volume fraction of host polymer in the reaction medium, describes a similar phenomenon viz. the rate coefficient for propagation increases with volume fraction. This would be expected on the evidence of graph 33 and the discussion of section 4.2.1.2 and can likewise be discounted by application of the same arguments.

4.2.1.4 Dependence of $k_p$ on Molecular Weight of Host Polymer

From graph 33, for a given value of solution viscosity, $k_p$ increases as the molecular weight of the host polymer decreases. As the usual correlation between solution viscosity and molecular weight has been shown to hold (graphs 23,24 and 25) at these concentrations, there is a greater volume
fraction of solute of lower molecular weight at a given viscosity. For example, at a value of $\log_{10} \kappa_{P}/\mu = 3.4$, the following apply:

<table>
<thead>
<tr>
<th>$\mu$</th>
<th>$\phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15,100</td>
<td>0.484</td>
</tr>
<tr>
<td>38,500</td>
<td>0.434</td>
</tr>
<tr>
<td>126,000</td>
<td>0.372</td>
</tr>
</tbody>
</table>

Although the invalidity of the $\kappa_P$ graphs has already been established (due to the varying value of $\kappa_P$) it is felt that the approach in this section is legitimate as no predictions of variation in $\kappa_P$ either side of $\log_{10} \kappa_P/\mu = 3.4$ are being made.

It will be noted that the concentration of polystyrene required to cause $\kappa_P$ to assume a given value reduced with increasing molecular weight. This is evidently a viscosity effect and underlines the premise that at the high viscosities studied here, $\kappa_P$ becomes viscosity-dependent and therefore diffusion-controlled.

4.2.1.5 The Form of the $\kappa_P$/Volume Fraction Graphs

Graph 34, although reflecting roughly the same trend exhibited by graph 33, has been chosen to illustrate the following speculation as the curves seem to relate more nearly to each other than those of $1/\gamma \kappa_P$ versus $\log$ (viscosity).
The form of the graphs seems to imply, were the experiments to be continued on to higher volume fractions of host polymer, that either of the two following events might occur:

i) The values for \( k_p \) "plateau out" at a level of \( \log k_p \geq 3.75 \);

ii) At the value of \( \log k_p = 3.75 \), a maximum occurs in the curves and they describe subsequently a monotonic decrease in \( k_p \) with increasing volume fraction.

Given the assertions of sections 4.2.1.2 and 4.2.1.3, it is more likely that (ii) is correct and the graphs might therefore develop the following form at even higher viscosities than studied here:

The graph of \( \log_{10} k_p/M \) vs. volume fraction for the solution of host polymer of molecular weight 126,000 reaches a maximum at a volume fraction of 0.51. This is interesting; if the curve follows the above development and is symmetrical about the maximum then it would indicate a finite value of
log_{10} k_p/M of about 3.75. As has already been shown (7-10) movement of monomer molecules in a crosslinked gel ceases and at a volume fraction of 100% the environment of the monomer molecules can be considered even less amenable to their displacement than in a gel. Thus, obtaining a value for k_p bears out the premise that assuming k_t to be invariate is incorrect.

4.2.1.6 Consideration of the Solution Properties of the Reaction Medium

The foregoing discussions highlight the necessity, in this study, to consider k_p and k_t jointly as the KINETIC RATIO. Its variation with the respect to the parameters viscosity and volume fraction of host polymer seem to be best described by comparing it with the value of k_p^2/k_t which obtains when the reaction is free of diffusion control. This value, 5.2 x 10^{-4} (calculated from values of k_p and k_t given in the Polymer Handbook (64), is divided into k_p^2/k_t calculated in each kinetic run and the quotient, the REDUCED KINETIC RATIO y, is treated as the variable on graphs 37 and 38.

Both plots show that a smooth correlation of a similar form occurs when the host polymer has a molecular weight of 15,100 or 38,500 but that this correlation breaks down possibly to be replaced by another when the host polymer's molecular weight is 126,000.

For Host Polymer m.w. = 15,100 or 38,500

Within the range of η and φ studied, the reduced kinetic ratio increases from a value of about unity (log_{10} y = 0). This accords with current
thought which holds that at low viscosities, the rate coefficients for propagation and termination are not very different from the values which would be expected when diffusion control is absent. In other words, the extent of diffusion control of the reaction increases steadily and does not, as some suggest (19, 27a, 32, 33, 40) only become significant when a certain viscosity or volume fraction is reached.

The graphs also indicate a levelling off in the value of \( \gamma \) at a value \( \log \gamma = 3.1 \). These observations are discussed more fully below.

It is likely that at some point (or over a range) between the two molecular weights, the properties of the polymer solution deviate from those observed at the lower molecular weight. If, as is more likely by intuition, the change occurs over a range of molecular weights, then the graph of \( \log \gamma \) vs \( \gamma \) including those molecular weights may look like this:

The three solid curves represent the molecular weights studied here and the dotted curves represent the hypothetical molecular weights – were they to
be studied. The proposed general pattern is obvious: the curves become less and less convex upwards until some critical molecular weight whose curve is labelled $A$ - a straight line. After this molecular weight the curves become progressively convex downwards. Such a proposition, however, requires that the curves for molecular weights greater than $A$, unless some constraint be applied, approach an abscissa in the same way that the curves before $A$ is reached level off to a plateau value.
4.3 The Fit of Current Results to Models wherein Volume Fraction describes the Course of Polymerisation

4.3.1 Introduction

Marten and Hemielec's model (27a) predicts a limiting volume fraction in the polymerisation of styrene at temperatures below 80°C. Hence the model cannot be applied to all the results in this study, as they do not all exhibit this phenomenon. Runs 1-1, 1-3, 1-4 and 1-5 are all relevant; each displays a limiting conversion.

At 100% conversion, the contents of the dilatometer used in this study would be totally polystyrene with a density of 1.050 g cm\(^{-3}\) at 50°C (assuming that density is independent of molecular weight)

\[
\Delta V = V_i - m
\]

\[
\frac{\Delta V}{1.050}
\]

where \(\Delta V\) = volume change on polymerisation;
\(V_i\) = initial volume;
\(m\) = total mass of dilatometer contents

Then the meniscus drop at 100% conversion is given by

\[
d = \frac{\Delta V}{\pi r^2}
\]  \(\text{(4.2)}\)

Where \(r\) = capillary radius
A table may thus be drawn up:

<table>
<thead>
<tr>
<th>Run</th>
<th>( V_t/\text{cm}^3 )</th>
<th>m/g</th>
<th>( \Delta V/\text{cm}^3 )</th>
<th>d/cm</th>
<th>( x_L/% )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>17.393</td>
<td>16.770</td>
<td>1.422</td>
<td>243.2</td>
<td>2.528</td>
</tr>
<tr>
<td>1-3</td>
<td>18.532</td>
<td>17.545</td>
<td>1.822</td>
<td>311.6</td>
<td>2.439</td>
</tr>
<tr>
<td>1-4</td>
<td>19.363</td>
<td>18.162</td>
<td>2.066</td>
<td>353.4</td>
<td>2.165</td>
</tr>
<tr>
<td>1-5</td>
<td>18.039</td>
<td>16.764</td>
<td>2.070</td>
<td>354.0</td>
<td>1.511</td>
</tr>
</tbody>
</table>

\( x_L \), the Limiting Conversion is calculated by:

\[
\frac{h_1 - h_f}{d} \quad (4.3)
\]

\( h_1 \) and \( h_f \), the initial and final meniscus heights, are obtained from the graphs for each run.

The figures in the table above for percentage conversion are remarkably consistent and represent the final stage of conversion up to the gel point. To them must be added, of course, the percentage of polystyrene already in the system to get a figure for total effective conversion. In this respect, the run with reference 1.5 cannot be investigated further as the relevant density/composition graph is not sufficiently discriminating.

<table>
<thead>
<tr>
<th>Run</th>
<th>%PS (v/v)</th>
<th>( x_L )</th>
<th>Total PS at cessation of run</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
<td>51.6</td>
<td>2.53</td>
<td>54.15</td>
</tr>
<tr>
<td>1-3</td>
<td>41.2</td>
<td>2.44</td>
<td>43 63</td>
</tr>
<tr>
<td>1-4</td>
<td>36.5</td>
<td>2.17</td>
<td>38.67</td>
</tr>
</tbody>
</table>
The glass transition temperature (27a) of the styrene/polystyrene mixtures with these final compositions is always less than 20°C. It can fairly be assured, therefore, that the cessation of polymerisation is not due to the trapping of radical species in a glassy matrix.

4.3.2.1 A Comparison with the Work of Marten and Hamielec

The equation which these co-authors developed (27a) to predict conversion with time is:

\[
\frac{dx}{dt} = \left(\frac{kp^3}{k \tau, \alpha} \right) \left( \frac{K_m}{K_{m, \text{crit}}} \right)^n \exp \left\{ -B \left( \frac{1}{V_f} - \frac{1}{V_{f, \text{crit}}}, \frac{1}{2} \right) \exp \left( \frac{A \left(1 - \frac{1}{V_f} \right)}{V_{f, \text{crit}}} \right) \right\} x \left( \frac{f k_d [I]_0}{1 - \xi x} \right)^n (1-x) \exp \left( -k_d \frac{t}{2} \right) \quad (4.1)
\]

This equation (4.1) is not separable because the term $1-\xi x$ is present; so an analytical solution of 4.1 is not possible. It was hoped to be able to plot out the course of the current polymerisations according to this equation to judge the fit of the experiment data to the model of Marten and Hamielec. However, linear interpolation between temperature and initiator concentrations either side of those employed here should yield limits to conversion between which the limits in this study ought to fit.

From Fig 2. at 45°C (Ref. 27a)

[I]_0 = 0.025 moldm^{-3} \rightarrow X_L = 98.5%

[I]_0 = 0.0125 moldm^{-3} \rightarrow X_L = 87%
From Fig 3. at 60°C (Ref 27a)

\[ [II]_0 = 0.0268 \text{ mol dm}^{-3} \rightarrow x_L = 90\% \]

\[ [II]_0 = 0.0164 \text{ mol dm}^{-3} \rightarrow x_L = 91.5\% \]

4.3.2.2 Interpretation of \( x_L \) as a function of \( (T, \text{ and } [II]_0) \).

Before applying these results, it is interesting to note the unexpected reversal of the variation of \( x_L \) with \([II]_0\) if the temperature is changed from 45°C to 60°C. Under normal circumstances, an increase in \([II]_0\) should lead to a greater \( x_L \). A greater number of kinetic chains, reducing the average molecular weight of the product, should lower the reaction viscosity. This, in turn, by virtue of a reduced or delayed effect on \( k_L \), would be expected to allow the polymerisation to progress further before cessation. Such an observation is borne out at 45°C. At 60°C, however, the relationship appears to be reversed. It is unlikely that the reasoning above cannot be applied and so the likely explanation is that the limiting conversions are the same and that the difference arises from printing accuracy of the graphs. It is quite probable that as the temperature rises, the effect of \([II]_0\) differences - if small, as here, - becomes less. The strong dependence of viscosity on temperature which causes a large decrease in viscosity on heating from 45°C to 60°C will ensure that the more subtle effect of change in \([II]_0\) on \( x_L \) becomes less significant.
4.3.2.3 Conformity of the Current Results to the Volume Fraction Model

From 4.3.2.1, at 45°C and $[I]_o = 0.02 \text{ mol dm}^{-3}$, one would expect $98.5\% < x_L > 87\%$. At 60°C, $[I]_o = 0.02 \text{ mol dm}^{-3}$ should lead to $91.5\% > x_L > 90\%$ (or, with the reasoning in 4.3.2.2, $x_L = 91.5\%$ or $x_L = 90\%$). So, the values of $x_L$ at 50°C should, if the model in 27a is correct, lie between 98.5% and 87%. The table in 4.3.1 does not bear this out, though. All the polymerisations under consideration have $x_L$ far below 87%.

In 27a, Marten and Hamielec make the following assumptions:

1. The termination reaction becomes diffusion-controlled when $D_t$, becomes equal to or less than $D_t$, crit.
2. The termination reaction becomes diffusion-controlled before the occurrence of entanglement.

Whilst not contradicting, these two assumptions may not be mutually applicable. In other words, the failure of the model in 27a to account for the current observations may be because, under these circumstances, entanglement and diffusion control take effect at different stages of the reaction.

It is important to remember that the design of the experiments in this study ensures that the species under investigation-polystyryl radicals—are very different in comparison with the molecules forming the environment in which they react.
For a polymerisation from zero conversion, the radicals (developing species) may be considered to be "of a size" with the surrounding terminated molecules. Then entanglement and diffusion control begin, if not together, within a very short span of time. When the current method is employed to study radical behaviour, the environment is necessarily contrasting in character. Indeed, as the graphs (26) show, the host polymer solutions are all formulated in a region of distinct chain entanglement. Thus any model which seeks to describe the course of a polymerisation on the basis of diffusion control becoming effective well before chain entanglement will not succeed in the high conversion regimes simulated here. Whilst the foregoing arguments do not disprove the validity of Marten and Hamielec's work (which, as they have shown, fits reasonably well at medium high conversions from zero) it does describe a validity limit for this particular volume fraction approach. Namely such an approach will not be applicable in cases where radicals are generated in an entangled environment.

4.3.2.4  Why the Model Breaks Down (27a)

The arguments used in this paper utilise ideas proposed by Bueche (47). In this work, Bueche considers the phenomena of diffusion and viscosity in terms of segmental motion of polymer chains. Where the arguments of Marten and Hamielec break down is most likely in their application of Bueche's segmental-motion based theory to polymeric radicals in high-viscosity media viz. surround by highly-entangled inert molecules. The equation quoted by Bueche (47) on which is based the work of Marten and Hamielec is:
According to Bueche, this equation is quite general provided that entanglements are not present. However, if the diffusing molecule cannot move without dragging surrounding molecules with it, its motion will not be completely random due to entanglements. Thus the statistical basis on which 4.4 is founded becomes invalid. The situation may be redressed for entangled molecules provided that those considered, to use Bueche's terminology, are $N$ segments long. In this case, with tight mutual entanglement, the combined centre of mass will move at random. Effectively, the chains behave as a single chain with $2N$ segments. In the high-viscosity media of the current study, however, growing polymer radicals will not approach the length of host polymer molecules. So the reasoning of Bueche applied to tangled situations will not describe what must - and there is no choice here - be visualised as a small molecule, dissimilar to its surroundings, experiencing hindrance of its motion. Such hindrance will not be due solely to mechanical entanglements; it seems likely that the unpaired electron of the polymeric free radicals may also dictate that the motion of the radicals be perturbed by the presence of $\pi$-electrons in the polystyrene host molecules. It is telling that kinetic run 1-4 shows the greatest discrepancy from the limiting conversion predicted by Marten and Hamielec; this reaction was carried out in a solution of host polymer with molecular weight greater than in 1-1 and 1-3.
This observation supports the ideas outlined above by confirming that the greater the opportunity for hindrance the lower is the agreement with a theory (27a) which predicts conversion based on volume fraction where the environment of growing radicals is very different from the radicals themselves.
4.4 Fitting Current Results to Other Models.

4.4.1 The Model of O'Driscoll

From 1976 onwards, O'Driscoll - with a series of co-workers - published a series of papers which examines high-conversion kinetics (31,49,51,65,66,67). It would be disingenuous to attempt to apply the proposals firmly here, as the papers dealt with vinyl monomers other than styrene. However, as a theory based on the ideas of volume fraction, it pays to examine briefly its main points.

4.4.2 Chain Entanglement

The model is developed in Ref 31. Cardenas and O'Driscoll commence with the equation:

\[ K_e = X^n \sigma_p \]  

By recasting this equation as:

\[ \log K_e = \beta \log X + \log \sigma_p \]  

And using Bueche's value of \( \beta = 1 \) (32,33) the critical molecular weight for entanglement may be deduced. Division by the repeat unit weight of polystyrene yields then the following critical constants for entanglement of the host polymers:

PS1: \( K_e = 6,918 \)
PS3: \( K_c = 13,800 \)
PS4: \( K_c = 25,704 \) but see footnote on page 72
PS2: \( K_c = 40,738 \)

Hence the critical constant for chain entanglement is seen to vary with the molecular weight of the host. Entanglement theories depend upon a growing radical being identical with its environment. This is not the case here where radicals develop in a pre-formed medium; this could explain why \( K_c \) vs \( M_c \) is a straight line which is not horizontal. It would be expected that the constant remain so; three conclusions may be drawn:

i) The adjustable parameters \( a_G \) and \( a \) depend on a fixed value of \( K_c \) obtaining throughout the polymerisation. As the current system represents four "snapshots" of a reaction, and \( K_c \) appears to vary, the model of Cardenas and O'Driscoll - with just two adjustable parameters - is not universally applicable.

ii) More adjustable parameters may need to be incorporated to take account of this feature - changing \( K_c \).

iii) Simple entanglement theories may not apply to reactions carried out in media whose host polymer is anionically-polymerised styrene. Effects of narrow ranges of molecular weight are likely to upset the statistical foundation of such theories if simply treated.
4.4.3 The model of Brooks and Bogunjoko

This model (Ref 52) considers the correlation between viscosity of the reaction medium and the kinetic coefficients on the basis of previous work carried out by Brooks (37).

It is difficult to draw such far reaching conclusions in this study - the severely restrictive practical nature of the high viscosities involved meant that only a narrow range of conditions vis-a-vis refs. 37 and 52 could be investigated. However, the observations in section 4.2 above lead to the following tentative conclusion.

As discussed in section 4.2 above, it cannot be assumed that $k_\alpha$ and $k_\beta$ are invariate. We must therefore consider them jointly as the kinetic ratio, $k_\alpha^2 k_\beta^{-1}$. Moreover, in order to counter the effect of different variations in each coefficient with conversion, the reduced kinetic ratio is more suitable for study. Graphs 27 and 28 apply. The correlation of $\gamma$ with viscosity - is seen to be, in general, far better than that with volume fraction. It is difficult, in fact, to plot graph 28 with conviction. Graph 27 indicates that the two lower molecular weight host polymers constitute a system which conforms best to a viscosity correlation - bearing out the observations of Brooks in 1977 (37). The shape of the graphs is not exactly coincident for two reasons:

i) Brooks plotted $\log \left( k_\alpha/k_\alpha^2 f \right)$ vs viscosity rather than $k_\alpha^2/k_\alpha$, as here;

ii) Brooks assumed that $f$ did not vary with viscosity.
In the current study, it was found that $f$ did vary with viscosity (see next section). Nevertheless, the roughly parallel techniques and monomers used in both studies support the fact that the current study's findings bear out the framework of Brook's 1977 model. Namely, that chain termination reactions are controlled:

1) above a certain limiting size of radicals involved in termination;

1i) with a correlation best expressed in terms of viscosity rather than volume fraction.

Hence from this study it may be proposed that the same model applies and that two populations of terminating radicals exist.

Further support for this model would be lent if the polymer formed by the reaction could be distinguished from host polymer. Shifts in MWD may then indicate population demarcation. However, such distinction could not be made with G.P.C. so the model remains strongly indicated and supported, if not confirmed.

4.5 The Effect of Viscosity on Initiator Efficiency

The gradient of graph 30, at $t = 0$, yields, in conjunction with section 1.8.2 and figures from table 3.2.1, a value of 0.29 for initiator efficiency. With a view to highlighting an extreme case, the experiment to determine $f$ was carried out on the solution of highest viscosity; molecular weight of host polymer = 126,000. This has a zero-shear viscosity of
around 35.1 PaS at a volume fraction of 0.453. (See Table 2.1 and Section 2.4.7.) It did not prove possible, within the laboratory time available, to investigate this further; a definite effect of solution viscosity on initiator effect was confirmed, though. Russel et al. (40) described a model wherein the rate of propagation ensures that the radicals formed during initiator decomposition do not diffuse apart but undergo recombination. This would explain the fall in $f$ at raised viscosities which was observed here. However, the phenomenon must be hedged; only the one result was obtained and a direct comparison with the work in Ref 40 cannot be made; moreover, the materials under inspection in Ref 40 were different (MMA rather than styrene). Figure 3, however, indicates a rough value of $f = 0.3$ for AIBN at 50°C in MMA; this appears roughly consistent with the present result although the concentrations used were different then and now.

With all the provisos outlined above, it was felt best to analyse the current results in terms of a constant value of $f$. It was felt to be rash to interpret the result too far in the absence of further practical work. Additionally, comparisons with others' work rests on making the same - if justified - assumptions; and constancy of $f$ has hitherto been observed. The arguments of Kulkarni and Mashelkar (38) (Section 1.4.1) are very convincing.
FINAL CONCLUSIONS

This study has ascertained the following:

1. Previous well-established relationships between solution viscosity and polymer content and molecular weight do not always hold true for the high-conversion systems simulated here;

2. The rate coefficient for propagation varies with the volume fraction of host polymer and solution viscosity;

3. Viscosity is the physical property of such media, rather than volume fraction, which better describes variations in rate coefficients;

4. It is incorrect, at any point in the regimes here studied, to apply constant values to $k_o$ and $k_t$;

5. Assumptions made during derivations of volume-fraction based termination models lead to model breakdown in the systems studied here;

6. A model involving two populations of terminating radicals, whose degree of entanglement is closely paralleled by viscosity variation, is a better fit to the current results;

7. It is possible that initiator efficiency is affected by solution viscosity, being reduced at high viscosities.
RECOMMENDATIONS FOR FURTHER STUDY

1. Similar studies should be carried out, at the same previously uninvestigated viscosities, on solutions of host polymer in non-source monomers. By this means, m.w.d. effects may be observed by separation of pre- and post-formed polymer.

2. The same types of study in (1) would also yield information which would be independent of any thermodynamic or electronic effects between solvent and host.

3. The size of the growing radicals may have an effect on these results; a series of initiator concentrations would characterise these.

4. Altering the viscosity and keeping the host's molecular weight constant could yield useful information; temperature series investigations would enable such to be carried out.

5. Useful information would be furnished by investigating polymer formed in a similar environment to itself; to this end attempts should be made to polymerise from zero viscosity to those investigated here.
REFERENCES


60. BROOKS, B.W.: Private Communication (1986).


APPENDIX I

Monomer Depletion Curves
and graphs referred to in
the text
Graph 1
Initial Rate Determination
Kinetic Experiment 1-1
Graph 2
Initial Rate Determination
Kinetic Experiment 1-2
Graph 3
Initial Rate Determination
Kinetic Experiment 1-3
Graph 4
Initial Rate Determination
Kinetic Experiment 1-4
Graph 5
Initial Rate Determination
Kinetic Experiment 1-5
Graph 6
Initial Rate Determination
Kinetic Experiment 1-6
Graph 7
Initial Rate Determination
Kinetic Experiment 2-1
Graph 8
Initial Rate Determination
Kinetic Experiment 2-2
Graph 9
Initial Rate Determination
Kinetic Experiment 2-3
Graph 10
Initial Rate Determination
Kinetic Experiment 2-4
Graph 11
Initial Rate Determination
Kinetic Experiment 3-1
Graph 12
Initial Rate Determination
Kinetic Experiment 3-2
TEXT BOUND INTO THE SPINE
Graph 13
Initial Rate Determination
Kinetic Experiment 3-3
Graph 14
Initial Rate Determination
Kinetic Experiment 3-4

Meniscus Height/cm

Time/min

0 10 20 30 40 50 60 70 80 90 100 110 120 130
0 11 12 13 14 15 16 17 18 19 20 21 22
Graph 15
Initial Rate Determination
Kinetic Experiment 3-5
Graph 16
Initial Rate Determination
Kinetic Experiment 3-6
Graph 17
Monomer Concentration vs Polymer Concentration, PS I
Graph 18
Monomer Concentration vs Polymer Concentration, PS2
Graph 19
Monomer Concentration vs
Polymer Concentration, PS3
Graph 20
Monomer Concentration vs Solution Density, PS1
Graph 2.1
Monomer Concentration vs Solution Density, PS2
Graph 23
Log Zero-shear Viscosity vs Polymer Concentration, PS1
Graph 2.4: Log Zero-shear Viscosity vs Polymer Concentration, PS2
Graph 25
Log Zero-shear Viscosity vs Polymer Concentration, PS3
Graph 26.

\[ \log [\eta] \quad \text{Pa s} \]

- \( \Delta: \bar{M}_V = 15,100 \) (PS1)
- \( \Theta: \bar{M}_V = 38,500 \) (PS3)
- \( \Box: \bar{M}_V = 126,000 \) (PS2)
- \( \times: \bar{M}_V = 64,000 \) (PS4)
Graph 26a
Log Zero-shear Viscosity vs Polymer Concentration, PS4

\[ \log \eta \text{ [Pa.s]} \]

- 36
- 40
- 44
- 48
- 52
- 56
- 60

\( [\text{PS4}]/% \)
Graph 2.7
Relationship between Reduced Kinetic Ratio and Solution Viscosity

Reduced Kinetic Ratios:
- $\bar{M}_v = 125,000$
- $\bar{M}_v = 38,500$
- $\bar{M}_v = 15,100$
Graph 28
Relationship between Reduced Kinetic Ratio and Volume Fraction of Host Polymer

\( \Delta: \bar{M}_v = 15,100 \)

\( \square: \bar{M}_v = 38,500 \)

\( \circ: \bar{M}_v = 126,000 \)
Graph 29
Spectrophotometer Calibration Curve

Absorbance

$[\text{dpph}] \times 10^{-4} \text{ mol dm}^{-3}$
Graph 30
DPPH Depletion Curve
Graph 31
GPC Calibration Curve

Fractional Elution Volume
(Relative to toluene marker as 100% elution).
Graph 32
Solution Density versus Polymer Concentration - all host polymers.
TEXT CUT OFF IN ORIGINAL
Graph 33

Variation of Rate
Coefficient of Propagation with solution viscosity.
Graph 34

Variation of Rate Coefficient for Propagation with Volume Fraction of Host Polymer

\[ \log_{10} \text{ cpd dm}^{-3} \text{ mol}^{-1} \text{ sec}^{-1} \]
Graph 35

Variation of Rate Coefficient for Termination with Solution Viscosity.

\[ k_t \text{/(dm}^3\text{mol}^{-1}\text{Sec}^{-1}) \]

\[ \log_{10} \gamma / \text{PaS} \]

- $\bar{M}_v = 15,100$
- $\bar{M}_v = 38,500$
- $\bar{M}_v = 126,000$
Graph 36

Variation of Rate Coefficient for Termination with Volume fraction of Host Polymer.
APPENDIX II

Gel Permeation Chromatograms for each host polymer.

Elution volumes of 0.3µl are marked below each peak

cf graph 31.
Experimental Data—Kinetic Experiments

All these data consist of pairs comprising a time (in minutes) since the start of the reaction and a meniscus height (in cm) read off the dilatometer scale. The data were plotted directly to give the graphs in Appendix I; the tangents to these graphs at \( t = 0 \) then yield a rate, \( R_0 \), from which the kinetic parameters (\( k_a, k_1, \) and \( \gamma \)) were calculated. The limiting conversions exhibited by runs 1-1, 1-3, 1-4 and 1-5 are apparent from these data; they are not apparent on the graphs for reasons of space. Sample calculations for the major derivations are presented in Appendix IV.
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APPENDIX IV – SAMPLE CALCULATIONS
1) Calculation of Rate of Polymerisation for kinetic experiment 1-1

(Ref: Graph 1)

Initial gradient = \(18.0 - 12.1 = \frac{0.1475 \text{ cm min}^{-1}}{40}\)

Capillary radius = 0.0629 cm

\[\cdot \text{ volume change} = \pi (0.0629)^2 \times 0.1475\]

\[= \frac{0.0018 \text{ cm}^3 \text{ min}^{-1}}{60}\]

Dilatometer contents weigh 16.7704 g

\[\cdot \text{ initial polymerising volume} = 17.3931 \text{ cm}^3\]

(using a density of 0.9642 g cm\(^{-3}\))

Hence at one minute, volume in dilatometer

\[= 17.3931 - 0.0018 = 17.3913 \text{ cm}^3\]

\[\cdot \text{ density at one minute} = \frac{16.7704}{17.3913} = 0.9643 \text{ g cm}^{-3}\]

\[\cdot \text{ at one minute, the concentration of styrene is 4.4 mol dm}^{-3}\]

(Ref: Graph 20)

Hence initial \(R_o\) = 4.17 - 4.14 = \(5 \times 10^{-5} \text{ mol dm}^2\text{sec}^{-1}\)
Calculation of $\psi$, the reduced kinetic ratio, for kinetic Experiment 1-1

Equation 1.14 is: 

$$R_{n} = k_{o} (M)^{2} \left( \frac{2f k_{d} (I)}{k_{t}} \right)$$

$$= R_{n}^2 = k_{o}^2 (M)^{2} \cdot 2f k_{d} (I)$$

$$k_{o}^2 = \frac{R_{n}^2}{2f k_{d} (I) (M)^{2}}$$

For kinetic Experiment 1-1, $[I] = 0.0203$ mol dm$^{-3}$

$[M] = 4.17$ mol dm$^{-3}$

and Ref. 63 gives: $k_{d} = 2.984 \times 10^{10}$ sec$^{-1}$

This yields: $k_{o}^2 k_{t}^{-1} = 258,000 R_{n}^2$

Ref. 63 also provides, for styrene at 50°C,

$$k_{o} = 182 \text{ dm}^{2} \text{ mol}^{-1} \text{ sec}^{-1}$$

Hence the value of $k_{o}^2 k_{t}^{-1}$ in the absence of diffusion control,

$$k_{o}^2 k_{t}^{-1} = (182)^{2} = 5.2 \times 10^{-4} \text{ dm}^{2} \text{ mol}^{-1} \text{ sec}^{-1}$$

This has been designated $\alpha$ in this study.

Thus $\psi$, the Reduced Kinetic Ratio, is
\[ \frac{k_p^2 k_t^{-1}}{k_{v0}^2 k_{t0}^{-1}} = \frac{1}{\alpha} \]

Using all the figures above yields:

\[ \gamma = \frac{0.183}{5.2 \times 10^{-4}} \approx 353 \text{ to 3 figures} \]

\( \gamma \), being a ratio, is dimensionless.
Experimental Values used in Calculation of Rates of Polymerisation and Kinetic Ratio

<table>
<thead>
<tr>
<th>Ref</th>
<th>Initial Mass in Dilatometer/g</th>
<th>[L]/mol dm⁻²</th>
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</tbody>
</table>

The capillary attached to the dilatometer throughout the three series of kinetic experiments had a radius of 0.0629cm.
APPENDIX V — NOMENCLATURE
c - Concentration

$C^*, C^{**}$ - Critical Concentrations

D - diffusion coefficient of substance $x$; diffusivity

E - entanglement density

F - flux of substance $x$

f - initiator efficiency

g - acceleration due to gravity

I - initiator molecule

I. - initiator radical

K - a Mark-Houwink constant

K* - a critical constant

k - rate coefficient for decomposition

k. - rate coefficient for initiation

k* - rate coefficient for propagation

k. - rate coefficient for termination

k. - rate coefficient for cage I formation

k. - rate coefficient for cage I exit and reassociation

k$\beta$ - rate coefficient for formation of cage II from cage I

k$\alpha$ - rate coefficient for segmental diffusion

k$\gamma$ - rate coefficient for translational diffusion

k$\alpha$ - rate coefficient for radical reaction

M - molecular weight average (subscript $v \equiv$ viscosity average; subscript $w \equiv$ weight average; subscript $n \equiv$ number average)

M - monomer molecule

M. - monomer radical, length $x$

N - Avogadro's number, molecular weight (Tulig & Tirrell)
\( N_c \) - characteristic chain length

\( P_{AD} \) - correction factor (steric/directional)

\( p \) - degree of polymerisation

\( R \) - radius

\( R_\cdot \) - general radical species

\( R_e \) - transition-state end separation

\( R_i \) - rate of initiator decomposition

\( R_1 \) - rate of initiation

\( R_p \) - rate of polymerisation

\( r \) - encounter distance, radius

\( T \) - temperature

\( t \) - time

\( V \) - volume, molar volume

\( V_f \) - free volume

\( w_p \) - weight fraction of polymer

\( \bar{X}_c \) - average chain length

\( \bar{X}'' \) - critical value of number-average chain length to cause entanglement

\( x \) - fractional conversion of monomer to polymer

\( x_0 \) - hydrodynamic radius divided by the square root of the chain length

\( \alpha \) - a Mark-Houwink constant; a dimensionless group (Balke and Hamielec); coefficient of cubic expansion; the kinetic ratio at zero diffusion control \((k_{pc}^2/k_{tc})\)

\( \beta \) - an exponent in work by Cardenas and O'Driscoll relating volume fraction to entanglement

\( \Delta H_{\text{m(vap)}} \) - enthalpy change on mixing (vapourisation)
5 - jump distance; correction factor in work by Pioni et al relating segmental diffusion to molecular parameters.

\( \eta \) - viscosity
\( \eta_s \) - microviscosity
\( \eta_{\text{rel}} \) - relative viscosity
\( \eta_{\text{sp}} \) - specific viscosity
\( \overrightarrow{\eta} \) - specific viscosity
\( \overrightarrow{[\eta]} \) - specific viscosity
\( \gamma \) - kinetic chain length
\( \rho \) - density
\( \tau \) - dimensionless time
\( \phi \) - jump frequency/volume fraction of polymer present in a simulated polymerisation system
\( \gamma \) - the reduced kinetic ratio

The following subscripts were used throughout:

- \( m \) denotes monomer;
- \( p \) denotes polymer;
- \( s \) denotes solvent;
- \( o \) denotes absence of diffusion control

subscript \( o \) also denotes a value at \( t = o \); the context makes clear the significance of this subscript.