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Propagation Rate Coefficients from Electron Spin Resonance Studies of the Emulsion Polymerization of Methyl Methacrylate

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ABSTRACT: The first results are reported for the quantitative application of ESR spectroscopy to emulsion polymerization kinetics. When this technique, in conjunction with dilatometric rate measurements, was applied to the seeded emulsion polymerization of methyl methacrylate at 50 °C, the dependence of the propagation rate coefficient (k_p) on the weight fraction of polymer (w_p) was found to be $k_p = k_p^0$ ($0.33 \leq w_p \leq 0.84$) and $k_p = k_p^0 \exp[-29.8(w_p - 0.84)]$ ($0.84 \leq w_p \leq 0.99$), where $k_p^0 = 790 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These results reflect the passage of the latex particles through their glass transition point (at $w_p = 0.84$), leading to the propagation step being controlled by the diffusion of monomer to the propagation site. The observed decrease in k_p for $w_p > 0.84$ appears to be less dramatic than that predicted by current free volume theories.

Introduction

We have reported previously¹ how it is possible to utilize modern ESR spectrometers (possessing both long-term field stability and high sensitivity) for the detection of free radicals in the emulsion polymerization of certain monomers (e.g., methyl methacrylate). The accumulation of ESR spectra using frozen samples opens up the possibility of measuring directly the time evolution of the free-radical concentration during emulsion polymerizations. Furthermore, such direct quantitative measurements of the free-radical concentration when coupled with concomitant measurements of the instantaneous polymerization rate allow the propagation rate coefficient (k_p) to be determined directly over a relatively wide range of polymer concen-

trations. We report here the first application of this method, the system chosen for study being the emulsion polymerization of methyl methacrylate. The values determined for k_p by this direct ESR method are virtually independent of any model-based assumptions. The major uncertainty in the method arises from the necessity of calibrating the ESR spectrometer.

The method provides in principle a means of measuring absolute values for k_p . In practice, it provided in this study accurate results for the relative values of k_p as the system passed through the glass transition point and then proceeded beyond it, due to the consumption of monomer. Melville and co-workers² have previously reported that the propagation rate coefficient for methyl methacrylate de-

creases significantly at high conversions during polymerization in bulk, although excessive scatter in their data prevented any quantitative description. We present the results of a quantitative study of the variation of the propagation rate coefficient with conversion in seeded emulsion polymerizations at 50.0 °C. The weight fraction of polymer (w_p) in the particles varied over the range 0.33–0.99. As the glass transition point occurred at $w_p \approx 0.84$, this showed clearly that propagation continued, albeit at a decreased rate, well beyond the glass transition point in emulsion polymerization systems. This contrasts with the behavior reported for bulk systems.

Experimental Procedures

The dilatometric method devised for measuring the fractional conversion of monomer to polymer as a function of time at 50.0 °C has been described in detail previously,³ as has the procedure for making the ESR measurements.¹ All kinetic studies were performed by using seed latices. Only those runs where new particle nucleation was absent (as determined by transmission electron microscopy) are presented below. The seed latices were characterized by methods described elsewhere.³ The unswollen radius of the seed latex used in runs RE 17–19 was 46 nm, whereas that for all other runs was 34 nm. Both latices were essentially monodisperse (coefficients of variation were 8 and 12%, respectively). The number-average molecular weights of the polymer constituting the latex particles were determined by gel permeation chromatography to be 0.87×10^6 and 1.2×10^6 , respectively, with corresponding polydispersity indices of 2.0 and 1.80.

Samples for study by ESR were removed under vacuum from the dilatometer during the course of the polymerization. The samples were collected in standard quartz ESR sample tubes (3-mm i.d.), sealed, and quickly frozen to 77 K in liquid nitrogen. This procedure stops the polymerization and cryogenically traps the propagating radicals without any decrease in concentration. All samples were examined by using a Bruker 200D X-band spectrometer interfaced to a PDP 11/34 computer for data acquisition and manipulation. Samples were measured at 100 K and a microwave power of 50 dB (2.0 μ W). Above this microwave power some power saturation of the samples was observed. Recording of spectra at 100 K has three distinct advantages in sensitivity terms in this system: (a) the aqueous emulsion system is in the solid phase, and hence absorption of microwaves by water is greatly reduced, allowing larger samples to be investigated; (b) there is a secondary increase in sensitivity due to the temperature dependence of the Boltzmann factor; and (c) the radical concentration is stable, and hence the ESR signal can be accumulated to increase the sensitivity.

Radical concentrations were calculated by double integration of the observed ESR signal, this value being compared with a similar double integration of a suitable standard run under similar instrumental conditions. Primary and secondary standards were prepared for use in this work. The primary standard consisted of DPPH in benzene prepared and sealed under vacuum. To allow for the difference in dielectric properties between the primary standard and the frozen aqueous emulsion polymerization system, a secondary standard was employed. This standard contained DPPH, methyl methacrylate, Aerosol MA80, seed latex, and water and was similar in composition to the emulsion polymerization system. This standard was outgassed and sealed under vacuum. Use of these standards allowed a dielectric attenuation factor for the emulsion system to be calculated.

Results and Discussion

Limiting Conversion in Methyl Methacrylate Emulsion Systems. An important observation in the current study was that the emulsion polymerizations of methyl methacrylate proceeded readily to essentially complete conversion. It has been reported^{4,5} that polymerization of methyl methacrylate in both bulk and emulsion systems ceases well short of 100% conversion at 50.0 °C. The complete conversion in emulsion polymerization was verified because we wished to study systems containing extremely high weight fractions of polymer. An unam-

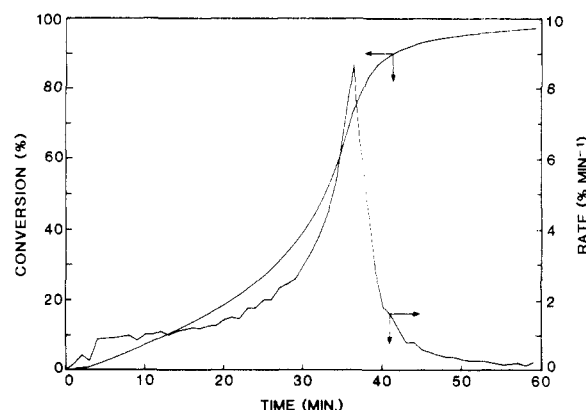


Figure 1. Characteristic plots of the conversion and instantaneous rate of polymerization as a function of time for the seeded emulsion polymerization of methyl methacrylate.

biguous result was obtained here because the dilatometric method used to measure the fractional conversion could be checked by several independent techniques.

A plot of the fractional conversion of monomer to polymer vs. time for the seeded emulsion polymerization of methyl methacrylate is presented in Figure 1. Also shown in the same diagram is the instantaneous rate of polymerization as a function of time obtained by numerical differentiation of the data used to construct the previous curve. The rate of polymerization is characterized by a rapid approach to an approximate steady state, followed by a relatively long period of almost constant rate.³ A very rapid increase in rate then followed. This corresponds to the occurrence of the Trommsdorff gel effect, after which the rate dropped off sharply. The shape of the rate curve has been discussed elsewhere³ and will not be considered further. In all of the seeded emulsion polymerizations studied here, the polymerizations appeared to proceed to complete conversion. This observation differs from the results obtained by Horie et al.⁴ for the bulk polymerizations of methyl methacrylate and by Friis and Hamielec⁵ for the emulsion polymerization of the same monomer. These authors reported that the rate of polymerization dropped to near zero at ca. 80–85% conversion of monomer to polymer at the temperature of the present studies (50.0 °C). It was found necessary in the studies reported here, however, to monitor the polymerization for approximately 3–24 h in order to observe complete conversion, and it is significant that neither Horie et al. nor Friis and Hamielec measured the conversion over extended periods of time. Notwithstanding these experimental differences, there does appear to be a fundamental difference in the "limiting" conversions observed in bulk and emulsion polymerizations of methyl methacrylate.

The observation described above of essentially complete conversion of monomer to polymer in the present study was initially based upon dilatometric measurements. Since there appeared to be a discrepancy between this result and those reported previously, several additional experiments were performed to confirm the extent of conversion of monomer to polymer. These experiments included the gravimetric determination of the polymer content at 99% conversion as determined by dilatometry. The gravimetric results were in excellent agreement with the dilatometric results, irrespective of whether the latex samples were dried at temperatures above 50.0 °C or below. It was also found that when an emulsion system at its limiting conversion at 50.0 °C was heated to 65.0 °C, no further polymerization could be induced, even though initiator was present.

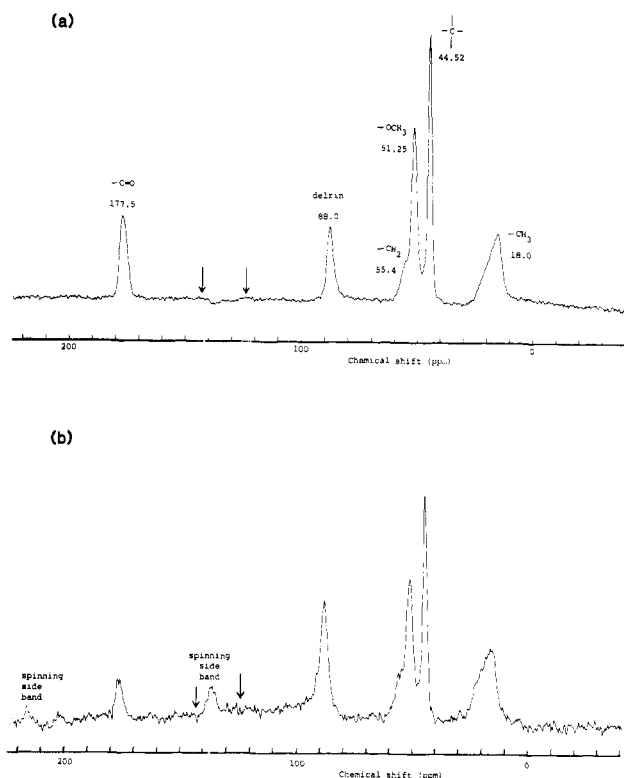


Figure 2. ^{13}C magic-angle NMR spectra of the polymer at limiting conversion: (a) with cross-polarization; (b) without cross-polarization. The arrows indicate the expected positions of the $\text{C}=\text{C}$ resonances of the monomer.

Two spectroscopic experiments were also performed to test the completeness of conversion of monomer to polymer. As reported previously,¹ the addition of styrene monomer to an emulsion polymerization of methyl methacrylate at a limiting conversion of near 100% caused the ESR spectrum to be transformed quantitatively from that exhibited by poly(methyl methacrylate) free radicals to that displayed by polystyryl free radicals. This again suggests the absence of polymerizable methyl methacrylate in the system. We note in this context that the diffusion coefficients of styrene and methyl methacrylate monomers in poly(methyl methacrylate) particles of high weight fraction of polymer are expected to be comparable in magnitude.

Evidence of complete conversion was also obtained by using magic-angle spinning ^{13}C NMR spectroscopy, both with and without cross-polarization. Typical spectra for emulsion-polymerized samples at limiting conversion are shown in Figure 2. No resonances that were attributable to $\text{C}=\text{C}$ double bonds or $\text{C}=\text{O}$ adjacent to $\text{C}=\text{C}$ were observed, suggesting that polymerization of monomer was essentially complete. Earnshaw et al.⁶ have shown that as little as 1% of unreacted methyl methacrylate monomer can be distinguished by the $\text{C}=\text{O}$ resonance in such experiments. When a bulk polymerization of methyl methacrylate was performed at 50 °C and allowed to proceed to the (apparent) limiting conversion, resonances due to $\text{C}=\text{C}$ double bonds in unreacted monomer could be detected. Their integrated intensities indicated that the limiting conversion for bulk polymerization of methyl methacrylate at 50 °C was ca. 83%, in good agreement with the results of Horie et al.⁴

The limiting conversions after emulsion and bulk polymerizations at 50 °C were also determined by dissolving the monomer/polymer and obtaining high-resolution NMR spectra; values of ca. 99% and 85%, respectively, were obtained.

The foregoing results show that the rate of polymerization did not drop to zero in the emulsion polymerizations of methyl methacrylate reported here when the monomer concentration in the latex particles fell below that corresponding to the glass transition point. This contrasts with the results obtained both in these studies and previously for bulk systems, where the rate of polymerization was indeed found to decline dramatically once the monomer concentration fell below that corresponding to the glass transition point. The difference between the present results and those reported by Friis and Hamielec for the same emulsion polymerization may be tentatively ascribed to the latter authors' shorter observation times. Note that because of the small concentration of both free radicals and monomer in the aqueous phase, polymerization in the water can be shown by calculation to make a negligible contribution to the overall polymerization rate in emulsion systems.

The explanation for the different results obtained in emulsion and bulk polymerizations is not immediately apparent. One possibility is that in emulsion systems, small quantities of water are imbibed by the latex particles, thus plasticizing the polymer. However, as shown below, the glass transition points for bulk and emulsion systems do not appear to occur at significantly different volume fractions of polymer; any effect of water in emulsion systems thus seems likely to be small. A second possible cause for the observed differences may in part be associated with the rate of supply of monomer to the free radicals at monomer concentrations below that corresponding to the glass transition point. In the glassy state, polymerization would be expected to become diffusion controlled, the rate of polymerization being determined *inter alia* by the rate at which monomer is supplied by diffusion to the propagating free radicals. In the emulsion polymerization studies reported here, the radius of the latex particles was of the order of 50 nm. On average, monomer in the particles would not be required to diffuse further than, say, half this distance to become available to the free radicals for polymerization. In bulk polymerizations, however, the average distance between free radicals at, say, a concentration of 10^{-6} mol dm^{-3} would be of the order of 100 nm. This means that monomer would be required to diffuse a distance some 4 times greater than that in the emulsion polymerization case in order to become available for propagation. Since the time required to diffuse a given distance varies as the square of that distance, the average time required for the diffusion of monomer to the free radicals in bulk systems may be at least an order of magnitude greater than that for emulsion polymerization. For this reason, monomer may be supplied at a slower rate in bulk systems than in emulsion systems, and the rate of polymerization would be reduced accordingly. It should be stressed that it follows from the foregoing discussion that the observation that the rate of polymerization drops essentially to zero below the glass transition point does not of necessity imply that the propagation rate coefficient k_p is also near zero. The free radicals may simply be starved of monomer. This suggests that it may be necessary to monitor bulk systems over long periods of time (e.g., weeks) in order to detect high conversion polymerization in systems in the glassy state.

There is, however, a third important difference between emulsion and bulk polymerizations that may contribute very significantly to the differences in observed behavior. In bulk polymerizations at high conversions the free radicals are generated in pairs in a highly viscous medium. Their ability to diffuse apart, even if they escape geminate

Table I
Determination of Propagation Rate Constant for Methyl Methacrylate at 50.0 °C

run	designation time, min	C_M , mol dm ⁻³	w_p	$R_p/10^{-4}$, mol dm ⁻³ s ⁻¹	$[R\cdot]/10^{-7}$, mol dm ⁻³	$N_c/10^{16}$, dm ⁻³	\bar{n}	k_p , ^a dm ³ mol ⁻¹ s ⁻¹
RE17	14	6.6	0.33	2.74	0.50 ± 0.13	7.8	0.39	830 ± 220
	29	5.0	0.51	7.04	1.03 ± 0.19	7.9	0.79	1360 ± 250
	37	1.9	0.83	14.8	9.7 ± 0.7	8.0	7.3	820 ± 60
	45	0.66	0.94	1.47	107 ± 7	8.1	80	20.8 ± 1.4
	53	0.43	0.96	0.62	153 ± 9	8.1	114	9.3 ± 0.6
RE18	14	6.6	0.33	2.71	0.27 ± 0.13	7.8	0.21	1500 ± 700
	29	5.1	0.51	7.10	0.94 ± 0.18	7.9	0.72	1490 ± 290
	37	1.8	0.84	17.4	11.8 ± 0.8	8.0	8.9	800 ± 50
	45	0.54	0.95	1.48	111 ± 7	8.0	84	24.8 ± 1.6
	53	0.30	0.97	0.68	166 ± 10	8.0	125	13.6 ± 0.8
RE19	14	6.6	0.33	2.67	0.39 ± 0.13	7.9	0.30	1040 ± 350
	29	4.9	0.52	7.66	1.42 ± 0.19	8.0	1.07	1090 ± 150
	37	1.6	0.86	12.8	17.9 ± 1.1	8.1	13.3	457 ± 28
	45	0.56	0.95	1.51	119 ± 7	8.2	88	22.9 ± 1.4
	53	0.33	0.97	0.54	170 ± 10	8.2	125	9.7 ± 0.6
RE20	12	6.6	0.33	2.97	0.39 ± 0.13	17.4	0.14	1200 ± 400
	27	5.0	0.51	7.69	2.89 ± 0.26	17.6	0.99	530 ± 50
	35	1.3	0.89	9.29	31.9 ± 1.9	17.9	10.7	224 ± 13
	43	0.52	0.96	1.20	110 ± 7	18.0	36.9	21.2 ± 1.4
	51	0.30	0.97	0.66	152 ± 9	18.0	51	14.3 ± 0.9

^a Only data with a precision of ±20% or better was used to calculate k_p .

recombination, is greatly reduced compared with that for low viscosity systems. The close proximity of the initial pair of radicals means that propagation events when they do occur are likely to lead to residual termination^{7,8} (i.e., termination events that arise because the free-radical chain ends possess spatial mobility even in the glassy state as a consequence of the addition of monomer molecules in the propagation step). By way of contrast, in emulsion systems, the free radicals are generated in the low viscosity aqueous phase for the entirety of the polymerization process. These enter the latex particles essentially one at a time. Such single file entry of free radicals into latex particles could significantly reduce the rate of residual termination, allowing polymerization at high conversions to proceed more readily in emulsion systems than in bulk systems.

Determination of the Propagation Rate Coefficient.

Some typical results obtained for the rate of polymerization (R_p) as measured by dilatometry and the corresponding total concentration of free radicals ($[R\cdot]$) in the entire system as determined by ESR measurements are presented in Table I. Values for the average number of free radicals per particle (\bar{n}) and the propagation rate coefficient at 50 °C were calculated from such data by using

$$\bar{n} = [R\cdot]N_A/N_C \quad (1)$$

$$k_p = R_p/(C_M[R\cdot]) \quad (2)$$

where N_A is Avogadro's constant, N_C is the particle number concentration, and C_M is the monomer concentration in the latex particles. Some derived values are also listed in Table I. Note that the value of N_c increases slightly during the course of interval III of seeded emulsion polymerizations because polymerization is accompanied by a decrease in the total volume of the system.

The runs designated RE 17, RE 18, and RE 19 in Table I were designed to be similar so that the reproducibility of the methods could be assessed. Comparative results for \bar{n} as a function of the weight fraction of polymer in the latex particles (w_p) for the three different runs are displayed in Figure 3. The reproducibility of \bar{n} was satisfactory (better than 5%) at high weight fractions of polymer but dropped off sharply at lower weight fractions when the average free-radical concentration was near the limit of detection of the ESR spectrometer.

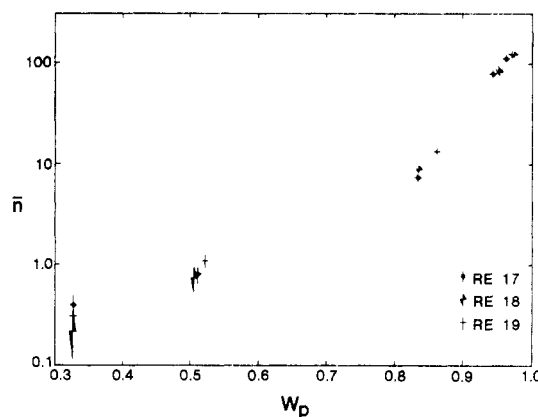


Figure 3. Plot of \bar{n} vs. weight fraction of polymer for three similar runs to illustrate the reproducibility of the results.

The results presented in Table I show that the free-radical concentration varied from about 3×10^{-8} mol dm⁻³ at low conversions to about 2×10^{-5} mol dm⁻³ at high conversions. The values of \bar{n} correspondingly varied from about 0.2 to 125. The former value was that evident in interval II (polymerization in the presence of monomer droplets) of the emulsion polymerization, whereas the latter pertained to the end of interval III (polymerization in the absence of monomer droplets). The observation that \bar{n} becomes large late in interval III suggests that the rates at which the termination events (both bimolecular termination and exit) occur during the Trommsdorff gel effect may decline significantly; it is likely that the rate coefficient for entry of free radicals into the particles does not change so dramatically during this period.

The values determined for k_p as a function of the weight fraction of polymer are plotted in Figure 4. The results suggest that for values of w_p less than that corresponding to the glass transition composition at the experimental temperature, the value of k_p was approximately constant. Its mean value was calculated from

$$k_p = \sum_i w_i k_{pi} / \sum_i w_i$$

where w_i is the weighting factor for the i th measurement of k_p . The weighting factor was set equal to the reciprocal of the precision of the value of k_p . Only results for which the precision of the data was better than 20% were in-

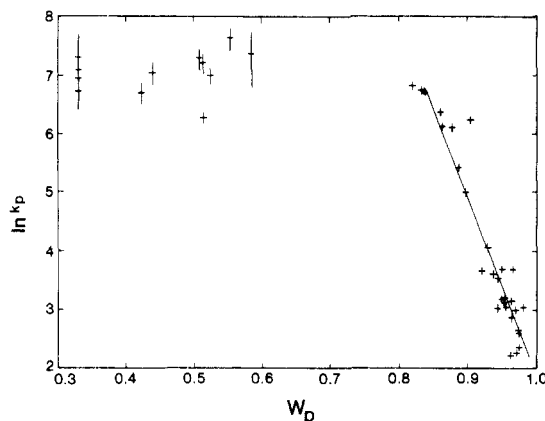


Figure 4. Plot of the variation of the propagation rate constant with the weight fraction of polymer for methyl methacrylate at 50.0 °C (all data included).

cluded in this mean value calculation. The average value of k_p so calculated for monomer concentrations exceeding that corresponding to the glass transition point was $790 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. In addition to the standard deviation in the value of k_p calculated from random variations that is quoted in this result, an additional systematic uncertainty of perhaps $\pm 30\%$ should be added because of possible absolute errors in the calibration of the ESR spectrometer. Values of k_p for methyl methacrylate at 50.0 °C reported in the literature span the range $200\text{--}1200 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ if the values of k_p reported at lower temperatures⁹ are taken into account. This range clearly encompasses the mean value of k_p found in these studies. Korus and O'Driscoll,⁹ however, have shown that a least squares regression analysis of an Arrhenius plot of the literature values for k_p at different temperatures gives $k_p = 450 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. (The precision here has been estimated from the lines of maximum and minimum slopes.) This average value for k_p is smaller than the value determined in the present study, but the precision of the two sets of data is insufficient to allow any inference to be drawn as to whether the difference between these two values is significant (i.e., to infer that k_p in viscous emulsion polymerization systems, which may contain trace quantities of water, is significantly greater than that for polymerizations conducted at low conversions, and hence at a lower viscosity, but in some cases performed in the presence of solvents). Note that Kamachi et al.¹⁰ estimated $k_p = 187 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for the polymerization of methyl methacrylate at room temperature by measurement of the free-radical concentration by ESR combined with a single value for the conversion determined by precipitation of the polymer.

When the monomer concentration in the latex particles fell below that corresponding to the glass transition point at the polymerization temperature, the value of k_p was found to decrease with increasing weight fraction of polymer in the particles (see Figure 4). The existence of an analogous knee-point for the termination rate coefficient of methyl methacrylate at the glass transition point has been reported previously³ in the emulsion systems. The results presented here suggest that k_p decreases approximately exponentially with the weight fraction of polymer in the latex particles at high weight fractions of polymer. The least squares regression line for $w_p \geq 0.84$ was found to be expressed by

$$k_p = k_p^0 \exp[-29.8(w_p - 0.84)] \quad (3)$$

where $k_p^0 = 790 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. Note that the experimental uncertainties in k_p decrease significantly at higher w_p

(because $[R\cdot]$ is then higher). Moreover, since the absolute (systematic) uncertainty in k_p is independent of w_p , eq 3 should be quite an accurate representation of the relative variation of k_p with w_p : i.e., most of the uncertainty in the parameters given in eq 3 lies in the value of k_p^0 . The uncertainty in the value of the ratio k_p/k_p^0 as a function of w_p for higher w_p values ($w_p > 0.8$) was determined from the scatter of the data points to be of the order of $\pm 25\%$. Equation 3 has been written in terms of the experimentally determined quantity w_p , the weight fraction of polymer. This parameter can be related to the more usual parameter, the volume fraction of polymer ϕ_p , by assuming ideal mixing of monomer with polymer; this yields $\phi_p = \{(d_p/d_m)/w_p + [1 - (d_p/d_m)]\}^{-1}$, where d_p and d_m are the densities of the polymer and monomer, respectively.

The observed decrease in k_p at high conversions may be associated with the diffusion control of the propagation reaction in the glassy state. The rate-determining step under these conditions might be expected to be the diffusion of monomer to the sites of the propagating free radicals. The monomer concentration at the onset of the observed reduction in k_p was ca. 1.8 mol dm^{-3} , corresponding to a mean distance of separation of the monomer molecules of about 1 nm. Consumption of monomer in the propagation step thus requires monomer molecules to diffuse significant distances through a medium composed largely of polymer chains.

Soh and Sundberg¹¹ have adapted the Rabinowitch model¹² for diffusion-controlled processes to account for diffusion-controlled propagation reactions. They justified their application of this model, which is strictly only applicable to small molecules that are similar in size, on the basis that the propagating ends of macroradicals possess mobility that is comparable to that of the monomer molecules. According to Soh and Sundberg, the observed propagation rate coefficient k_p at high conversions can be written in terms of two limiting rate coefficients:

$$1/k_p = 1/k_p^0 + 1/k_{p\text{vfi}} \quad (4)$$

Here k_p^0 corresponds to the rate coefficient in the absence of diffusion control and $k_{p\text{vfi}}$ is its value when there is absolute diffusion control. The latter rate coefficient is given by the Smoluchowski-type expression

$$k_{p\text{vfi}} = (N_A/10^3)4\pi R_{AB}D_{MO} \exp(1/v_{fm} - 1/v_f) \quad (5)$$

where R_{AB} is the collision radius for the monomer and the growing free radical, D_{MO} is the self-diffusion coefficient for the pure monomer, and v_{fm} and v_f are the fractional free volumes of the pure monomer and the swollen latex particles, respectively. Following Soh and Sundberg, we set $R_{AB} = 0.74 \text{ nm}$ and $v_{fm} = 0.164$ and calculated v_f from

$$v_f = v_{fm}(1 - \phi_p) + v_{fp}\phi_p \quad (6)$$

where v_{fp} is the fractional free volume of pure polymer ($=0.0187$). Values of D_{MO} in the range $10^{-5}\text{--}10^{-6} \text{ cm}^2 \text{ s}^{-1}$ are considered by Sundberg¹³ to be appropriate for methyl methacrylate. Figure 5 presents a comparison of the predictions of eq 4 and 5 with the experimental results as summarized by eq 3. Curves are presented for two values of D_{MO} : 1×10^{-6} and $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$. It is apparent that near the glass transition point the latter value of D_{MO} predicts values for k_p that are in fair agreement with the experimental results.

Note that better agreement between theory and experiment could be achieved by increasing the value of D_{MO} to greater than $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$; such values, however, would appear to be too large to be physically reasonable. Note also that for large values of w_p beyond the glass

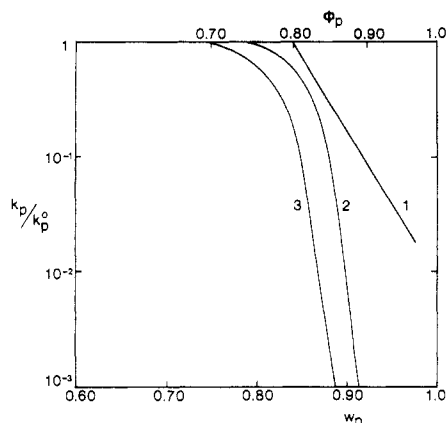


Figure 5. Variation of the propagation rate constant with the weight fraction of polymer: (1) experimental results; (2, 3) theoretical predictions of the free volume theory with $D_{MO} = 1 \times 10^{-6}$ and $1 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively.

transition point eq 4 and 5 predict an extremely rapid decrease in k_p with w_p . The experimentally determined decrease in k_p is much less dramatic, resulting in the theoretical values for k_p being several orders of magnitude less than the observed values if $w_p > 0.90$. Clearly, eq 4 and 5 must be used with caution at high weight fractions of polymer.

Conclusions

It is apparent that quantitative ESR measurements in combination with dilatometric data provide a method with considerable potential for the measurement of propagation rate coefficients. The values obtained are essentially free of any model-based assumptions. Absolute accuracy is about $\pm 40\%$, while relative accuracy (as the variation of k_p with w_p) is $\pm 25\%$. For methyl methacrylate at 50°C , we obtained

$$k_p = k_p^0, \quad 0.33 \leq w_p \leq 0.84$$

$$= k_p^0 \exp\{-29.8[w_p - 0.84]\}, \quad 0.84 > w_p \geq 0.99$$

where $k_p^0 = 790 \pm 300 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. These results show that for propagation a mechanistic transition occurs at the glass transition point ($w_p = 0.84$), so that the rate-determining step becomes the diffusion of monomer to the propagation site. It is particularly noteworthy that the technique described here can be applied to systems containing very high proportions of polymer; and indeed, the experimental uncertainties decrease with increasing w_p .

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Changes of Liquid Crystalline Polymer Structure with Temperature. 6. Distortion of One-Dimensional Order in Smectic B Polymer

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ABSTRACT: The character of one-dimensional order in a smectic polymer with mesogenic side groups and long spacers was studied by means of SAXS experiments, polarized microscopy, and electron microscopy over a wide temperature range, including the clearing temperature. It was demonstrated that the electron density distribution along the normal-to-smectic plane is a complicated function, characteristic of three-component systems. Such state is due to microphase separation of different fragments of macromolecules. The damping of correlation in smectic layer arrangements has an exponential form with correlation lengths of 460–600 Å. The temperature increase leads to decreasing layer-packing perfection and thermal expansion of interlayer and intralayer packing. In the isotropic state a weak fluctuation of electron density, which was associated with the correlation hole effect, was observed.

Introduction

It is quite evident that the changes of one-dimensional order in layered liquid crystalline (LC) polymers (i.e., smectics) with temperature, especially in the vicinity of phase transitions, have not been sufficiently investigated up to the present time. The available data indicate a

decrease of the orientational order parameter during transition into the isotropic melt state (near the clearing points T_{cl}).¹⁻³ For some smectic polymers, as has been found in ref 4–7, the degree of perfection of the layered order increases with temperature rise. However, up to now the nature of the temperature dependence of structural