Radical Termination and Radical Concentrations during the Batch Emulsion Polymerization of Methyl Methacrylate Studied by Electron Spin Resonance Spectroscopy

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ABSTRACT: Electron spin resonance (ESR) spectroscopy has been employed to monitor occluded radical concentrations during the unseeded batch emulsion polymerization of methyl methacrylate. A cryogenic quenching procedure has been used to record ESR spectra periodically during the course of the reaction. The occluded radical concentration first increases, reaching a maximum at a time corresponding to almost 100% conversion and then slowly decays due to "residual termination". The decay period exhibits second-order kinetics and reveals a rate constant (k_t) of 410 mol^{-1} dm^3 s^{-1} at 333 K for a particle size of 72 nm. The variation of the decay profile with initiator concentration, surfactant concentration, and temperature has also been examined.

Introduction

Emulsion polymerization techniques are widely used in the commercial manufacture of a very wide range of polymeric materials. Despite their widescale use, however, there are many mechanistic aspects of the technique which still remain poorly understood.

In a typical emulsion system an oil-in-water emulsion of a sparingly soluble monomer is maintained by mechanical agitation in the presence of a suitable surfactant (emulsifying agent).[1] The thermal decomposition of the initiator (e.g., peroxodisulfate anions) generates a primary radical (e.g., sulfate radical anions) in the aqueous phase which, hence, needs to transfer across the phase boundary before polymerization can proceed.

The process of initiation itself is not a simple one. It is widely accepted that an initiating species, such as the sulfate radical anion, is unlikely to readily transfer from the aqueous to the organic phase. The concept that the addition of several monomer units to the primary radical would be required before transfer becomes feasible was first suggested by Priest.[2] Recent data suggest that the rate-determining step for radical entry into a particle is the aqueous-phase propagation to a critical oligomeric size which enables entry to be successful. In the case of the emulsion polymerization of styrene the data suggest a critical oligomeric size of between two and five monomer units, but nearer to the former than the latter.[3] Naturally, the critical oligomeric size would be expected to vary from one monomer to another. Alternative fates for these oligomeric radicals in the aqueous phase would be further propagation or termination, and in the organic phase desorption from the particle. The last, however, is thought to be unlikely for radicals which have achieved the critical oligomeric size.[3]

Once entry of the initiating radical into a particle has been achieved, polymerization proceeds with the monomer being continually replenished by fresh monomer from the emulsion droplets. Thus, latex particles are generated, swollen by the presence of monomer. Termination of the growing polymer chain can occur upon entry of a second initiating radical into the same particle.

Termination is also a complicated process.[4] The two radical coils meet each other by translational diffusion and it follows, therefore, that once the latex particles are large enough, they may contain several radical chains. Contact between the radical centers and, hence, termination follow conformation reorientations of the polymer chains. At low conversions translational mobility is probably rapid, but at high conversions, the polymer chains will be so interwoven that diffusion will become difficult. Under these circumstances some radical centers would become so occluded within dead polymer molecules that they would be protected from termination and a high residual radical content within the latex results. However, it has been suggested that the radical centers can still wander and terminate by "residual termination" ("propagation diffusion").[5-7] The termination process, therefore, continues until, at conversions close to 100%, there would be a 50:50 chance of each latex particle containing one remaining unterminated radical center.

The number of particles per cubic decimeter obviously varies with particle size which itself is a function of the "recipe" used in the preparation of the latex. However, if we assume that there is a 50:50 chance of a particle containing a residual radical and that the detection limit of a modern ESR spectrometer is ca. 10^{-7} mol of radicals/dm^3, then it should be possible to detect the presence of unterminated radical chains by ESR spectroscopy, providing there are about 10^{17} particles/dm^3. Much higher radical concentrations would be expected during the course of the polymerization, particularly during the period when conversions were approaching 100%.

With these observations in mind we have undertaken a series of experiments involving the batch emulsion polymerization of methyl methacrylate (MMA). Experiments undertaken by two other groups of workers involving this monomer but employing different preparative techniques confirm the possibility that occluded radicals can be observed by ESR during the course of such a reaction.[8-11] It appears that ESR can also be employed to monitor propagating radicals during the course of the bulk polymerization of the same monomer.[12-14]

The object of our experiments was to monitor the occluded radical concentration from the onset of the reaction exotherm, until such a time as it either achieved a steady value or decayed away to a near-zero concentration. These experiments should provide information leading to a better insight into radical termination at very high conversions.

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The first direct observations of propagating radicals were reported by Ballard et al. during batch emulsion polymerization of MMA.[8,9] There are two alternative approaches. The first involves the use of continuous rapid flow techniques in which the emulsion is pumped through the spectrometer cavity. Due to the high dielectric of water this technique requires a flat cell (of path length ca. 1 mm) which reduces the volume of the sample which can be examined. It does, however, allow continuous monitoring of the radical concentration. An alternative approach is to freeze-quench a representative sample. Since ice has a significantly lower dielectric than water, much larger sample volumes are possible than with the rapid flow technique. Providing the freeze-quenching procedure is undertaken immediately after removing the representative sample (before significant kinetic relaxation can result) each sample presents a "snapshot" of the radical concentration at the sampling time. This latter technique has been selected for the experiments now reported.

Experimental Section

The emulsion polymerization of MMA was undertaken by employing a single charge batch reactor as described previously.[15] The standard recipe consisted of 150 g of MMA, 3 g of sodium lauryl sulfate [(SLS), as emulsifying agent], 0.75 g of dipotassium peroxodisulfate [(KP), as initiator] and deionized water to a total final weight of 500 g. Dissolved oxygen was removed as described[15] and the reaction was undertaken at 333 K under a blanket of nitrogen.

Experiments were also undertaken using this standard recipe at 323 and 328 K. Other experiments were undertaken varying the KP weight between 0.15 and 1.5 g (with a SLS weight of 3 g) and varying the SLS weight between 2.25 and 6.0 g (with a KP weight of 0.75 g).

A redox couple (ammonium peroxodisulfate–sodium disulfite) was also used as an alternative initiator. The concentration of the reagents in the couple and their rate of addition to the 150 g of MMA and 3 g of SLS in 345.3 g of water were arranged so as to achieve the same reaction exotherm time and temperature as observed by employing 0.75 g of KP. This was achieved by adding equal volumes of solutions of 0.85 g of ammonium peroxodisulfate and 0.85 g of sodium disulfite (both in 20 cm^3 of water) at a rate of 20 cm^3/h with respect to both solutions.

Samples were withdrawn, for ESR investigation, at various times during the course of the polymerization and rapidly quenched in 4-mm, paramagnetic-free, quartz sample tubes by freezing to 77 K in liquid nitrogen. ESR spectra were recorded on a Varian E3 spectrometer with 100-kHz magnetic field modulation with the sample temperature controlled by means of a Varian E4557 variable-temperature unit. All ESR spectra were recorded as a single scan at 173 K and, in order to maximize spectral intensities, were recorded at a microwave power of 5 mW and with a modulation amplitude of 1 mT. Estimates of radical concentrations (per cubic decimeter of MMA) were obtained by employing the Varian strong pitch reference sample as a standard. As with all ESR calibrations the resulting concentrations are considered to be accurate to ±50%.

Percentage conversion was monitored by withdrawing representative samples from the reaction mixture at 5-min intervals. The procedure involved freezing a 2-mL sample to liquid nitrogen temperature and evacuating to dryness in a vacuum oven at 313 K for 24 h, followed by gravimetric determination of percentage solids.

Particle size determinations (number average) were undertaken using a Coulter N4 submicron particle analyzer.

Results and Discussion

As a preliminary to ESR measurements a number of experiments were undertaken, at 333 K, employing the standard recipe detailed above, with the aim of characterizing the system. These experiments indicate an exotherm maximum approximately 17 min after commencement of the reaction with a scatter from run to run of about 2 min. The exotherm itself reaches a temperature of 354 ± 1 K. In addition each reaction was monitored periodically to determine percentage conversion to polymer. In all of the "standard" runs undertaken almost complete conversion (i.e., >95%) was achieved about 6 min after the exotherm maximum. Typical percent conversion and reaction temperature (exotherm) vs time plots for the standard recipe are presented in Figure 1.

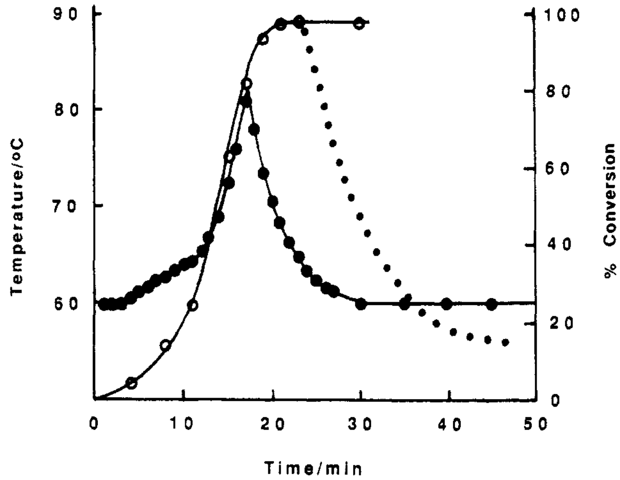

Figure 1. Percentage conversion (○) and reaction temperature (exotherm) (●) as a function of reaction time for a typical standard recipe emulsion polymerization of methyl methacrylate (in water) at an external thermostat temperature of 60 °C. The dotted line indicates the decay curve for occluded radicals (in arbitrary concentration units) for comparison purposes. Greater detail of this last curve is presented in Figure 3.

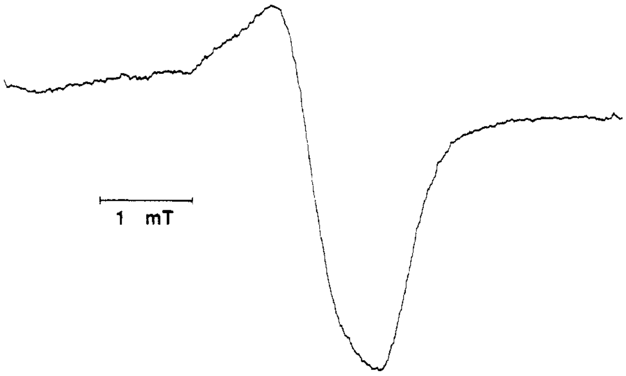

Figure 2. ESR spectrum, recorded at 173 K, of a representative sample taken 28 min after commencement of the batch emulsion polymerization of methyl methacrylate (standard recipe) at a reaction temperature of 333 K.

During the course of the polymerization representative samples were withdrawn for ESR examination. Very little ESR activity was observed during the early stages of the polymerization, and it can, therefore, be assumed that the occluded radical concentrations are below the detection limit of the spectrometer. The first measurable spectrum intensities were obtained at approximately the time of the exotherm maximum (17 min after commencement of reaction). Thereafter the spectrum intensity increased, reaching a maximum after approximately 23 min (i.e., about 6 min after the exotherm maximum), and then decreased, reaching low levels again after a reaction time of between 40 and 50 min. A typical spectrum, recorded at 173 K, is shown in Figure 2.

As would be expected for a spectrum of a frozen solution, the spectrum illustrated in Figure 2 shows virtually no identifiable hyperfine structure. However, the spectrum appears to arise from the same radical species during the course of these measurements. This was deduced by

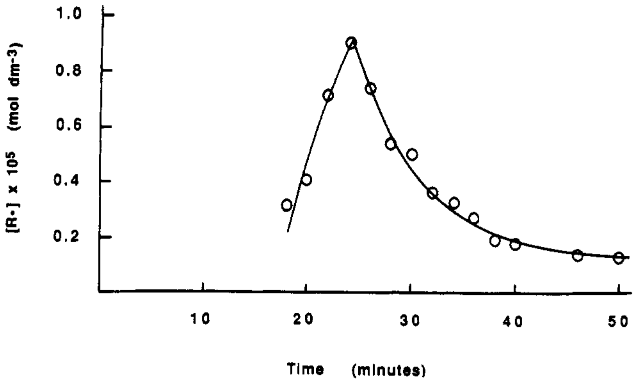

Figure 3. Occluded radical concentration (per cubic decimeter of polymer), monitored by ESR spectroscopy, as a function of reaction time for a typical batch emulsion polymerization of methyl methacrylate (standard recipe) at a reaction temperature of 333 K.

Table I
Parameters Obtained for the Batch Emulsion Polymerization of Methyl Methacrylate, at 333 K, at Different KP and SLS Concentrations

[KP]/g[a]	[SLS]/g[a]	particle size/nm	10^5[R*]*b*/mol dm^{-3}	*n*[c]
Variation of Initiator Concentration				
1.50	3.0	68	0.75	0.9
0.75	3.0	72	0.9	1.3
0.15	3.0	81	1.25	2.5
Variation of Surfactant Concentration				
0.75	6.0	61	0.5	0.4
0.75	3.0	72	0.9	1.3
0.75	2.25	78	1.5	2.7

[a] Per 500 g of reaction mixture. [b] The highest concentration (per dm^3 of polymer) achieved by the occluded radicals during typical runs (see Figure 3 as an example). [c] Maximum number of radicals per particle achieved during the reaction.

examining the growth and then the decline in the spectrum intensity at several points on either side of its central point. This analysis shows that the radical species involved remained consistent during both the growth and decay periods. Unfortunately, however, the lack of observable hyperfine structure in the ESR spectrum makes it impossible to unambiguously assign the spectrum to a single radical species. Other workers, employing spectrometers with repetitive scan facilities, have observed spectra with hyperfine structure attributable to the poly(methyl methacrylate) propagating radical.[8,10] We assume, that the major contribution to our spectra is also the poly(methyl methacrylate) propagating radical. However, the possibility that there may also be a contribution from peroxyl radicals, formed by reaction of the poly(methyl methacrylate) propagating radicals with oxygen, cannot be totally excluded although the rigorous exclusion of oxygen from the reaction system should minimize this possibility.

Figure 3 shows the variation in radical concentration during the course of a typical standard reaction. The maximum radical concentration occurs about 6 min after the reaction exotherm maximum and is achieved during the very latest stages of the reaction (i.e., between 95 and 98% conversion). The maximum concentration of radicals occluded within the polymer particles during a typical standard run is about 10^{-5} mol/dm^3 of polymer. Previous research, in which methyl methacrylate is either the sole or the predominant monomer, has indicated similar levels of radical activity. For example, approximately the same radical concentrations have been noted during the seeded batch emulsion polymerization of methyl methacrylate[8,9] and during the semicontinuous emulsion polymerization of a methyl methacrylate copolymer.[10,11] Slightly higher levels (ca. 10^{-4} mol dm^{-3}) appear to have been observed during the bulk polymerization of methyl methacrylate.[13] It is pleasing to note that all of these different systems indicate similar radical concentrations to those reported herein. A typical particle size in our experiments of 72 nm (indicating that 1 dm^3 of emulsion would contain 1.36×10^{18} particles) corresponds to an average of 1.3 radicals/particle. This level of radical activity within the particles is similar to those observed by Westmoreland et al. during the semicontinuous emulsion copolymerization of methyl methacrylate (with butyl acrylate and methacrylic acid).[10]

The data presented in Figure 3 show several interesting features. First, occluded radical concentrations remain very small (i.e., close to the detection limit of the spectrometer) until about the same time as the reaction exotherm maximum is achieved (corresponding to about 75% conversion). They then increase steeply, reaching their highest concentrations at approximately the same time as the reaction achieves 95–98% conversion (i.e., 6 min after the reaction exotherm). Thereafter, their concentration decreases to levels roughly consistent with between 0 and 0.25 radicals/particle.

The first appearance of significant occluded radical concentrations must correspond to the changing nature of the polymeric particles as the monomer levels decrease. Their first appearance, therefore, is related to the point where translational mobility has reduced sufficiently to prevent rapid radical–radical termination.

The maximum occluded radical concentration is reached at a point where only a small percentage (possibly as little as 1–3%) of unreacted monomer remains. Although initiating radicals are still being generated by the thermal decomposition of dipotassium peroxodisulfate, the number of new radicals achieving the critical oligomeric size is rapidly declining at this stage. Thus, radical–radical termination can only be achieved between radicals already occluded within the particles, with the small amount of residual monomer enabling propagation to accommodate termination. During this period of occluded radical decay, therefore, the kinetics of the system would be expected to follow the simple expression $-d(R^*)/dt = k_t[R^*]^2$ where R* refers to occluded radicals. Consequently, if radical–radical termination is occurring within the particles, the decrease in occluded radical concentration would be expected to be second order with respect to R*.

Kinetic aspects of our results will be discussed later within this paper.

Variation in Surfactant Concentration. Experiments were undertaken in which the SLS concentration was lowered and raised above that of the standard recipe with the KP concentration unchanged at 0.75 g (per 500 g of reaction mixture). A change in the SLS concentration would be expected to have a small effect upon the rate of KP decomposition.[16] However, the major effect is to change the size and, therefore, the number of particles present.[17] In their experiments involving the semicontinuous emulsion copolymerization of 8 BA/91 MMA/1 MAA Westmoreland et al.[11] noted an increase in occluded radical concentration with particle size. Our results for the batch emulsion polymerization of MMA also indicate an increase in occluded radical concentration with particle size (see Table I) although the range of particle size covered in our experiments is rather smaller than that covered by Westmoreland et al.[10,11]

The increase in the number of particles present as the SLS concentration increases is in accord with the Smith–Ewart theory,[17] and it would be reasonable to assume that the concentration of occluded radicals per particle should be proportional to the particle volume. The experimental observations, therefore, follow expectations in this respect.

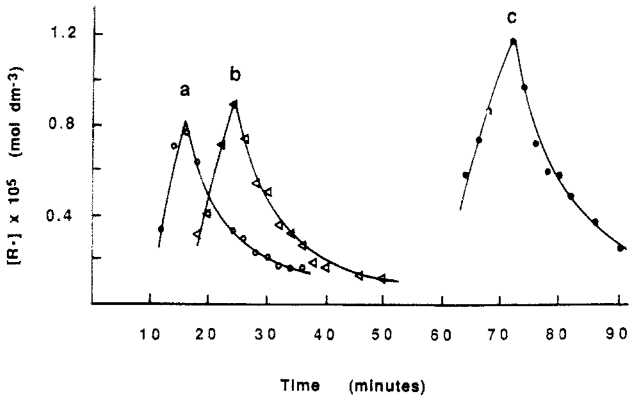

Figure 4. Influence of varying the KP concentration on the occluded radical concentration (per cubic decimeter of polymer), for the batch emulsion polymerization of methyl methacrylate at a reaction temperature of 333 K: [KP] = (a) 1.50 g, (b) 0.75 g, and (c) 0.15 g in a total reaction mixture of 500 g.

The time of the reaction exotherm, and hence the time at which the maximum occluded radical concentration is achieved, increases with a decreasing SLS concentration.

Variation in Initiator Concentration. Experiments were also undertaken in which the KP concentration was lowered and raised above that of the standard recipe with the SLS concentration remaining unchanged at 3.0 g. The experimental results obtained are illustrated in Figure 4. As expected, a decrease in KP concentration delays the reaction exotherm and results in a consequent delay in the time at which the maximum occluded concentration also results in an increase in particle size and, therefore, also results in an increase in occluded radical concentration with particle size (see also Table I).

One result to emerge from the experiments involving the variation of the SLS and KP concentrations is that the number of occluded radicals per particle (at the occluded radical maximum) increases with particle volume irrespective of whether the change in particle volume has been induced by varying the SLS or the KP concentrations.

Kinetics of Radical Decay. All of the experiments described above have been undertaken by employing KP as the initiator. One problem with such a system is that the initiator continues to supply radicals to the system long after the reaction exotherm. It is possible, therefore, that new radicals of critical oligomeric size can still be formed from small amounts of monomer remaining unreacted in the aqueous phase and that these new oligomeric radicals are responsible for the decay of the occluded radicals.

In order to distinguish between the above possibility and conventional polymeric radical–radical termination, further experiments were undertaken, employing the ammonium peroxodisulfate–sodium disulfite redox couple. The concentration of these redox reagents and their rate of addition were adjusted to give the same exotherm time and exotherm temperature as for the standard recipe. Under these conditions the occluded radicals reached the same maximum concentration as that reached with KP as initiator. In two further experiments the rate of addition of the redox initiator was maintained for a period of 6 min after the exotherm (this corresponding to the time at which the occluded radicals reach their maximum concentration), but then in one experiment the addition was terminated (thus significantly reducing the concentration of radicals in the aqueous phase) while in the other experiment the rate of addition was doubled (thus considerably increasing the concentration of radicals in the aqueous phase). The occluded radical concentrations and their decay curves were indistinguishable in all of these experiments. Conversions are high during this decay period (i.e., >96%) and so the diffusion rates of small molecules within the polymer are much reduced. Consequently, it can be anticipated that propagating polymeric radicals are predominantly removed by residual termination (propagation diffusion). The above observations support this view. Even so, small but significant monomer concentrations remain and during the course of the radical decay in our standard experiment (employing KP as initiator) propagating radicals of critical oligomeric size are still being formed. The rate of decomposition of KP is very much dependent upon the concentration of species such as SLS and methyl methacrylate.[18] For example, at 50 °C, about 1% decomposition has occurred after 60 min in "pure" water whereas in the presence of 2% v/v methyl methacrylate ca. 9% decomposition has occurred. Clearly, sufficient KP remains during the period of radical decay observed in our standard system to provide a supply of initiating radicals and hence, also, to create propagating radicals of critical oligomeric size.

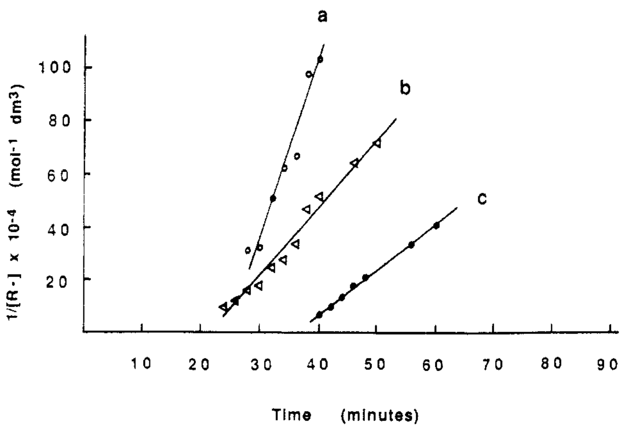

Figure 5. Inverse occluded radical concentration (per cubic decimeter of polymer) as a function of reaction time for the batch emulsion polymerization of methyl methacrylate at a reaction temperature of 333 K: [SLS] = (a) 6.0, (b) 3.0, and (c) 2.25 g in a total reaction mixture of 500 g.

In a particularly relevant experiment Zhu et al.[13] have shown that radicals are occluded during the bulk polymerization of methyl methacrylate employing UV illumination of 2,2′-azobis(2-methylpropionitrile) as a source of initiating radicals. When UV illumination was discontinued (and, consequently, when no new initiating radicals were being formed), it was found that the occluded radical concentration remained unchanged for several months. Although there is some evidence that the termination mechanism may differ in bulk compared to emulsion systems,[19] this latter observation is interesting when compared to the results just described, and termination involving newly entered propagating radicals, as well as long-established propagating radicals, cannot be excluded.

A kinetic analysis of the decay curves for all systems indicates that the decay follows second-order kinetics; typical 1/[R*] plots are presented in Figure 5.

Our results (summarized in Table II) are remarkably similar to those of Westmoreland et al.[11] (for the semicontinuous emulsion copolymerization of methyl methacrylate) who obtained a value for k_t of 340 dm^3 mol^{-1} s^{-1} at 333 K for a particle size of 50 nm and of 20 dm^3 mol^{-1} s^{-1} at 333 K for a particle size of 500 nm. In comparing results obtained by employing different techniques, it is important to remember that factors such as reaction vessel, stirrer design (size and shape), and stirrer speed can significantly influence the kinetic parameters of emulsion systems.

Nevertheless, our results (summarized in Tables I and II) and those obtained by Westmoreland et al. cited above

Table II
Parameters Obtained, for the Batch Emulsion Polymerization of Methyl Methacrylate at 333 K, for the Polymeric Radical–Radical Termination Rate Constant (k_t), at Different KP and SLS Concentrations

[KP]/g[a]	[SLS]/g[a]	particle size/nm	k_t/mol^{-1} dm^3 s^{-1}
Variation of Initiator Concentration			
1.50	3.0	68	975
0.75	3.0	72	410
0.15	3.0	81	305
Variation of Surfactant Concentration			
0.75	6.0	61	430
0.75	3.0	72	410
0.75	2.25	78	290

[a] Per 500 g of reaction mixture.

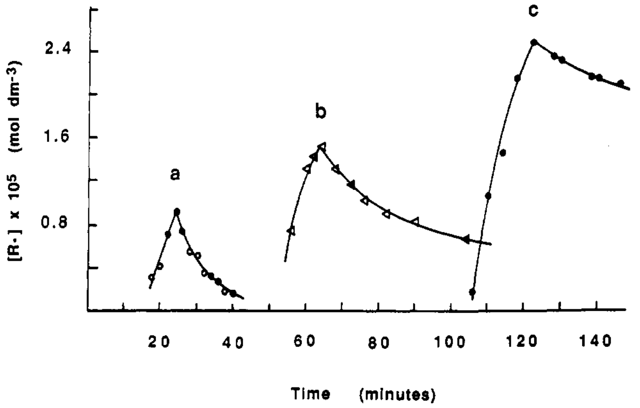

Figure 6. Influence of varying the reaction temperature on the occluded radical concentration (per cubic decimeter of polymer) for the batch emulsion polymerization of methyl methacrylate at (a) 333 K (reaction exotherm maximum at 17 min), (b) 328 K (reaction exotherm maximum at 52 min), and (c) 323 K (reaction exotherm maximum at 105 min).

for the semicontinuous system both indicate that k_t increases as particle size decreases. This could be a consequence of a greater rate of diffusion in the smaller particles. Alternatively, if small propagating radicals of critical oligomeric size are still available within the aqueous phase, the more favorable surface/volume ratio in smaller particles could also have a significant influence.

It should also be noted when results are compared that in our batch emulsion polymerizations the reaction temperature is still returning to that of the external thermostat bath (60 °C) during the early stages of the radical decay. For example, for the standard recipe, the reaction mixture is at a temperature of about 64–65 °C at the onset of the radical decay, returning to a temperature of 60 °C about 30 min after commencement of the reaction (see Figure 1).

Influence of Reaction Temperature. A further range of experiments, employing KP as the initiator in the standard recipe, were undertaken by varying the reaction temperature.

Several interesting features emerge from these experiments (see Figure 6). As expected, a decrease in the reaction temperature delays the reaction exotherm due to the reduced rate of radical production in the aqueous phase. This results in a corresponding delay in the time at which the occluded radicals achieve their maximum concentration. The occluded radicals also achieve higher concentrations as the reaction temperature is lowered. Two factors contribute to this feature. First, the lower rate of decomposition of KP results in a larger particle size and, secondly, the lower reaction temperature results in a lower value for k_t, thus allowing an increase in the occluded radical population.

A further feature of these results is the anticipated lower rate of occluded radical decay at lower temperatures [k_t = 410 mol^{-1} dm^3 s^{-1} at 333 K (particle size 72 nm), 35 mol^{-1} dm^3 s^{-1} at 328 K (particle size 135 nm), and 5 mol^{-1} dm^3 s^{-1} at 323 K (particle size 240 nm)]. In principle, it should be possible to obtain a guide to the activation energy for the termination reaction from these results but, unfortunately, this is precluded by the fact that the particle size also changes with reaction temperature.

Conclusions

Quantitative ESR measurements (employing the cryogenic quenching technique) have enabled values for the polymeric radical–radical termination rate constant, k_t, to be determined for the batch emulsion polymerization of methyl methacrylate at 333 K. These values represent the first values obtained by this method (previous results have concentrated on either seeded or semicontinuous techniques). The values obtained correspond to conversions approaching 100% and are, hence, due to residual termination processes. Although absolute ESR concentrations are only accurate to ±50%, the value obtained (410 mol^{-1} dm^3 s^{-1} for the standard recipe, particle size 72 nm) is in good agreement with others. For example, Ballard et al. have determined values of ca. 100 mol^{-1} dm^3 s^{-1} at 50 °C for samples at about 90% conversion by employing a seed of particle size 150 nm[19,20] and Westmoreland et al. have obtained values of 340 and 20 mol^{-1} dm^3 s^{-1} at 60 °C for particle sizes of 50 and 500 nm, respectively, by employing the semicontinuous approach and conversions of ca. 95–98%.[11] Our value is considerably below that observed in bulk polymerizations taken to low conversion,[12] but this difference is anticipated in view of the highly viscous nature of latex particles at conversions approaching 100%.

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