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REACTION TEMPERATURE PROFILES AND RADICAL CONCENTRATION MEASUREMENTS ON BATCH EMULSION COPOLYMERIZATIONS OF METHYL METHACRYLATE AND BUTYL ACRYLATE

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Abstract—Electron spin resonance (ESR) spectroscopy has been employed to monitor the occluded radical concentration during the batch (unseeded) emulsion copolymerization of methyl methacrylate and butyl acrylate. Occluded radical concentrations, above the detection limit of the ESR spectrometer, are only observed at methyl methacrylate mole fractions >0.96. The occluded radicals reach a maximum concentration at high conversion (*ca* 95%) and thereafter their concentraion declines via a second order termination process. The variation in the maximum reaction temperature and the time at which this maximum occurs with mole fraction has also been monitored and is discussed. The most surprising feature of these latter observations is that the rate of polymerization is much faster for butyl acrylate than for methyl methacrylate despite the greater propagation rate constant of the latter.

INTRODUCTION

Emulsion polymerization techniques are widely used in the commercial manufacture of a broad range of polymeric materials. 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). The thermal decomposition of the initiator (e.g. peroxodisulphate anions) generates a primary radical (e.g. sulphate radical anions) in the aqueous phase which, hence, needs to transfer across the phase boundary before polymerization can proceed.

It is widely accepted that a primary radical is unlikely to transfer readily 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 [1]. Recent data suggest that the rate-determining step for successful entry of a radical into a particle is aqueous-phase propagation to a critical oligomeric size. 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 latter, however, is thought to be unlikely for radicals which have achieved the critical oligomeric size [2].

Once entry of the initiating radical into a particle has been achieved, polymerization proceeds with the monomer being continually replenished from the emulsion droplets. Thus, latex particles are generated, swollen by the presence of unreacted monomer.

Termination of a growing polymer chain within a particle can occur as soon as a second initiating radical enters the same particle. At low conversions translational mobility is relatively rapid so the number of unterminated radical chains (i.e. the number of radicals per particle) remains low. However, as the volume of the particles and conversion percentage increase there is an increasing possibility of finding several unterminated chains in each particle. At high conversions, diffusion within the interwoven polymer chains becomes more difficult and some radical centres become so occluded within dead polymer molecules that they are protected from termination and a high residual radical content within the latex would be expected. However, it has been suggested that the radical centres can still wander and terminate by "residual termination" ("propagation diffusion") [3–5]. In principal, therefore, the termination process could, continue until, at conversions close to 100%, there would be a 50:50 chance of each latex particle containing one remaining unterminated radical centre.

The number of particles is controlled by many factors including the "recipe" used in the preparation of the latex. Nevertheless, radical concentrations high enough to be detected by electron spin resonance (ESR) spectroscopy would be anticipated at high conversions in such systems and have, indeed, been observed. However, considering that information concerning the nature and concentration of propagating radicals is vital in order to understand the emulsion polymerization process, it is surprising that ESR spectroscopy has not been more fully applied to these systems.

The first direct observations of propagating radicals during batch emulsion polymerization of methyl methacrylate were reported by Ballard *et al.* [6, 7].

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There are two alternative approaches. The first involves the use of a closed-loop continuous flow technique in which the emulsion is pumped through the spectrometer cavity [8, 9]. This approach has the disadvantage that the high dielectric of water requires the use of a flat aqueous 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 [6, 7, 10, 11]. Since ice has a significantly lower dielectric than water, much larger sample volumes are possible than with the continuous flow technique. Providing the freeze-quenching procedure is undertaken before significant kinetic relaxation can result, a "snapshot" of the radical concentration at the sampling time is obtained.

This latter technique has been selected for our experiments. We have previously reported a series of experiments involving the batch emulsion polymerization of methyl methacrylate (MMA) [12]. The object of these experiments was to monitor occluded radical concentrations from the onset of the reaction exotherm, until such a time as they either achieved a steady value or decayed away to a near zero concentration. These experiments showed that the occluded radical concentration increases noticeably once *ca* 80% conversion has been achieved, reaching a maximum at a time corresponding to near complete conversion, and then slowly decays due to "residual termination". The decay exhibits second-order kinetics with a termination rate constant of 410 $\mathrm{mol^{-1}}$ $\mathrm{dm^{3}\ sec^{-1}}$ at 333 K for a particle size of 72 nm. This value was the first obtained by this method (previous results having concentrated on either seeded or semi-continuous techniques) and is in good agreement with others [11].

We now describe the results of a further series of experiments in which we have undertaken the copolymerization of methyl methacrylate and butyl acrylate (BA) over a range of compositions. The object of these new experiments was to examine how the incorporation of a second monomer into the polymer [thus forming a copolymer with different characteristics from poly(methyl methacrylate)] influences the ability of the radical centre to terminate as the overall composition (and, hence, nature) of the copolymer changes.

EXPERIMENTAL PROCEDURES

The emulsion polymerization of MMA was undertaken employing a single charge batch reactor and full details of the vessel design and reaction protocol have been fully described previously [13]. The standard "recipe" for the preparation of poly(methyl methacrylate) homopolymer consisted of 150 g MMA, 3 g sodium lauryl sulphate [(SLS), as the emulsifying agent], 0.75 g of dipotassium peroxodisulphate [(KP), as the initiator] and de-ionised water (346.25 g) to a total final mass of 500 g. A series of experiments were also undertaken employing MMA and BA as comonomers with comonomer mole fractions ranging from 0.9 to 0.0 with respect to BA. In these latter experiments the volumes of the comonomers were arranged such that their total mass was 150 g. Dissolved oxygen was removed as previously described [13] and all reactions were undertaken at an external thermostat temperature of 333 K under a blanket of nitrogen. Both of the monomers were used as supplied (MMA—B.D.H and BA—Lancaster Synthesis) in order to reproduce as closely as possible the conditions under which these reactions are undertaken commercially. As such the monomers were stabilised with 0.01% quinol and 200 ppm MeHX, respectively, as inhibitors.

Samples were withdrawn, for ESR investigation, at various times during the course of the polymerization and immediately 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 maximise spectral intensities, were recorded at a microwave power of 5 mW and with a modulation amplitude of 1 mT. Estimates of radical concentrations (per $\mathrm{dm^{3}}$ of monomer) were obtained employing the Varian strong pitch reference sample as a standard and, as with all ESR calibrations, they are considered to be accurate to ±50%.

RESULTS AND DISCUSSION

Although our main interest in these experiments was to discover how the intensity of the ESR spectrum varied with time during the preparation of various MMA–BA copolymers the reaction temperature was also monitored for each preparation. These latter measurements also presented some interesting features which are described below.

Variation in reaction temperature with comonomer composition

The maximum reaction temperature for the homopolymerization of MMA, using the batch technique described herein, was found to be 354 ± 1 K (see also Ref. [12]) and for the homopolymerization of BA to be 358 ± 1 K. Some typical reaction temperature profiles are shown in Fig. 1 and the maximum temperature achieved for the various (initial) comonomer mole fractions is illustrated in Fig. 2.

The total area beneath each temperature profile changes little with comonomer composition but the maximum reaction temperature arises much earlier for the homopolymerization of BA than it does for

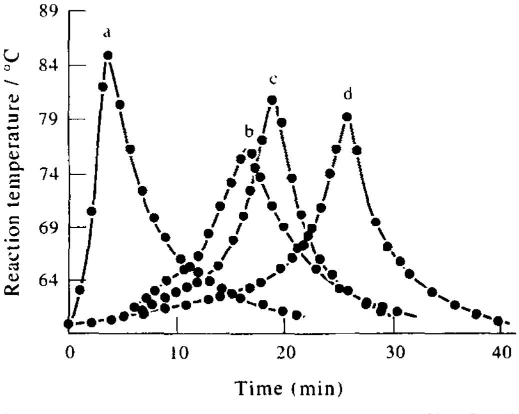

Fig. 1. Some typical reaction temperature profiles for the emulsion copolymerization of methyl methacrylate and butyl acrylate at an external thermostat temperature of 333 K. Methyl methacrylate mole fractions are (a) 0.0, (b) 0.2, (c) 1.0 and (d) 0.8.

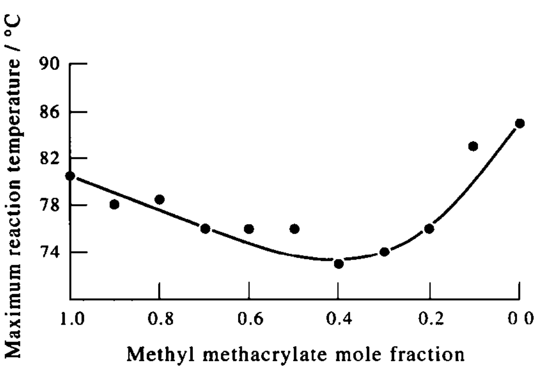

Fig. 2. The variation in maximum reaction temperature with initial comonomer mole fraction for the batch emulsion copolymerization of methyl methacrylate and butyl acrylate at an external thermostat temperature of 333 K.

the homopolymerization of MMA. Exactly the same latter observation has been made for this system by Emelie *et al.* [14] even though their experimental conditions varied in several ways from ours.

There are several factors to consider here. In emulsion systems the rate of polymerization (R_p) is given by

$$R_p = k_p \cdot [M] \cdot (n/N_A) \cdot N_p$$

(k_p is the propagation rate constant, n the number of radicals per particle, N_A Avogadro's number and N_p the average particle number per unit volume). Taking the respective k_p values as ≈650 dm^3 mol^{-1} sec^{-1} for MMA (at 323 K) [15] and ≈450 dm^3 mol^{-1} sec^{-1} for BA (at 323 K) [16] the earlier maximum in the reaction temperature for BA contrasts with the expected difference in the rate of polymerization based on the two k_p values. Note also that the two initial monomer concentrations differ in our experiments {[MMA] = 2.95 mol dm^{-3}; [BA] = 2.27 mol dm^{-3}} such as to favour a greater R_p for MMA. Emelie *et al.* have attributed this contrast with expectation to a much greater value of n for BA than for MMA [14] but, unfortunately, at this stage of the polymerization radical concentrations in our experiments lie below the detection limit of the spectrometer (see later) so this cannot be verified experimentally. In addition, there is no reason to suppose that the average particle number per unit volume is the same in these two homopolymerizations.

The reaction temperature profiles in the centre of the mole fraction range are broader and have a lower maximum temperature than those nearer to either of the homopolymers (see Fig. 2). Assuming that the maximum reaction temperature qualitatively reflects the maximum rate of polymerization then the latter decreases towards the middle of the mole fraction range. For a binary emulsion system such as this the overall rate of propagation at any mole fraction can be expressed in terms of four kinetic functions (k_M, k_B, r_M and r_B), the monomer concentrations [M] and [B], and their mole fractions x_M and x_B (where B represents butyl acrylate and M represents methyl methacrylate) [17], i.e.

$$k_p = [1/(r_B/k_B + r_M/k_M([M]/[B]))] \cdot \{[r_M([M]/[B] + 1)]x_M + [r_B + ([M]/[B])]x_B\}.$$

However, assuming that the maximum rate of propagation occurs at about 50% conversion it is the value of k_p at 50% conversion (allowing for feed composition drift) which is important. We have calculated a series of such values and these calculations clearly show (see Table 1) a steady decline in the value of k_p with MMA mole fraction both at the commencement of the reactions and at 50% conversion (i.e. allowing for feed composition drift). Since these values do not follow the experimental trends, qualitatively expressed in Fig. 2, we are forced to the conclusion that it must be the change in the $n \cdot N_p$ term, and the increasing importance of this term at high BA mole fractions, that is responsible for the higher rate of homopolymerization of BA compared to MMA and also for the increasing rate of polymerization at about 50% conversion.

Variation in the time at which the maximum reaction temperature occurred with comonomer composition

Part of our investigations of this system also included a study of the time at which the reaction temperature reached a maximum as a function of mole fraction. For the homopolymerization of BA the maximum occurs after *ca* 4 min and for MMA after *ca* 17 min. The much shorter time for the former is accompanied by a higher maximum reaction temperature as detailed above. As explained above, this copolymerization system has also been investigated by Emelie *et al.* [14] although with some variations in reaction conditions such as temperature (323 K), monomer:water ratio, initiating system and surfactant. However, they too observed a much earlier temperature maximum for the homopolymerization of BA and, in addition, these same workers also studied a single copolymerization ($x_M = 0.5$). In the latter case the maximum reaction temperature occurred at virtually the same time as that for the homopolymerization of MMA.

Our results cover a much greater comonomer mole fraction range (0.1–0.9 in 0.1 increments) and the times at which the resulting maximum reaction temperature occurred are presented in Fig. 3.

We anticipated a gradual change in the time at which the maximum reaction temperature occurred with mole fraction between those of the two

Table 1. The values of kp initially (i.e. at the commencement of the reaction) and at 50% conversion (i.e. allowing for feed composition drift with monomer consumption)

	Initial values (i.e. 0% conversion)										
x_M	1	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1	0
kp/dm^3 mol^{-1} sec^{-1}	650	643	633	623	612	598	582	563	538	503	450
	Values at 50% conversion										
x_M	1	0.86	0.73	0.60	0.48	0.36	0.25	0.16	0.08	0.03	0
kp/dm^3 mol^{-1} sec^{-1}	650	640	627	612	596	575	552	526	496	469	450

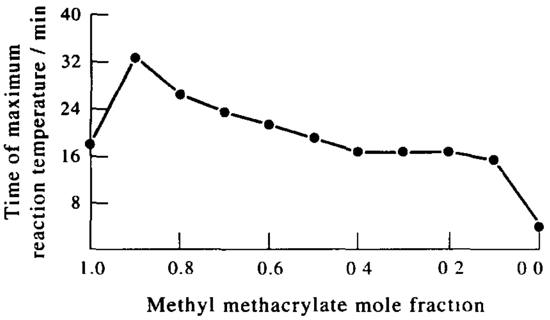

Fig. 3. The variation in the time at which the maximum reaction temperature occurred with initial comonomer mole fraction for the batch emulsion copolymerization of methyl methacrylate and butyl acrylate.

homopolymers but Fig. 3 clearly shows a more complex pattern of behaviour. However, it is interesting to note that our time for the 0.5 mole fraction lies close to that for the homopolymerization of MMA, in accord with the observations of Emelie *et al.* [14].

There are, in fact, two surprising features to Fig. 3. First, at many mole fractions, but principally those between $x_B = 0$ and 0.6, the time at which the maximum reaction temperature occurs is greater than that for either homopolymerization. Secondly, there is a sudden decrease in this time at low mole fractions (i.e. 0–0.1) of either comonomer. It is not easy to see why a small mole fraction of either BA or MMA should have such a marked effect.

This is, of course, a complicated system. The overall comonomer concentration increases as the MMA mole fraction increases and consequently the initial monomer:water ratio slowly changes with mole fraction. Emelie *et al.* have shown that an increasing ratio (in our case as the MMA mole fraction increases) delays the reaction exotherm in this system [16], and the same is true in other systems [18, 19]. Also, there is considerable evidence to suggest that monomers have an influence on the rate of decomposition of the peroxodisulphate anion [20] and it is likely that there is no single simple explanation of this feature.

Variation in occluded radical concentration with comonomer composition

In a previous publication we have studied the variation in radical concentration during the course of the homopolymerization of MMA for typical "standard" reaction conditions [12]. In this system the maximum radical concentration occurs about 6 min after the maximum reaction temperature and is achieved during the very latest stages of the reaction (i.e. between about 95 and 98% conversion). The maximum concentration of radicals occluded within the polymer particles during a typical "standard" run is about 10^{-5} mol per dm^3 of polymer. Previous research under slightly different conditions, in which MMA 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 MMA [6, 7] and during the semi-continuous emulsion polymerization of an MMA copolymer [10, 11].

It is important to remember that occluded radical concentrations only exceed the detection limit of the ESR spectrometer in the very last stages of polymerization. Presumably, during much of the polymerization plasticization of the latex by unreacted monomer allows termination to proceed sufficiently rapidly to prevent significant occluded radical concentrations to develop. However, at very low unreacted monomer levels plasticization is reduced to a point where translational mobility is insufficient to maintain rapid termination. In addition, of course, the much higher particle volumes expected at high conversions will be more likely to sustain more than one radical per particle than the smaller particles present in the earlier stages of the polymerization. In experiments undertaken at a comonomer mole fraction <0.9 with respect to MMA we failed to observe any significant level of radical activity. In fact, only experiments with a mole fraction between 1.0 and 0.96 (with respect to MMA) gave rise to any significant ESR activity thus indicating much greater translational mobility in poly(butyl acrylate) than in poly(methyl methacrylate). This is consistent with the T_g values of the two homopolymers [poly(methyl methacrylate) ≈ 373 K and poly(butyl acrylate) ≈ 220 K] with that for poly(methyl methacrylate) being significantly above both the external thermostat and maximum reaction temperatures [21].

In all of these latter experiments the maximum ESR intensity was observed between 6 and 8 min after the maximum reaction temperature (which, itself, was progressively delayed upon increasing BA mole fraction over this range, see above). The relevant plots of radical concentrations for each experiment in the MMA mole fraction range 0.97–1.0 are presented in Fig. 4. It can be clearly seen that the maximum radical concentration achieved declines rapidly as the mole fraction of BA in the feed increases. At a BA feed mole fraction of 0.04 only a small radical concentration of *ca* 10^{-6} mol per dm^3 polymer was observed. At higher BA mole fractions the radical concentration fell below that detectable under the measurement conditions.

In all cases the rate of ESR spectral decay is second

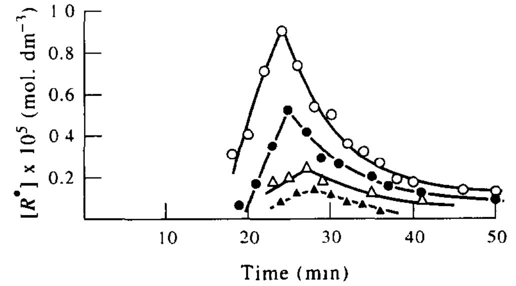

Fig. 4. Occluded radical concentration (per cubic decimetre of polymer), monitored by ESR spectroscopy, as a function of reaction time for the batch emulsion copolymerization of methyl methacrylate and butyl acrylate at an external thermostat temperature of 333 K. Methyl methacrylate mole fractions: 1.0 (○), 0.99 (●), 0.98 (△) and 0.97 (▲).

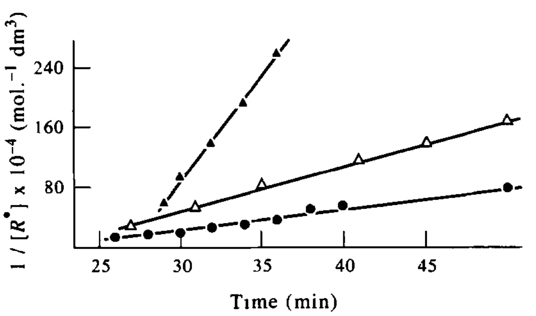

Fig. 5. Inverse occluded radical concentration (per dm^3 of polymer) as a function of reaction time for the batch emulsion copolymerization of methyl methacrylate and butyl acrylate at an external thermostat temperature of 333 K. Methyl methacrylate mole fractions: 1.0 (●), 0.98 (△) and 0.97 (▲).

order (see Fig. 5) with respect to occluded radicals with the rate of decay increasing as the BA feed mole fraction increases. This increase in the rate of occluded radical decay with increasing BA content is, of course, consistent with the failure to observe occluded radicals in copolymerizations in which the initial feed BA mole fraction exceeds 0.05.

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