Communications to the Editor

Application of Electron Spin Resonance Spectroscopy to Emulsion Polymerization

Although free radical byproducts have previously been detected by ESR in emulsion polymerization systems,[1] propagating free radicals apparently have not been observed directly. This failure presumably results from the low concentration (ca. 10^{-7} mol dm^{-3} of latex[2]) of propagating free radicals in such systems. The advent of commercial ESR spectrometers, which have enhanced sensitivity and high field stability, allows the acquisition of cumulative-scan data. This opens up the possibility of detecting free radicals in suitable emulsion polymerization systems. The quantitative measurement of the free radical concentration in such systems when coupled with the concomitant measurement of the polymerization rate enables the propagation rate coefficient to be determined directly. Apart from such quantitative goals, the direct observation of ESR spectra of the propagating species is qualitatively useful in guiding mechanistic deductions.

The heterogeneous nature of an emulsion polymerization system renders difficult the direct exploitation of in situ ESR spectroscopy (e.g., using rapid flow techniques). Spectra are most readily obtained in these systems by sample removal, followed by quenching. Recent studies[3] have shown that in a typical emulsion polymerization system (styrene at 50.0 °C), the kinetic relaxation time of the free radical concentration is ca. 10^3 s. It should thus be possible to freeze an emulsion polymerization sample without the occurrence of significant changes in the free radical concentration. Freezing permits a much greater sample size to be placed in the ESR cavity since solid ice has a significantly lower dielectric constant than liquid water (which is a major constituent in most emulsion polymerization systems). The presence of liquid water always places a severe restriction on the ESR sample size because its dielectric properties tend to reduce the quality factor of the cavity and hence the signal intensity, to an impracticably low value.[4] An additional benefit of cooling to ca. 100 K is that there is a significant increase in sensitivity due to the Boltzmann factor.

This paper reports the successful application of electron spin resonance to the identification and measurement of the concentration of propagating free radicals in the emulsion polymerization of methyl methacrylate. Some preliminary observations with styrene are also reported. A subsequent publication will show how it is possible to combine these ESR techniques with kinetic studies to deduce the rate coefficients for propagation and also to obtain additional mechanistic information.

Experimental Section. The kinetics of the emulsion polymerizations were followed dilatometrically as described previously.[3] These measurements yielded the fractional conversion of monomer to polymer at the moment when any sample was removed (via a tap incorporated into the base of the dilatometer) for ESR spectroscopy. Quartz ESR tubes could be connected both to this tap and to a vacuum line.

A typical experiment was performed as follows: An Aerosol MA80 solution (0.909 g in 60.0 cm^3 of water) was placed in the dilatometer, and distilled methyl methacrylate (MMA) (22.2 g) added. The mixture was emulsified by vigorous stirring and a poly(methyl methacrylate) seed latex (30.7 g, containing 16.0% (w/w) polymer) of known particle radius (34 nm) added. This seeded mixture was stirred for 12 h at room temperature. The monomer swollen seed particles were next equilibrated with the emulsion droplets at 50.0 °C, degassed on a vacuum line, and flushed with nitrogen. Degassed potassium peroxydisulfate solution was then added under a stream of nitrogen to initiate polymerization. Samples for ESR study were removed into evacuated ESR tubes (3.0 mm internal diameter) after various polymerization times and frozen by immersion in liquid nitrogen. The tubes were then sealed and stored in liquid nitrogen.

ESR spectra were recorded at 100 K and also at 323 K,

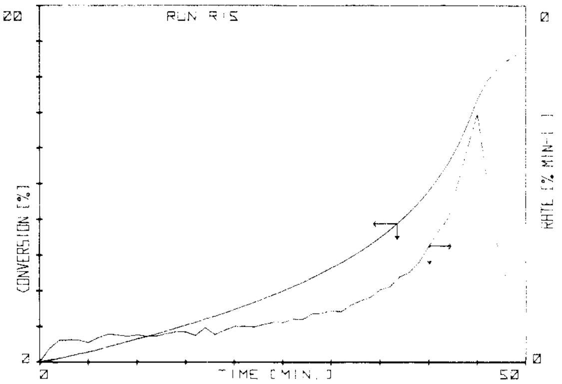

Figure 1. Fractional conversion and rate of polymerization as a function of time for a typical seeded MMA emulsion polymerization at 50 °C.

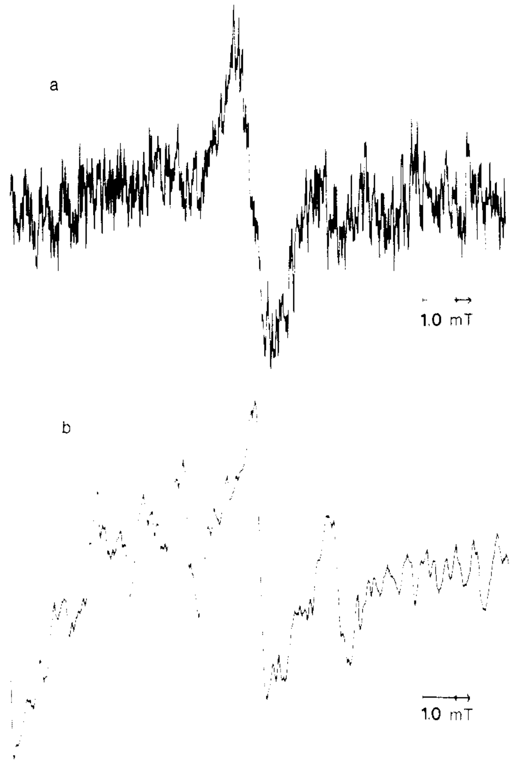

Figure 2. ESR spectra of samples taken from seeded emulsion polymerizations of MMA: (a) 200 s single scan at 100 K after 15 min polymerization; (b) 10 scans of the same sample.

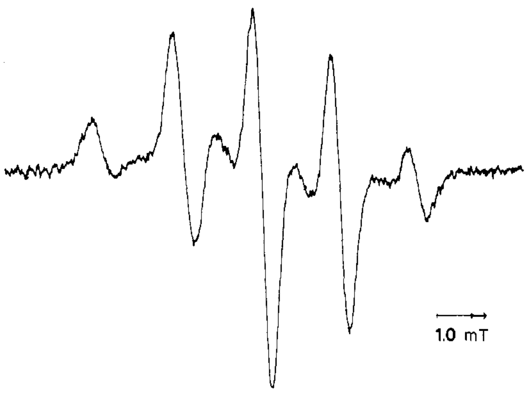

Figure 3. ESR spectrum at 100 K of a sample removed from the seeded MMA emulsion polymerization 60 min after commencement of polymerization.

with a Bruker ES 200D, interfaced to a PDP11-34 computer. The latter facility permitted both signal accumulation and the subsequent computation of the radical concentration by double integration and comparison with appropriate standards.

The absence of significant particle nucleation in all the systems studied was established by electron microscopy.

Results and Discussion. Polymerization. Typical fractional conversion and rate of polymerization vs. time curves for a seeded MMA emulsion polymerization are shown in Figure 1. After a brief induction period, there was a short approach (lasting only a few minutes) to an approximate steady state. This was followed by a period of approximately constant rate (of ca. 30-min duration), almost all of which corresponds to interval II of a classical ab initio emulsion polymerization (i.e., in the absence of particle nucleation and with growth of the seed latex particles occurring in the presence of monomer droplets). A region characterized by a rapid increase in rate then ensued, after which the rate declined as complete conversion of monomer to polymer was approached. This entire region corresponds to interval III of an ab initio emulsion polymerization (i.e., polymerization of monomer within the latex particles after exhaustion of the monomer droplets at the end of interval II). The increase in rate (by almost an order of magnitude) can be attributed to the Norrish–Trommsdorff gel effect.[5]

ESR Spectra. Constant Rate Period. A typical single-scan ESR spectrum of samples taken in the region of constant rate is shown in Figure 2a. The signal was of very low intensity, being close to the limit of resolution of the spectrometer. This is reflected in the poor signal-to-noise ratio and is consistent with a low free-radical concentration in the seed particles. This is in accord with the relatively slow polymerization rate observed in the period of approximately constant rate. The spectrum shape is poorly resolved, although there is a strong central line and indications of the presence of fine structure between 2.5 and 6.0 mT from the center.

In order to improve the signal-to-noise ratio, the ESR signal was accumulated for 2000 s, resulting in the spectrum displayed in Figure 2b. The fine structure is now clearly apparent. Comparison with the spectrum observed at longer polymerization times, when the free radical concentration was higher, confirms that it was the poly(methyl methacrylate) propagating radical that was being observed.

Accelerating Rate Period. The ESR spectrum that was observed in the region of accelerating rate is shown in Figure 3. Note that the signal-to-noise ratio of the spectrum observed in interval III is considerably higher than that of the spectrum recorded in interval II. This is a consequence of a substantial increase in the radical concentration in this region. This increase may be attributed to a marked reduction in the bimolecular termination rate coefficient that accompanies the consumption of monomer within the latex particles after the monomer droplets have been exhausted.

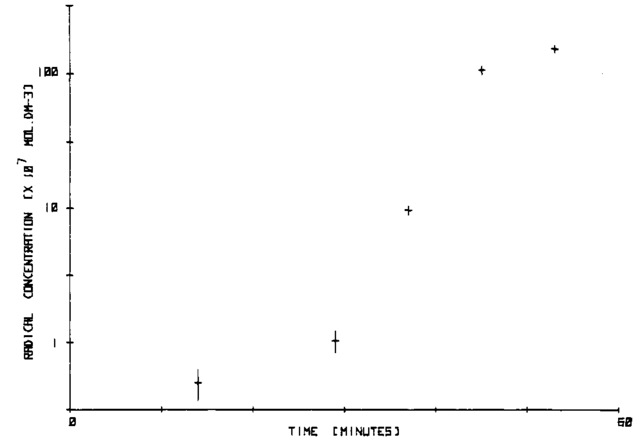

Figure 4. Radical concentration vs. polymerization time for seeded emulsion polymerization of MMA at 50 °C.

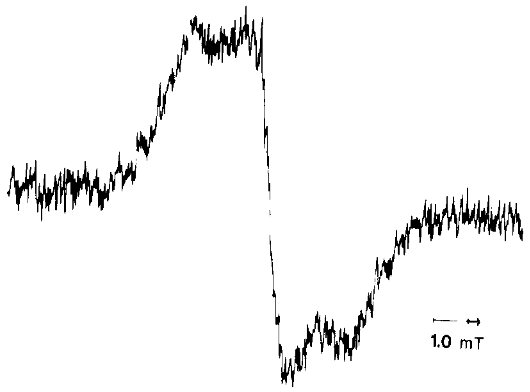

Figure 5. ESR spectrum at 100 K of a sample taken 60 min after the addition of styrene (25% (w/w) of polymer) to a fully polymerized (>99%) seeded MMA emulsion polymerization 165 min after initiation.

The ESR spectrum observed in interval III comprises five major lines (with hyperfine splitting of 2.5 mT) and four intermediate lines of much lower intensity. This 5 + 4 line alternating spectrum corresponds closely to that reported previously[6] for the poly(methyl methacrylate) propagating radical in a solid-state matrix.

The radicals are trapped within the latex particles and not in the aqueous phase. This was confirmed by removing a sample from the dilatometer at the end of interval III, placing it into a 1.0-mm internal diameter ESR tube without freezing, and recording the spectrum at 323 K. The spectrum was unchanged from that recorded at 100 K, confirming that the radicals were trapped within the latex particles. The spectrum was unchanged in shape and area after 16 h at 25 °C. Therefore, the radicals are in a solid and not a mobile phase. This conclusion was further confirmed by recording the spectrum at 323 K and then at 100 K and again at 323 K. No significant changes in shape were observed on freezing the sample and then melting it. These results indicate that the concentration of free radicals in the aqueous phase was too small to be detected. Given that the aqueous-phase monomer concentration is usually relatively small (ca. 0.15 mol dm^{-3}) compared with that in the particle (ca. 7.0 mol cm^{-3}),[7] we may conclude that the primary locus of polymerization in these seeded emulsion polymerizations of MMA was the latex particles. This is in conformity with the classical Harkins–Smith–Ewart viewpoint.[8,9] The alternative proposal by Medvedev[10] that polymerization occurs at the interface between the latex particles and the aqueous dispersion medium is unlikely to be correct for these systems.

Radical Concentration. The concentration of PMMA-propagating radicals in the sample of polymerization latex could be determined from the ESR spectra. Figure 4 shows that the radical concentration vs. polymerization time curve is sigmoidal in shape. This displays three regions of radical concentration: (i) a low value (ca. 10^{-7} mol dm^{-3}) during interval II; (ii) a rapid increase during the period of accelerating rate in interval III; (iii) a limiting value of ca. 10^{-5} mol dm^{-3} at complete conversion. The value of $\bar{n}$ (the average number of free radicals per latex particle) was ca. 100 at the end of interval III. A quantitative treatment of the relationship between the radical concentration and the polymerization rate will be presented in a subsequent paper.

Styrene Polymerization. No ESR spectrum was observed for samples taken from ab initio emulsion polymerizations of styrene. Radicals could be detected, however, by the postaddition of distilled styrene (ca. 25% (w/w) on polymer) to the seeded MMA emulsion polymerization mixture 165 min after the addition of initiator (cf. Tanaka et al.[11]). Note that this postaddition of styrene was performed in the absence of oxygen and at a time when the dilatometric measurements indicated that the polymerization of MMA was essentially complete (>99%).

The spectrum of a sample taken 60 min after the postaddition of styrene in the manner described above is shown in Figure 5. It can be attributed to the polystyryl-propagating radical in a solid matrix. The spectrum appears to consist of a broad triplet with a hyperfine splitting of ca. 2.6 mT and a width at half-height of 1.4 mT. The radical concentration was found to be the same as that of the poly(methyl methacrylate) radicals prior to the addition of styrene. This suggests that termination reactions do not occur at an appreciable rate at polymer concentrations above 80% (w/w) in this system. The absence of a detectable spectrum associated with a propagating radical in the emulsion polymerization of styrene may thus be attributed to (a) a low radical concentration in the latex particles, (b) the broadness of the lines in any such spectrum of radicals in the solid state, and (c) the ease with which the polystyryl-propagating radical is power saturated.

The techniques reported in this paper will have important future applications in quantitative kinetic studies of emulsion polymerization systems. The direct measurement of the average number of free radicals per particle as a function of time when coupled with rate measurements allows the determination of the rate coefficients for the microscopic events (e.g., free radical propagation, entry, desorption, and termination) that govern emulsion polymerization kinetics. In this way, extensive mechanistic deductions become possible.

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Registry No. Methyl methacrylate, 80-62-6; styrene, 100-42-5.

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