Continuous ESR Measurement of Propagating Free-Radical Concentrations for Batch Emulsion Polymerization of Methyl Methacrylate

Hsiu-Rong Chang,[†] Hsing-Yeh Parker,[‡] and David G. Westmoreland*,[†]

Research Laboratories, Rohm and Haas Company, Spring House, Pennsylvania 19477, and Bristol, Pennsylvania 19007

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Free-radical emulsion polymerization is an extremely important process for synthesis of a wide variety of polymer systems and thus has been widely studied for many years. However, one of the more difficult problems in fully understanding emulsion polymerization is the characterization of the propagating free radicals involved in the process. Information about the nature and the concentration of the propagating free radicals is vital for the ultimate development of a complete understanding of the complex emulsion polymerization process. While ESR has been applied previously to the study of bulk polymerization,[1] it is only rather recently that modern ESR techniques have been applied to study propagating free radicals in batch emulsion polymerization of methyl methacrylate[2] (MMA) and in semicontinuous emulsion polymerization of a PMMA copolymer.[3,4] Recent work[5] in our laboratory has developed a closed-loop flow system which allowed continual ESR analysis of semicontinuous emulsion polymerization without freezing intermediate samples. This new technique has two limitations when applied to batch emulsion polymerization. First, during the autoacceleration period it is difficult to collect ESR magnetic field sweep signals that can thoroughly characterize the rapidly changing radical concentration. Second, closed-loop flow of latexes containing high levels of monomer is problematical. Thus our laboratory has been interested in further developing our techniques, and we report here on the development of a continuous flow technique using ESR to allow study of propagating free-radical concentrations on an essentially continuous basis during a batch emulsion polymerization of MMA. The utility of this technique is illustrated by the measurement of free-radical concentrations for two particle size latexes of an MMA polymerization system.

In carrying out these experiments, we have used a custom-built experimental setup designed specifically for coupling an emulsion polymerization directly to an ESR spectrometer. A complete setup for carrying out an emulsion polymerization is placed in a fume hood on a table directly over the ESR magnet. A custom-built glass polymerization reactor is used which has a water jacket for thermal control and an exit tube for material to be transferred to the cavity of the ESR spectrometer. After the batch emulsion polymerization reaction has been initiated, the polymerizing latex is allowed to flow by gravity out of the reactor, through the ESR cavity, and then into a reservoir below the cavity. A custom-built ESR flat cell (13 mm wide and 0.3 mm thick) and Dewar insert are used to allow the latex to flow through the cavity; more details on the experimental setup have been reported elsewhere.[5] During the experiment the ESR spectrometer is operated at constant magnetic field such that the measurement point is at the top of one of the peaks of the nine-line PMMA propagating radical ESR spectrum; the intensity at the peak maximum is then monitored as the reaction proceeds. Our results to date do not detect any change in line width during the portion of the reaction where we can readily detect the radical signal. The free-radical concentration at the end of the run is calibrated by obtaining a time-averaged magnetic field sweep spectrum and comparing its peak area from double integration to standard solutions of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyl-*N*-oxy. The radical concentrations should be regarded as approximate at this time.

Batch emulsion polymerizations of MMA were carried out under a nitrogen atmosphere in the 5-L glass reactor described above according to the following procedure. An emulsified monomer mixture containing 148 g of water, 6.05 g of 45% sodium dodecyldiphenyloxide disulfonate solution, and 544 g of MMA was added to 2233 g of water at 50 °C. In the case of 230-nm particle size runs, 167 g of PMMA seed latex (16.6% solids) was also added to the initial reactor charge. The polymerization was initiated with 0.408 g of sodium sulfoxylate formaldehyde and 0.408 g of sodium persulfate, each dissolved in 28 g of water, with the initiation temperature being about 46 °C. The temperature of the reaction mixture was monitored by a thermocouple, and the conversion was measured by solid content analysis of samples withdrawn periodically from the reactor during the polymerization. The temperature in the cavity of the ESR spectrometer was set at 55 °C. The ESR spectrometer is a Bruker Instruments Model ESP-300 equipped with a computerized data system.

The experiment described above was carried out to study the synthesis of relatively high molecular weight PMMA, with M_w of about 3–6 million. The signal for the propagating free radical of PMMA was continuously monitored during the synthesis with the collection of data points every 2.6 s. Figure 1 shows conversion and free-radical concentration data for an MMA polymerization which achieved a final particle size of about 110 nm. The reaction begins very slowly, and the propagating free-radical concentration is low enough to be near or below our detection limit. Later there is a period in which the reaction accelerates to its maximum rate as indicated by conversion, which is observed in Figure 1 in the time range of about 18–22 min. The propagating radical concentration starts to increase noticeably at about 40% conversion, but most of the increase occurs in the range of 80–90% conversion. When the propagating free-radical concentration reaches its maximum, the conversion is about 93% complete. Even after the reaction is essentially complete, the propagating free-radical concentration continues to maintain that constant value during our observation time. We infer from this phenomenon that the free radicals remaining at the end of the polymerization are "trapped" in the polymer matrix, which is well below its T_g value even at the peak reaction temperature of about 58 °C. In the time that it was possible for us to observe the free radicals in this experiment, there is no discernible loss of ESR signal intensity.

We have also carried out a similar reaction to the first one but in this case used a seed latex to achieve a larger particle size of about 230 nm. Figure 2 shows the analogous ESR data for the propagating free-radical concentration for this polymerization. There are a number of similarities, including a lag time of low propagating radical concentration and a rapid increase in free-radical concentration as the polymerization achieves a high rate. One difference

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[†] Rohm and Haas Co., Spring House, PA 19477.

[‡] Rohm and Haas Co., Bristol, PA 19007.

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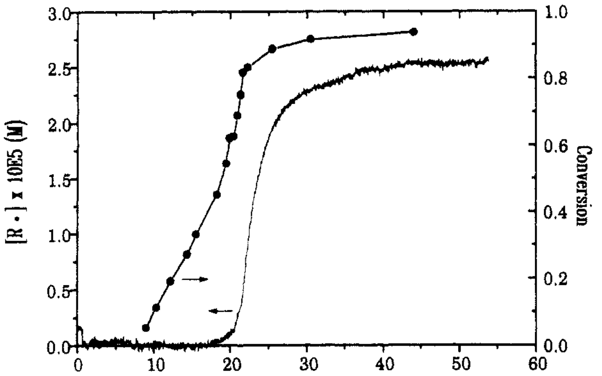

Figure 1. Conversion (filled circles) and propagating free-radical concentration (based on emulsion volume) versus time for a 110-nm batch emulsion polymerization reaction of MMA.

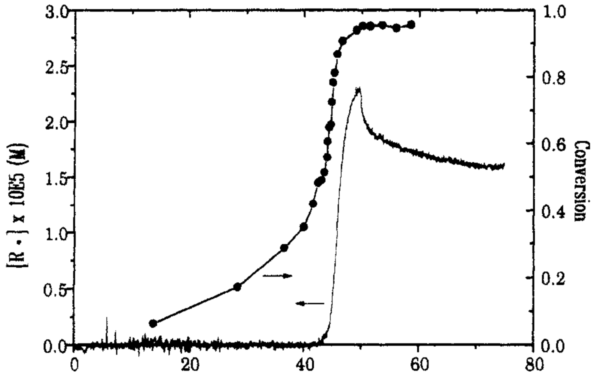

Figure 2. Conversion (filled circles) and propagating free-radical concentration (based on emulsion volume) versus time for a 230-nm batch emulsion polymerization reaction of MMA.

from the smaller particle size case is a longer delay time before the polymerization enters the high rate region and the free-radical concentration increases rapidly. Also, there is a notable and reproducible difference between the behavior of the 110-nm and the 230-nm polymerizations after the maximum free-radical concentration has been reached; the larger particle size reaction shows a decrease in the free-radical concentration after a short time at the maximum concentration, due to radical termination.

Values of $\bar{n}$, average number of radicals per particle, have been computed for these two different particle size systems. For comparison purposes, some selected values at various conversions are shown in Table I. As the data indicates, the maximum radical concentration based on the total particle volume, $[\mathrm{R}^\bullet]_\mathrm{p}$, is about the same for both particle size runs. These values translate to an $\bar{n}$ of around 75 for the 110-nm latex and around 560 for the 230-nm latex. Thus both systems show $\bar{n}$ values much greater than the classical value of 0.5 when they are at high conversion.

Table I
Radical Concentrations in Batch Emulsion Polymerization of MMA

time (min)	conversion	$[\mathrm{R}^\bullet]^a$ (M)	$[\mathrm{R}^\bullet]_\mathrm{p}{}^b$ (M)	$\bar{n}^c$
		110-nm Particle Size System		
19.5	0.546	6×10^{-7}	4×10^{-6}	2
21.4	0.750	3.5×10^{-6}	2.2×10^{-5}	11
25.6	0.887	2.0×10^{-5}	1.3×10^{-4}	65
30.5	0.915	2.3×10^{-5}	1.5×10^{-4}	75
		230-nm Particle Size System		
43.5	0.512	8×10^{-7}	5×10^{-6}	22
45.1	0.782	4.8×10^{-6}	3.0×10^{-5}	119
49.1	0.938	2.3×10^{-5}	1.5×10^{-4}	562
58.7	0.970	1.7×10^{-5}	1.1×10^{-4}	424

[a] $[\mathrm{R}^\bullet]$ is the radical concentration based on total emulsion volume. [b] $[\mathrm{R}^\bullet]_\mathrm{p}$ is the radical concentration based on total particle volume. [c] $\bar{n}$ is the average number of radicals per particle calculated by dividing $[\mathrm{R}^\bullet]$ by the particle concentration.

In the initial work which we have reported here, we have demonstrated the first, to our knowledge, direct experimental determination of the propagating free-radical concentration for a batch emulsion polymerization on an almost continuous basis. With this type of experiment we can monitor free-radical concentrations as they change relatively rapidly during batch emulsion polymerization reactions. An interesting difference in the case of batch emulsion polymerization of MMA for two different particle size latexes has been observed; we are currently exploring the nature of the free-radical termination reaction seen at the end of the experiment for the 230-nm particle size system and will discuss this further in the future.[6] A difference in kinetic behavior between different particle size polymerizations has been previously observed in semicontinuous emulsion polymerization of a PMMA copolymer,[3,4] but this system had a much larger difference in particle size (50 vs 500 nm). We also expect that the flow ESR technique described here should be extensible to some other batch emulsion polymerizations, such as those of styrene.

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References and Notes

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