Flow System for Continuous ESR Measurement of Propagating Free-Radical Concentrations during Semicontinuous Emulsion Polymerization

Willie Lau* and David G. Westmoreland*

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

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Emulsion polymerization is an extremely important process for the synthesis of a wide variety of polymers, especially on a commercial scale. One of the most difficult aspects in studying emulsion polymerization is to obtain information about the nature and concentration of propagating free radicals involved in the polymerization. Recently electron spin resonance (ESR) has been used to obtain very valuable information about propagating free radicals in both batch[1] and semicontinuous[2,3] emulsion polymerizations. This kind of information is crucial for determining key kinetic parameters of the emulsion polymerization process. We report here on the development of a new closed-loop flow system apparatus for the study of semicontinuous emulsion polymerization; the value of this technique for obtaining information on propagating free radicals during the polymerization process is shown in the case of a methyl methacrylate (MMA) polymerization.

In previous ESR studies of semicontinuous emulsion polymerizations, we have analyzed samples extracted from the reactor and frozen in dry ice to stabilize the propagating radicals, a procedure which takes about 15–20 s. We have been developing techniques to shorten this sampling time in order to extend ESR studies to systems with propagating radicals that have shorter lifetimes. In addition, we wanted to avoid as much as possible any changes in the sample which could be produced during the sampling and freezing process. The apparatus we have developed involves a closed-loop flow system (Figure 1) which circulates latex from the polymerization reactor through the ESR cavity for free-radical measurements and then returns the latex to the reactor. The reactor resides in a fume hood built on top of the magnet of a Bruker ESP 300 spectrometer. The microwave bridge has been relocated behind the magnet to accommodate placement of the reactor on top. A variable-temperature Dewar insert was custom built to house a special flat cell (0.3-mm sample thickness) which has both its inlet and outlet extending outside the cavity. The overall setup allows the circulation of latex from the polymerization reactor to the ESR cavity for measurement and the return of latex to the reactor without exposure to the atmosphere, maintaining conditions almost identical to those in the reactor.

The polymerization reactor is a glass-jacketed round-bottom flask with an outlet at the bottom. The temperature of the polymerization is controlled by the circulation of water from a thermal bath through the jacket. Latex is transported through poly(tetrafluoroethylene) tubing to the ESR flat cell. The transfer tubing is insulated with a thermal jacket to maintain reaction temperature and is equipped with a filter to remove any gel formed that might otherwise be trapped in the flat cell. A peristaltic pump is located after the flow cell which returns the latex to the polymerization reactor through poly(tetrafluoroethylene) tubing. The speed of the pump is adjustable, and the flow rate of the latex was kept at 50–70 mL/min. We estimated

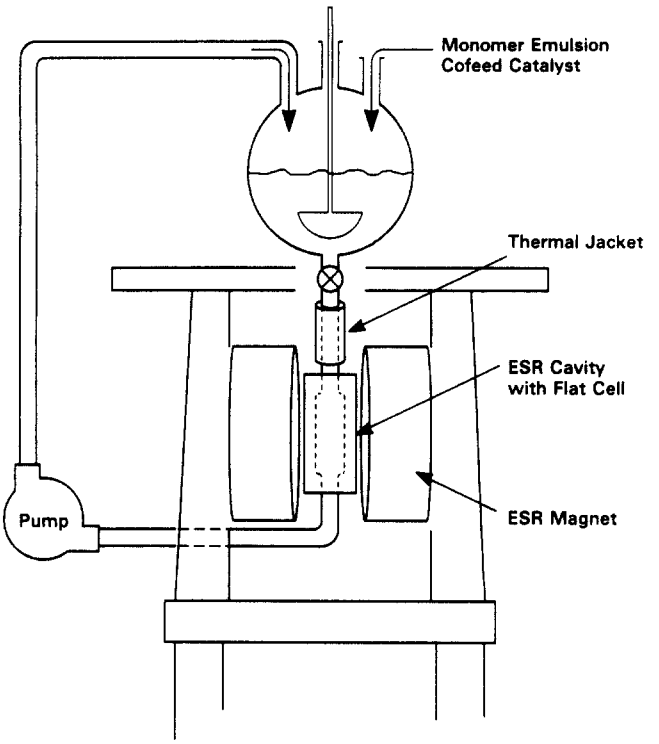

Figure 1. Schematic diagram for a closed-loop flow system used for ESR study of semicontinuous emulsion polymerization.

a total elapsed time of around 1–2 s for transfer of latex from the reactor outlet to the detection zone of the cavity. With the closed-loop approach, the bulk conditions of the polymerization in the reactor remain unperturbed.

A semicontinuous emulsion polymerization of 99/1 MMA/methacrylic acid (MAA) was carried out with a redox initiator system at 50 °C using the flow system with continual monitoring of the propagating radicals by ESR. The polymerization was designed to yield a final solids level and particle size of about 30% and 500 nm, respectively. The monomer emulsion and initiators were cofed with appropriate pumps over a period of about 2.5 h. The pump settings are adjusted to achieve a steady feed rate throughout the polymerization run. The latex was circulated continuously through the flow system for the duration of the polymerization run, and ESR measurements were made throughout the entire run at about 10-min intervals. The ESR spectra were recorded as a time average of 25 scans to improve the signal-to-noise level. The propagating radical concentrations were calculated by measurement of the total peak areas, derived from double integration of the spectra, and comparison to standard solutions of 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl. Small aliquots of the latex, withdrawn from the reactor each time an ESR spectrum was collected, were quenched with an inhibitor to stop further polymerization. These samples were analyzed for monomer concentrations, total polymer solids, and particle size.

The results for the MMA polymerization are summarized in Table I and Figure 2. The radicals detected by ESR are exclusively the pMMA propagating radicals with the same nine-line spectrum as observed previously.[2] The radical concentrations measured in the latex were calculated on the basis of total polymer volume, since it is unlikely for any radicals to have a significant lifetime in the aqueous phase. An analogous treatment was made for the monomer concentrations, since we operate under high conversion and thus expect the monomer being fed to diffuse into the polymer phase at a high rate. The total

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Table I
Parameters of Semicontinuous Emulsion Polymerization of 99 MMA/1 MAA at 50 °C Measured with ESR Flow System

monomer addition[a] (%)	convn[b] (%)	particle size (nm)	[M][c] (mol dm^{-3})	[R•][c] (10^{-4} mol dm^{-3})	$\bar{n}$[d]	k_p[e] (dm^3 s^{-1} mol^{-1})
17.6	88	260	1.3	5.0	3 670	12
39.0	92	340	0.94	6.4	10 060	5.8
57.7	92	390	0.92	6.8	15 810	3.8
72.6	92	440	0.93	7.6	22 190	2.7
87.7	92	460	0.91	7.9	28 000	2.2
98.8	92	480	0.85	7.5	29 860	2.2

[a] Based on the total monomer emulsion. [b] Calculated from in-process monomer concentrations. [c] Calculated based on the volume of the organic phase. [d] $\bar{n}$ is the average number of radicals per particle. [e] Apparent propagation rate constants calculated from eq 1.

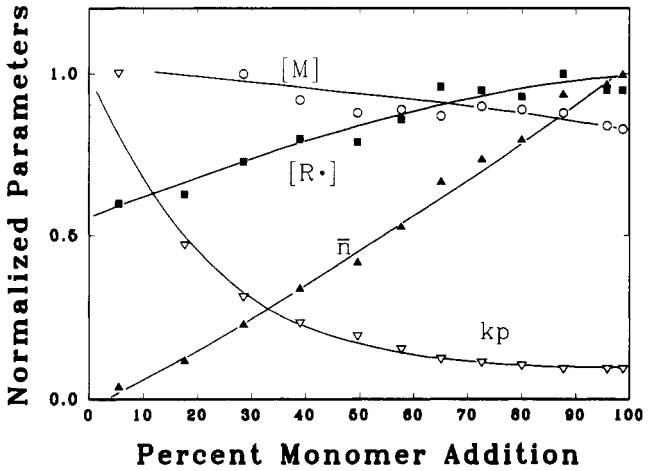

Figure 2. Plot of normalized values of kinetic parameters for the semicontinuous emulsion polymerization of 99/1 MMA/MAA at 50 °C.

number of particles was set with a polymer seed, and no new particles were detected in the polymerization. The conversions were calculated from monomer concentrations determined by a standard chromatographic method. Kinetic parameters were calculated based on eq 1 with details described previously.[2] It should be pointed out

$$\text{rate of polymerization} = k_p[R^\bullet][M] \quad (1)$$

that k_p determined from eq 1 is an apparent propagating rate constant which includes the effect of diffusion control which occurs at high conversion. These values are different from measurements at low conversion where diffusion is not a factor. A study of propagating free-radical concentration in bulk polymerization of MMA[4] demonstrated that care must be taken in measuring radical concentrations using ESR due to a changing dielectric constant during polymerization; in the case of emulsion polymerization the high water level dominates spectrometer tuning, and we have taken these effects into account.

As shown in Table I, the conversion based on monomer concentrations remained relatively constant throughout the run, indicating a steady-state condition as expected in a semicontinuous polymerization. The values of $\bar{n}$ (average number of radicals per particle) increase dramatically during the polymerization, although on a molar concentration basis the increase is smaller. A strikingly high $\bar{n}$ was observed in this polymerization, representing the highest value for $\bar{n}$ which has been reported to our knowledge. The decreasing apparent propagation rate constant, k_p, reflects a diffusionally controlled process. The high $\bar{n}$, together with the decreasing k_p, supports our previous speculation[2] that polymerization is not occurring homogeneously throughout the particles in this system. Thus we speculate that in a large-particle-size semicontinuous emulsion polymerization of a high-T_g polymer system at relatively low temperature and high conversion, diffusion of the monomer becomes rate limiting, and only those radicals residing near the surface of the particles are involved in the majority of the polymerization reactions. Using eq 1 and assuming a propagation rate constant from the literature[5] of ~70 dm^3 s^{-1} mol^{-1} for MMA at 50 °C, we estimate that less than 5% of the total pMMA propagating radicals detected are actively participating in the polymerization at the latter part of the run. We hypothesize that, due to the glassy state of the pMMA matrix at 50 °C, radicals near the center of the particles remain unterminated by either translational or propagation diffusion and eventually are "trapped",[6] resulting in an unusually high $\bar{n}$. The relatively small change in [R•] in comparison to the large change in $\bar{n}$ suggests the possibility of a minimum average volume requirement for the trapped radicals to remain unterminated. Under these conditions, k_p calculated based on the total radical population will have a lower than expected value. The subject of inhomogeneous polymerization in emulsion polymerization systems has also been addressed in a modeling study[7] which predicts nonuniform propagating radical distributions in large-particle systems during batch emulsion polymerization. Figure 2 shows plots of the major kinetic parameters on a normalized scale to show the changes throughout the polymerization. The plots show the increase of [R•] and $\bar{n}$, a decrease in k_p, and a constant [M], consistent with a gradual buildup of trapped radicals in the polymerization system. In the ESR spectra recorded throughout the polymerization, the trapped radicals are indistinguishable from the active radicals that carry out the bulk of the polymerization. The extent of this buildup of trapped radicals is a function of polymer composition, polymerization temperature, and particle size and will be reported separately.[8] Compared to our previous work using the frozen sample technique,[2,3] our new flow system can provide insight into a changing polymerization system in real time on a continuous basis.

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References and Notes

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(5) The value of ~70 dm^3 s^{-1} mol^{-1} for k_p was calculated from eq 3 of ref 1 using a value of 92% conversion. An estimate of the number of active propagating radicals can then be made from eq 1 of this paper.
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Registry No. MMA, 80-62-6; MAA, 79-41-4; (MMA)(MAA) (copolymer), 25086-15-1.