1048 *Macromolecules* **1990,** *23,* 1048–1053

In Situ Kinetic Studies of Microemulsion Polymerizations of Styrene and Methyl Methacrylate by Raman Spectroscopy

Lizhong Feng and K. Y. Simon Ng*

Department of Chemical and Metallurgical Engineering, Wayne State University, Detroit, Michigan 48202. *Received March 10, 1989; Revised Manuscript Received August 7, 1989*

ABSTRACT: The microemulsion polymerization kinetics of styrene and methyl methacrylate (MMA) in SDS/pentanol/water microemulsion systems was studied by the in situ Raman spectroscopic technique. The rate of polymerization in O/W microemulsion was investigated in detail as a function of temperature, of the nature of the initiators, and of the type and concentration of the monomer. The product latexes of microemulsion polymerization were studied by gel permeation chromatography (GPC) for molecular weight (MW) and molecular weight distribution (MWD). The GPC results were correlated with the Raman studies of the microemulsion polymerization kinetics.

I. Introduction

Microemulsions are thermodynamically stable, transparent or translucent, and homogeneous systems with a particle size of about 50–100 Å. While microemulsions can be used as potential media for polymerization in which better molecular weight (MW) and molecular weight distribution (MWD) may be achieved, little has been done on the kinetics of the polymerization. This may be due in part to the difficulties in directly obtaining kinetic data using most conventional analytical techniques, because of the relatively higher polymerization rate and the various complications associated with microemulsions.[1] Jayakrishnan et al.[2] investigated styrene and MMA microemulsion polymerization. They reported that the polymerization rates of their systems were slower than those in the classical emulsion systems. The microemulsion system was not transparent and stable during the polymerization process. Unstable and nonspherical latex particles were observed using transmission electron microscopy (TEM). In addition, they concluded that the adverse effect of the surfactant would result in a decreased reaction rate. The TEM observations of their microemulsion systems showed either no latex particles or extremely small, nonspherical particles. However, no information about MW and MWD was reported.

In another paper, Stoffer et al.[3] observed the solution behavior for MMA W/O microemulsion polymerizations initiated with oil- and water-soluble initiators. They reported that the effect of initiator on the size of the stability region of the microemulsion can be neglected and that an increase in initiator level would result in a decrease in MW and an increase in MWD, as in the case of the classical emulsion polymerization systems. However, the microemulsion polymerization trends and MW dependencies are the same for reactions initiated by both water- and oil-soluble initiators, which contradicts our previous findings.[1] For W/O microemulsion polymerization, Stoffer et al.[3] suggested that the polymerization would not occur in the aqueous phase. Although the estimated latex MW was over 1 million and the MWD reported was quite narrow, no definite trend for the MWD was observed. Their discussion did not explain the interrelationship between the MW and the rate changes observed when the initiator concentration varied.

Johnson et al.[4] studied styrene O/W microemulsion polymerization initiated by both water- and oil-soluble initiators, using photocorrelation spectroscopy. In microemulsion polymerization, one would expect a smaller size disparity because of the finer monomer dispersion. However, a bimodal molecular weight distribution was observed. Total conversion was reached in the reaction in less than 30 min, and the final latexes were stable and could be diluted. The kinetics of these systems were not reported.

In a more recent study, Candau et al.[5,6] investigated the acrylamide polymerization in an inverse microemulsion system. They reported a narrow MWD of the product latexes[5] using the ultracentrifugation technique. In a subsequent study, they used the dilatometric technique to investigate the polymerization kinetics. They claimed that a very high reaction rate and a high MW of the product latexes were found for their microemulsion systems. However, they did not explicitly address the relationships between MW, MWD, and the reaction kinetics.

The apparent discrepancy in the results of conversion, reaction rate, MW, and MWD of microemulsion polymerization studies reported has emphasized the necessity for a more effective and direct technique for studying microemulsion polymerization kinetics. This paper reports our on-going studies of styrene and MMA polymerizations in microemulsion using the laser Raman spectroscopy technique. Laser Raman spectroscopy is an excellent technique for the study of vinyl polymerization kinetics. It provides accurate conversion data, since it directly probes the breaking of the C=C bond and the formation of C–C bonds. Moreover, it may provide evidence for molecular interactions among polymer/monomer/surfactant/cosurfactant/initiator. The validity of this technique has been demonstrated for bulk polymerization of MMA and styrene,[7] for solution polymerization of acrylonitrile,[8] and for styrene microemulsion polymerization.[1] The latex products of the polymerizations were characterized by gel permeation chromatography (GPC), and the results are discussed and correlated with polymerization kinetics obtained from the Raman study.

II. Experimental Section

Materials. Styrene and methyl methacrylate (MMA) monomers were obtained from Fisher Scientific and were vacuum-distilled to eliminate the inhibitor. The distilled monomer was immediately stored at about 0 °C and used for experiments within several days. Sodium dodecylsulfate (SDS), obtained from Polyscience, was electrolytic pure. Pentanol was also obtained from Fisher Scientific. The oil-soluble initiator azobis(isobutyronitrile) (AIBN) was obtained from Eastman Kodak and the water-soluble initiator potassium persulfate (KPS) from Fisher Sci-

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* To whom correspondence should be addressed.

0024-9297/90/2223-1048$02.50/0

Table I
Composition and MW of Styrene/MMA Microemulsion Systems[a]

syst[b]	initiator, wt % on M	monomer, wt %	SDS, wt %	pentanol, wt %	water, wt %	M concn,[c] (M/SDS[d]), %	M_n, × 10^{-5}	M_w/M_n
s-K(5)-1	0.5	6.50	9.32	4.00	80.18	32.8 (0.70)	5.3	4.53
s-K(5)-2	0.5	5.83	8.29	7.19	78.69	27.3 (0.70)		
s-K(5)-3[e]	0.5	24.42	9.54	55.49	10.55	27.3 (2.56)	2.9	9.31
s-K(2)-1	0.2	6.50	9.32	4.00	80.18	32.8 (0.70)		
s-A(5)-1	0.5	6.50	9.32	4.00	80.18	32.8 (0.70)	8.4	4.64
s-A(5)-2	0.5	7.42	8.15	7.07	77.36	32.8 (0.91)	8.4	4.40
s-A(5)-3	0.5	7.39	8.54	7.04	77.03	32.2 (0.87)	6.2	4.17
s-A(5)-4	0.5	24.42	9.54	55.49	10.55	27.3 (2.56)	1.7	12.35
s-(0)-1	0.0	6.50	9.32	4.00	80.18	32.8 (0.70)		
m-K(5)-1	0.5	6.50	9.32	4.00	80.18	32.8 (0.70)		
m-A(5)-1	0.5	6.50	9.32	4.00	80.18	32.8 (0.70)	5.2	3.46
m-K(5)-2	0.5	6.24	9.38	9.38	75.00	25.0 (0.67)		
m-K-(5)-3	0.5	41.70	14.60	27.00	16.70	50.0 (2.86)	1.3	1.92
m-K(5)-4	0.5	15.92	5.77	41.97	36.34	25.0 (2.76)	4.3	3.95

[a] M, monomer, s, styrene, m, MMA (methyl methacrylate; A, AIBN; K, KPS. Polymerization temperature is at 60 °C unless stated otherwise. [b] Microemulsion system code. [c] Ratio of monomer/(monomer + pentanol + SDS) in weight percent. [d] Weight ratio of monomer/SDS. [e] Polymerization temperature at 50 °C. [f] Polymerization temperature at 80 °C.

entific, both having been finely ground before use. Water was doubly distilled.

Sample Preparation. Monomer-contained microemulsions were prepared by first mixing with the desired amount of SDS, pentanol, and the monomer (styrene or MMA) and then titrating with water to obtain a particular composition. To minimize the possibility of unwanted polymerization, the initiator was added and well mixed with the microemulsion at low temperature. A total of 2 cm^3 of sample at low temperature was put into a 5-mm-o.d. NMR tube with a J. Young valve (Brunfeldt Co.), carefully degassed under several thaw-and-freeze cycles, and sealed under vacuum. The sample was maintained at low temperature until mounted into the sample holder of the Raman spectrometer.

Laser Raman Spectrometer System and Sample Cell Holder. The laser source (514.5 nm) is a Coherent Innova-70 argon laser with three-stage light control mode. The Raman spectrometer is a Spex 1877 0.6m Triplemate with a Spex CD 2A compudrive. A Tracor-Northern large surface area rapid scan diode array detector was used, as described elsewhere.[1] A specially designed sample cell holder was used to allow uniform temperature control of the microemulsion polymerization. The circulating fluid was controlled to ±1 °C using a Nestlab RTE-5DD circulating bath. The sample holder was aligned to a satisfactory position for maximizing the Raman scattering signal, using a three-dimensionally adjustable metal support.

Gel Permeation Chromatography (GPC) and MW Determination. The MW and MWD were determined by gel permeation chromatography (GPC), using THF (at 35 °C) as the solvent. The latex samples to be measured were washed by excess cyclohexane at 20 °C, vacuum dried, and then dissolved in THF as 0.1 wt % solution. MW calibrations were made based on standard polystyrene (from PL Labs, up to 10^6 MW). Since some fraction of the latexes have very high MW values, the GPC results obtained are not absolute but can be compared to obtain the trends in MW and MWD.

III. Results and Discussion

The polymerization kinetics of styrene and MMA in an SDS/pentanol/water/monomer microemulsion system was studied. The effects of temperature, types of initiator and monomer, and concentrations of initiator and monomer on polymerization rate were investigated. The compositions of the microemulsion polymerization systems studied are given in detail in Table I. The systems were coded according to the types of monomer and initiator used, such as s-K(5)-1, which stands for *s*tyrene microemulsion system initiated with *K*PS (*0.5* wt %) with a composition of type "1". The monomer concentration (wt %) is defined as the ratio of monomer/(monomer + pentanol + SDS).

Raman spectra of microemulsion samples obtained during the polymerization process were stable, with good reproducibility. The spectra were taken at 2-min intervals. An exposure time of 1 s was used, with a total of 100 scans. A linear relationship between the monomer concentration in the microemulsion and the net integral area of the C=C double bond peak of the monomer was found,[1] indicating that the conversion can be computed reliably from the corresponding integrated C=C peak area.

The conversion of monomer in microemulsion polymerization is calculated based on the integrated peak area of C=C bond stretch at about 1631 cm^{-1}. The initial polymerization rates are calculated as (%/min),[1,8-10] based on the linear regression of the conversion data in the initial linear region, excluding the induction line. The correlation coefficients of the fits are generally better than 0.98. The microemulsion polymerization kinetics was found to depend on the microemulsion composition, type of initiator, and reaction temperature. The effect is particularly noticeable at the initial polymerization period. A characteristic pattern with KPS-initiated reaction and AIBN-initiated reaction in the O/W microemulsions was observed. The KPS-initiated polymerizations were found to start with a shorter induction time, while the AIBN-initiated ones were initiated more slowly but were observed to have a higher rate in the later stage of the microemulsion polymerization.

Effect of Temperature. Temperature effects were investigated for a styrene O/W microemulsion system (s-K(5)-1). The composition of this microemulsion was 6.50% styrene, 9.32% SDS, 4.00% pentanol, and 80.18% water and was initiated by 0.5% (wt % based on monomer) KPS. The polymerizations were conducted at 55, 60, and 80 °C (Figure 1, curves A–C), and the initial polymerization rates were found to be 5.0, 5.7, and 12.1%/min, respectively. It is obvious that the higher the temperature, the higher the initial rate. The activation energy based on the initial rates is about 8.2 kcal/mol within a temperature range of 25 °C. This activation energy is much lower than that of the styrene bulk polymerization, 19 kcal/mol.[7] The initial rates of the bulk polymerization were reported as 6%/h (0.1%/min) at 130 °C and 30%/h (0.5%/min) at 160 °C,[7] which are also significantly lower than the initial rates in microemulsion polymerization.

Initial rates of 6.0%/min and 10.4%/min were obtained for an MMA microemulsion polymerization system (m-

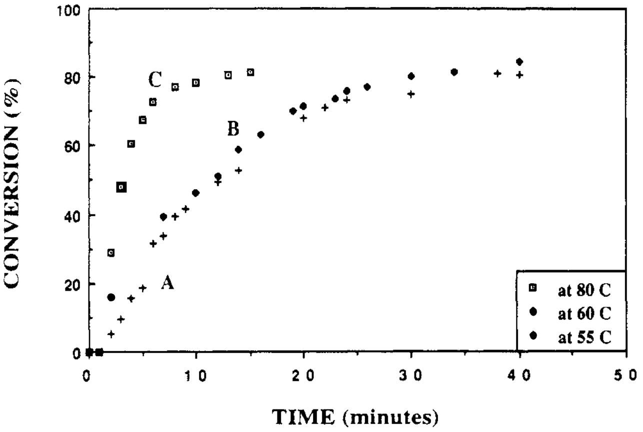

Figure 1. Conversion vs time curves of styrene O/W microemulsion polymerization initiated by 0.5% KPS: effect of temperature. (+) Curve A, at 55 °C; (◆) curve B, at 60 °C; (□) curve C, at 80 °C. The higher initial rate was observed at the higher temperature.

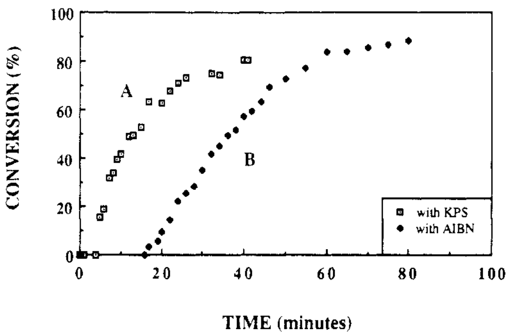

Figure 2. Conversion vs time curves of styrene O/W microemulsion polymerization at 60 °C: effect of the type of initiator at 0.5 wt % (based on monomer). (□) Curve A, initiated with KPS; (◆) curve B, initiated with AIBN. The KPS-initiated system shows a higher initial rate, while the AIBN-initiated one has a longer induction time and reaches higher conversion in the final stage.

K(5)-2) at 60 and 80 °C, respectively (not shown). The system was composed of 6.24% MMA, 9.38% SDS, 9.38% pentanol, and 75.00% water and was initiated by 0.5% KPS. The activation energy is calculated as 6.4 kcal/mol for the temperature range studied. This activation energy is also lower than the activation energy (9.6 kcal/mol) of the MMA bulk polymerization, where initial rates of 4.3%/h (0.072%/min) at 100 °C and 15%/h (0.25%/min) at 130 °C were observed.[7]

Effect of Initiator. In the O/W region, the conversion–time curves of the KPS-initiated reactions generally gave higher initial rates than the AIBN-initiated ones. Figure 2 shows the curves of styrene microemulsion polymerization, initiated with 0.5% KPS (curve A, s-K(5)-1) and 0.5% AIBN (curve B, s-A(5)-1) at 60 °C. The KPS-initiated sample (s-K(5)-1) showed an initial rate of 5.7%/min. The AIBN sample (s-A(5)-1) had a lower initial rate of 2.4%/min and a longer induction period. The former system reached a final conversion of about 80%, while the latter system had a slightly higher conversion before it leveled off. A similar initiator effect on styrene polymerization was also observed at a lower concentration of initiator (Figure 3, 0.2% initiator). The initial rate of the KPS-initiated polymerization (s-K(2)-1) is 4.2%/min, and the AIBN-initiated polymerization (s-A(2)-1) is 1.9%/min. It is apparent that KPS is more efficient in the initial period than AIBN (Figure 3, curve A). This may be explained by the fact that the water-insoluble AIBN must migrate into the oil phase through the water–oil interface to initiate the polymerization, while KPS can be dissociated readily in the continuous water phase.

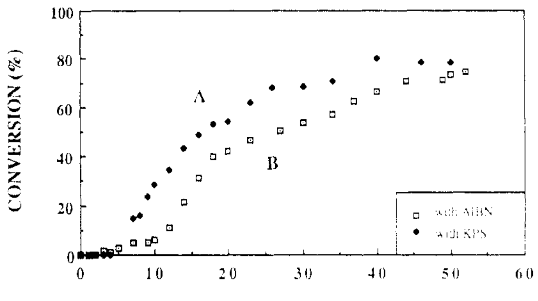

Figure 3. Conversion vs time curves of styrene O/W microemulsion polymerization at 60 °C: effect of the type of initiator at 0.2 wt %. (◆) Curve A, initiated with KPS; (□) curve B, initiated with AIBN. The two curves show close conversion at around 50 min. The AIBN-initiated system is lower in initial rate.

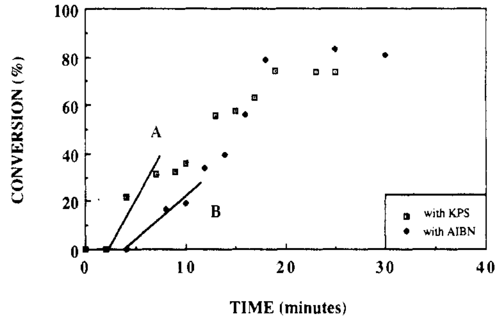

Figure 4. Conversion vs time curves of MMA O/W microemulsion polymerization: effect of the type of initiator at 0.5 wt %. (□) Curve A, initiated with KPS; (▲) curve B, initiated with AIBN. The AIBN-initiated one has a longer induction time and lower initial rate. However, at around 17 min the conversion value of curve B exceeds that of curve A, indicating that the AIBN-initiated MMA system can achieve higher conversion in the final stage than the KPS-initiated one.

For MMA systems, comparable initial kinetic behavior is observed for the KPS-initiated (Figure 4, curve A, m-K(5)-1) and AIBN-initiated (curve B, m-A(5)-1) polymerizations. The initial rates are 11.3%/min for the KPS-initiated system and 8.1%/min for the AIBN-initiated system. The initial rate difference can be attributed to an effect similar to that observed in the styrene system. It was noted, however, that at about 20 min the conversion of the AIBN-initiated polymerization exceeded the KPS-initiated polymerization.

When the above two styrene or MMA O/W microemulsion polymerizations are compared, it is found that the KPS- and AIBN-initiated polymerization kinetic behaviors are similar in manner: the reaction was initiated with a high initial rate after a short induction time, and the rate decreased and eventually leveled off. In the initiation stages, the polymerizations were found to be generally following first-order kinetics. On the other hand, with an identical microemulsion composition, KPS-initiated polymerizations showed higher initial rates than the AIBN-initiated reactions, while the latter resulted in higher final conversions.

The effects of initiator concentration, 0.5%, 0.2% and 0% KPS for styrene microemulsion (Figure 5, curve A (s-K(5)-1, curve B (s-K(2)-1), and curve C (s-(0)-1), respectively) at 60 °C were examined. The two curves with the initiator were very similar in shape, except that the 0.2% initiator polymerization showed a longer induction

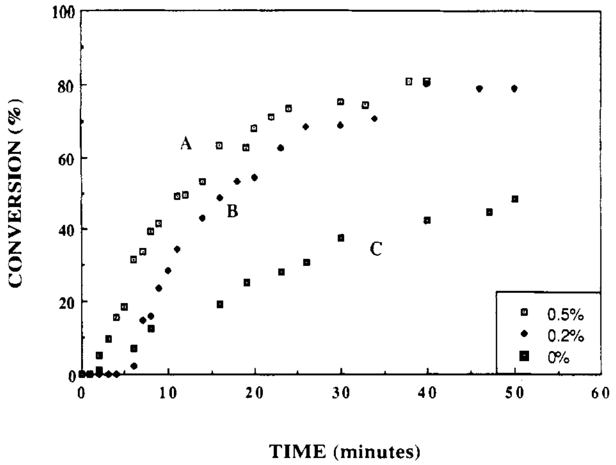

Figure 5. Conversion vs time curves of styrene O/W microemulsion polymerization initiated by KPS at 60 °C: effect of KPS concentration. (□) Curve A, initiated with 0.5% KPS; (◆) curve B, initiated with 0.2% KPS; (■) curve C, with 0% initiator. At initial stage, the rate of curve A is higher than curve B. However, in final stages curves A and B both have the same final conversion. The 0% initiator sample shows a much lower rate and final conversion value.

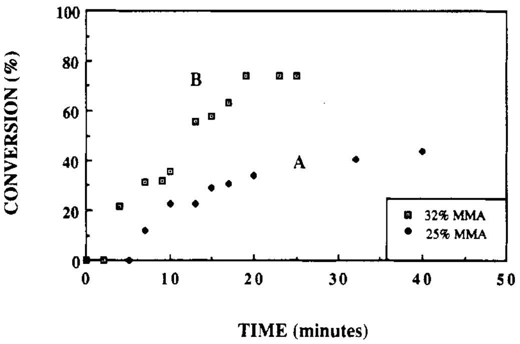

Figure 6. Conversion vs time curves of MMA O/W microemulsion polymerization initiated by 0.5 wt % KPS at 60 °C: effect of MMA concentration. (◆) Curve A, with 25% monomer concentration; (□) curve B, with 32.8% monomer concentration. Curve A shows a very low initial rate and final conversion, while with a higher MMA content curve B has a higher rate and conversion value.

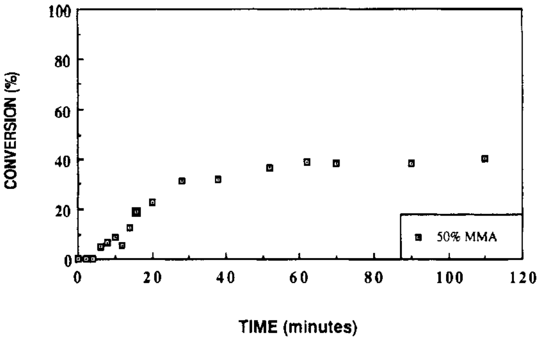

Figure 7. Conversion vs time curves of 50% MMA W/O microemulsion polymerization initiated by 0.5 wt % KPS at 60 °C. Low initial rate and final conversion are observed.

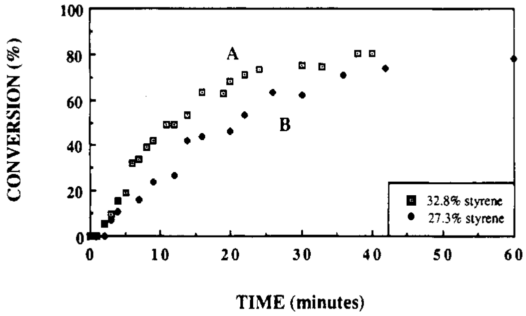

Figure 8. Conversion vs time curves of styrene O/W microemulsion polymerization initiated by 0.5 wt % KPS at 60 °C: effect of styrene concentration. (□) Curve A, with 32.8% monomer concentrations; (◆) curve B, with 27.3% monomer concentration. Curve A shows a higher conversion before 40 min, but the two curves reach similar final conversions.

period and a lower initial rate during the first several minutes. The system without initiator showed a much lower initial rate and final conversion compared to the others. The KPS-initiated styrene polymerization rates after the initiation period were found to be independent of the initiator concentration, although at the beginning the initial rate was dependent on the initiator concentration. This is in parallel to Candau et al.'s[6] study of acrylamide polymerization in inverse microemulsion, where the rate was essentially independent of the initiator concentration.

Effect of Monomer. In order to elucidate the monomer concentration effect, the reaction temperature and initiator concentration were kept constant for the following experiments. Figure 6 shows the kinetic behavior of 25% (curve A, m-K(5)-2) and 32.8% (curve B, m-K(5)-1) MMA microemulsion systems. The initial rate of 25% monomer sample is 6.0%/min, with a short induction period. The conversion curve leveled off at about 43% conversion at 40 min. The 32.8% monomer system has a shorter induction period, and the polymerization was maintained at a high rate of 11.3%/min during the first 20 min. The curve leveled off at about 75%. In the range of MMA concentration studied, initial O/W microemulsion polymerization rates and final conversion are found to be dependent on the monomer concentration. When monomer concentration is further increased, the microemulsion shifts to the W/O region. Figure 7 shows the conversion curve of a 50% MMA microemulsion system (m-K(5)-3) where the reaction rate was found to decrease rapidly after initiation. Moreover, the initial rate was significantly lower than in the O/W region.

The conversion curves for two styrene microemulsion systems (s-K(5)-2 and s-K(5)-1) of 27.3% and 32.8% styrene concentration are shown in Figure 8. The initial rate is 2.8%/min for the 27.3% styrene sample and 5.7%/min for the 32.8% styrene sample. The induction times for both polymerizations were about the same. At about 40 min, the higher initial monomer concentration curve began to level off, with a conversion of 80%, while the lower monomer concentration curve showed that the rate of polymerization also reached 76%. The polymerization continued at a slow rate, until it leveled off with 78% conversion at about 60 min. The change in monomer concentration seemed to affect only the initial kinetic behavior but not the final conversions. This is different from the results of the O/W MMA system observed.

Considering the effect of the type of monomer on the O/W microemulsion polymerization, it is noted that in the MMA system the polymerization is initiated much faster than in the styrene system. Since the solubility of MMA in water (1.56 wt % at 20 °C) is much higher than that of styrene (0.031 wt % at 25 °C),[11] it is likely that MMA polymerization occurs in the continuous phase of O/W microemulsion before the initiator migrates across the surfactant boundary into the oil phase. On the other hand, the less soluble styrene (in the continuous water phase) results in a lower initial rate.

According to studies by Jayakrishnan and Shah,[2] initial rates of MMA polymerization were lower in microe-

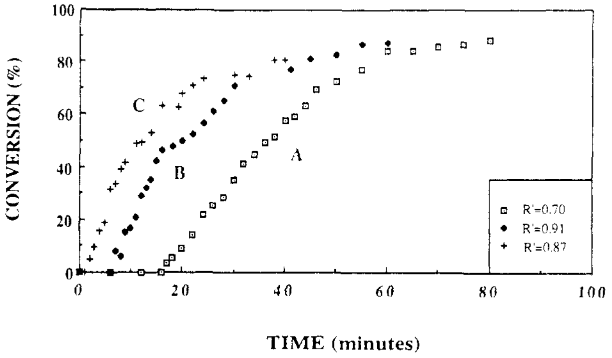

Figure 9. Conversion vs time curves of styrene O/W microemulsion polymerization initiated by 0.5 wt % AIBN; comparison of kinetic behavior of the corresponding three high MW sample latexes. (□) Curve A, with $R' = 0.70$ (ratio of monomer/SDS); (◆) curve B, with $R' = 0.91$, (+) curve C, with $R' = 0.87$. Curve B has unique multistage characteristics.

mulsion than in classical emulsion. There are also differences in rate resulting from adding the initiators in different ways, i.e., after the emulsification or mixed with the monomer prior to the emulsification. However, our results showed that the rate of polymerization was very high in both styrene and MMA O/W microemulsions, except for low MMA (25%) concentration (Figure 6, curve A, m-K(5)-2). The rate of microemulsion polymerization was in general so high that the conversion–time curve leveled off within 60–80 min. Jayakrishnan and Shah[2] suggested that a firm interface layer of surfactants, which can act as a barrier for initiator radicals diffusing into the core, may be responsible for the low polymerization rate. However, it has been shown by a number of investigators that microemulsion systems are usually quite dynamic.[12] This may explain our observation of a high rate of microemulsion polymerization.

GPC Measurement of MW and MWD. The GPC results of some of the latex samples showed different molecular weight distributions, judging from the different ratios of M_w/M_n (ratio of weight average molecular weight to number average molecular weight). It is interesting to note that styrene samples show a typical bimodal distribution behavior (Figure 10), while MMA samples do not show a multimodal distribution. The M_n and MWD (M_w/M_n) values of selected product latexes are shown in Table I.

The latex from the system with the original composition of 7.42% styrene, 8.15% SDS, 7.07% pentanol, and 77.36% water (Figure 9, curve B, s-A(5)-2) has the highest M_n, 8.4 × 10^5. The polymerization corresponds to a characteristic multistage conversion curve.[1] The nature of the multistage characteristics is not fully understood at this point. The other two systems (Figure 9, curve A (s-A(5)-1) and curve C (s-A(5)-3)), with slightly different original microemulsion compositions, result in latexes having M_n values of 8.4 × 10^5 and 6.2 × 10^5, respectively. All three samples were initiated by 0.5% AIBN at 60 °C. In each of the three polymerizations more than 80% conversion is reached after initiation. However, there were differences in the induction period, due possibly to different monomer/SDS ratios. A KPS-initiated system (Figure 1, curve B, s-K(5)-1) with the same original composition as system s-A(5)-1, however, showed a lower M_n value of 5.3 × 10^5 compared to the AIBN-initiated system. These results suggest that in O/W microemulsion the AIBN-initiated styrene polymerization latexes have higher M_n values then those from the KPS-initiated polymerization. This may be attributed to the high initial kinetic rate of the KPS-initiated polymerization observed. The molecular weight distribution was evaluated by the ratio of M_w/M_n. For latexes in systems s-K(5)-1 and s-A(5)-1, the ratios are 4.53 and 4.64, respectively, and show a similar bimodal distribution of molecular weight (Figure 10).

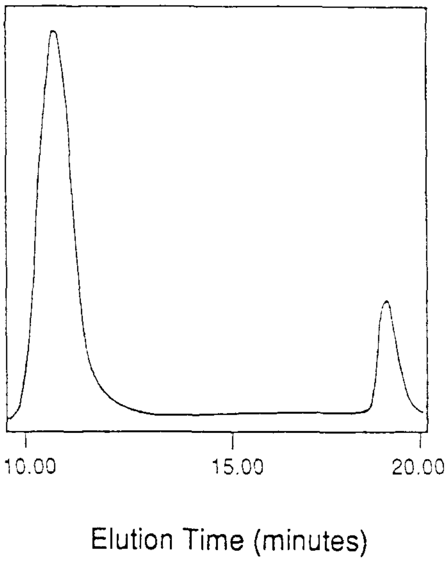

Figure 10. Molecular weight distribution of styrene microemulsion polymerization. A typical gel permeation chromatogram of styrene latex shows a bimodal distribution of molecular weight.

Our data shows that, in the W/O microemulsion region, the polymerizations initiated both by AIBN (s-A(5)-4) and by KPS (s-K(5)-3) result in a considerably lower M_n and higher values of M_w/M_n. It should be noted that, in the W/O region, the AIBN-initiated reaction has a higher initial rate than the KPS-initiated ones.[1] On the other hand, the GPC results again show bimodal molecular weight distribution for both latex samples from the W/O systems. Since high MW values may be the result of the small and uniform micelle size in the microemulsion, as was suggested by Candau et al.,[5] the relationship between the micelle size and the kinetic behavior in microemulsion polymerization needs further investigation.

The MW values for the MMA polymerization latex samples were found to be relatively lower than those from styrene systems. Of the two types of initiator, again the latex from the AIBN-initiated system (Figure 4, curve B, m-A(5)-1) had a slightly higher MW value compared to that of the KPS-initiated system (s-K(5)-4). The MMA system containing 50% MMA in (MMA + SDS + pentanol) showed the lowest M_n latex, 1.3 × 10^5 (m-K(5)-3), which corresponded to a very low final conversion in the kinetic curve (Figure 7). A relatively low M_n was also observed for latex from the styrene W/O systems (s-A(5)-4, s-K(5)-3). However, the W/O MMA latex (m-K(5)-3) had a very low MWD of 1.92, while the styrene systems exhibited a totally opposite trend in MWD values with 9.31 and 12.35 for the systems s-A(5)-4 and s-K(5)-3, respectively.

IV. Conclusions

In the MMA and styrene O/W microemulsion polymerizations, KPS-initiated systems in general result in a higher initial rate, while AIBN-initiated samples show higher final conversions. In the concentration range studied, the initiator concentration is found to have very little effect on the styrene systems. The monomer concentration significantly affects the kinetics of the MMA polymerization, especially in the later stages of monomer conversion, but would not cause much difference in the final conversion in styrene polymerizations. With the same microemulsion composition and initiator concentration, the initial rate for the O/W MMA polymerizations is faster than that in the O/W styrene case, which suggests that MMA polymerization might be initiated in the continuous aqueous phase. In the W/O microemulsion polymerizations, however, both the initial rate and final conversions are found to be lower compared to those of O/W microemulsion polymerization.

A GPC study of latexes from microemulsion polymerization shows the effect of the type of initiator, concentration, and type of monomer on the MW of the latex. For O/W systems, AIBN-initiated styrene polymerizations are observed to have a slightly higher M_n value than KPS-initiated systems. The MWD values are not much different for these latexes in certain areas of the O/W microemulsion region. The W/O microemulsion polymerization results in very low M_n for both monomers studied; however, the MWD trends are different for the styrene and MMA polymerization products. Comparison of kinetic study findings and GPC results indicates that, for microemulsion polymerization, the initial rate in the O/W region affects the MW value of the latex: generally, the higher the initial rate, the lower the MW.

We are performing a detailed kinetic analysis of the rate data obtained. Attempts will be made to develop a mathematical model to explain these observations. The results will be communicated in a separate paper in the near future.

Acknowledgment. We gratefully acknowledge financial support for our work from the Institute for Manufacturing Research of Wayne State University. We also thank the Analytial Chemistry Department of General Motors for the GPC analysis and the Chemistry Department of Wayne State University for allowing us to use the Raman spectrometer system.

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Registry No. MMA, 80-62-6; KPS, 7727-21-1; AIBN, 78-67-1; styrene, 100-42-5.

Conducting Polymer Blends: Polythiophene and Polypyrrole Blends with Polystyrene and Poly(bisphenol A carbonate)

Hsing Lin Wang, Levent Toppare,[†] and Jack E. Fernandez[*]

Department of Chemistry, University of South Florida, Tampa, Florida 33620.

Received June 13, 1989

ABSTRACT: Blends of the conducting polymers, polythiophene and polypyrrole, in the insulating host polymers, polystyrene and polycarbonate resin, have been prepared electrochemically. Threshold conductivities occur at ca. 18% for both conducting polymers in blends with polystyrene. With polycarbonate resin blends, polythiophene exhibits a threshold at ca. 12% and polypyrrole exhibits a threshold at ca. 7%. The low threshold conductivity of the polypyrrole/polycarbonate blends is attributed to blend homogeneity enhanced by hydrogen bonding. DSC confirms the presence of a homogeneous blend in this combination. TGA analysis suggests the presence of a 1:1 complex of PPy/PC in these blends. SEM is used to examine the electrode and solution sides of the film blends produced.

Introduction

Various aromatic compounds can be polymerized by electrochemical oxidation in solutions containing a supporting electrolyte.[1] Most studies have been devoted to polypyrroles and polythiophenes, which are generally prepared by the electrochemical oxidation of the monomers on a platinum or ITO electrode.[2–4] In situ doping during electrochemical polymerization yields free standing films that are relatively heavily doped with anions of the

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[†] Fulbright Research Fellow from the Middle East Technical University, Ankara, Turkey, 1988–1989.

0024-9297/90/2223-1053$02.50/0