

Polymerization of Methyl Methacrylate in 3-Component Cationic Microemulsion

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SYNOPSIS

Methyl methacrylate has been polymerized in three-component o/w microemulsions made with the cationic surfactant dodecyltrimethylammonium bromide (DTAB). The effects of temperature type and concentration of initiator (AIBN or potassium persulfate), and surfactant and monomer concentration on polymerization kinetics are investigated. Final conversions and reaction rates increase with increasing monomer and initiator concentrations and with higher reaction temperatures. The rate of polymerization shows initiation and termination intervals, but no constant rate interval is observed. Both molecular weight and particle size decrease as the concentration of initiator increases, regardless of type of initiator. Latexes with small particle size (< 70 nm) and high molecular weights (> 10⁶) were obtained in all cases. Activation energies for the microemulsion polymerization of MMA with AIBN (10.3 kcal/mol) and KPS (13.4 kcal/mol) are smaller than that of bulk polymerization using AIBN (20 kcal/mol). © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polymers with large molecular weights (> 10⁶) can be produced with fast reaction rates in both emulsion and microemulsion polymerization processes.¹⁻³ However, in the latter, stable direct or inverse latexes with particles smaller than 500 Å can be easily obtained.

Microemulsion polymerization was first reported by Stoffer and Bone^{4,5} in 1980. Since then, scores of papers have appeared on microemulsion polymerization of water-insoluble and water-soluble monomers.⁶⁻¹³ Most work has been done in four- or five-component microemulsions. The first report on polymerization in ternary microemulsions was made by our group.¹³ In that article, the polymerization of styrene in o/w microemulsions prepared with the cationic surfactant dodecyltrimethylammonium bromide (DTAB) was examined. Later, we reported the effect of type and concentration of initiator (AIBN or potassium persulfate) in the thermal polymerization of styrene in DTAB microemulsions,¹⁴

and showed that very stable latexes were produced and that particles had diameters between 20 and 35 nm depending on the concentration, but not type, of initiator. Polystyrene molecular weight decreased with increasing initiator concentration as $M_w \propto [I]^{-0.4}$. Polymerizations in ternary microemulsions made with an anionic surfactant (Aerosol OT) have also been recently reported.^{15,16}

Microemulsion polymerization of more polar monomers has not been systematically examined. It is known that emulsion polymerization of polar monomers differs substantially from that of sparingly water-soluble monomers such as styrene.¹⁷ The differences in the polymerization kinetics can be attributed to (i) an increased solubility of polar monomers in water, frequently with a predominance of true solubility over colloidal solubilization, which in itself leads to a diminished role of the emulsifier in the kinetics; (ii) a change in the properties of the interfacial layer (decreased interfacial energy), which causes a decrease in the adsorption of emulsifier; and (iii) a higher rate of surface formation of the polymer phase with respect to the rate of its stabilization by adsorbed emulsifier molecules, which is responsible for a flocculation mechanism for particle formation.

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Here, we report the polymerization of methyl methacrylate (MMA) in three-component o/w microemulsions made with DTAB. One-phase regions are detected at 25 and 60°C in this system near the water-rich corner. Thermal polymerization of these transparent, low-viscosity microemulsions is achieved using either water-soluble (potassium persulfate or V-50) or an oil-soluble (AIBN) initiator.

EXPERIMENTAL

Reagent-grade methyl methacrylate (MMA) from Scientific Polymer Products was passed through a DHR-4 inhibitor removal column (SPP) before use. Dodecyltrimethylammonium bromide (DTAB), with a purity greater than 99%, was from Tokyo Kasei. Hydroquinone and potassium persulfate (KPS) were reagent grade from Aldrich. 2,2-Azobisisobutyronitrile (AIBN) from DuPont and 2,2'-azobis(2-amidinopropane)dihydrochloride (V-50) from Wako were recrystallized from methanol. HPLC-grade tetrahydrofuran (Merck) was used as the mobile phase for molecular weight determinations.

The single-phase microemulsion region at 25°C was determined visually by titrating aqueous micellar solutions of DTAB with MMA. Phase boundaries were checked by preparing samples by weight in sealed glass ampules with compositions below and above the phase boundaries determined by titration. The phase diagram at 60°C was determined with MMA containing 10 ppm methyl ester hydroquinone (MEHQ) to inhibit thermal polymerization. Microemulsion conductivities were measured at 1000 Hz with an Orion 101 conductimeter and a Yellow Spring Instruments immersion cell (cell constant equal to 1.12 cm⁻¹).

Polymerization of MMA was carried out at 60°C in a 100 mL glass reactor. The reaction vessel was loaded with microemulsion and heated to 60°C before injecting a small amount of a concentrated aqueous solution of KPS. In the case of AIBN, a 7 wt % DTAB aqueous solution was loaded in the reactor and heated to 60°C before adding MMA containing the initiator at the required concentration. The sample becomes turbid when MMA is added but clears again in seconds. The reacting system was continuously stirred and sparged with nitrogen. Poly(methyl methacrylate) (PMMA) was isolated by filtration after precipitation with methanol.

Quasi-elastic light-scattering (QLS) measurements were made with equipment previously described.¹⁸ The magnitude of the scattering vector, q

$= (4\pi n/\lambda_0) \sin(\theta/2)$, was varied by changing the scattering angle, θ , from 30° to 120°. Here, n is the index of refraction and λ_0 ($= 488$ nm) is the wavelength of the light in vacuum. Intensity correlation data were analyzed by the method of cumulants to provide the average decay rate, $\langle \Gamma \rangle (= 2q^2 D)$, where D is the diffusion coefficient, and the variance, $\nu (= [\langle \Gamma \rangle^2 - \langle \Gamma^2 \rangle] / \langle \Gamma \rangle)$, which is a measure of the width of the distribution of the decay rates. The measured diffusion coefficients were represented in terms of apparent radii using Stokes law and assuming that the solvent has the viscosity of water. Latexes were diluted up to 1000 times before QLS measurements to minimize particle-particle interactions.

Molecular weights and molecular weight distributions were measured with a Shimadzu LC-4A liquid chromatograph and a refractive index detector using TSKH-gel Toyo Soda columns with molecular weight ranges from 10⁴ to 10⁷. Columns were calibrated using polystyrene molecular weight standards from Polyscience, Inc. PMMA molecular weights were corrected using the universal calibration method¹⁹ with the following Mark-Houwkins constants for PMMA²⁰: $a = 0.72$ and $K = 9.3 \times 10^{-5}$ dL/g.

RESULTS

One-phase microemulsions of MMA, DTAB, and water form at 25 and 60°C near the water-rich corner (Fig. 1). The one-phase region at 25°C is similar but slightly smaller than that at 60°C. One-phase microemulsions are transparent and fluid, except at high surfactant concentrations, where samples are also transparent (and nonbirefringent when examined through crossed polarizers) but highly viscous. Hence, upper-phase boundaries were not determined exactly. Conductivities are high (> 5 mS/cm) and increase with surfactant concentration and with temperature (Fig. 2). Conductivities also increase slightly upon MMA addition, go through a shallow maximum, and then decrease again (Fig. 2). This is probably due to hydrolysis of MMA as discussed below.

Conversion vs. reaction time as a function of MMA concentration for microemulsions made along a constant DTAB/water weight ratio of 7/93 are shown in Figure 3. Polymerization of these microemulsions is rapid (more than 60% conversion in 20 min) and the transparent microemulsions become increasingly turbid as the reaction proceeds. Initial reaction rates are independent of MMA concentra-

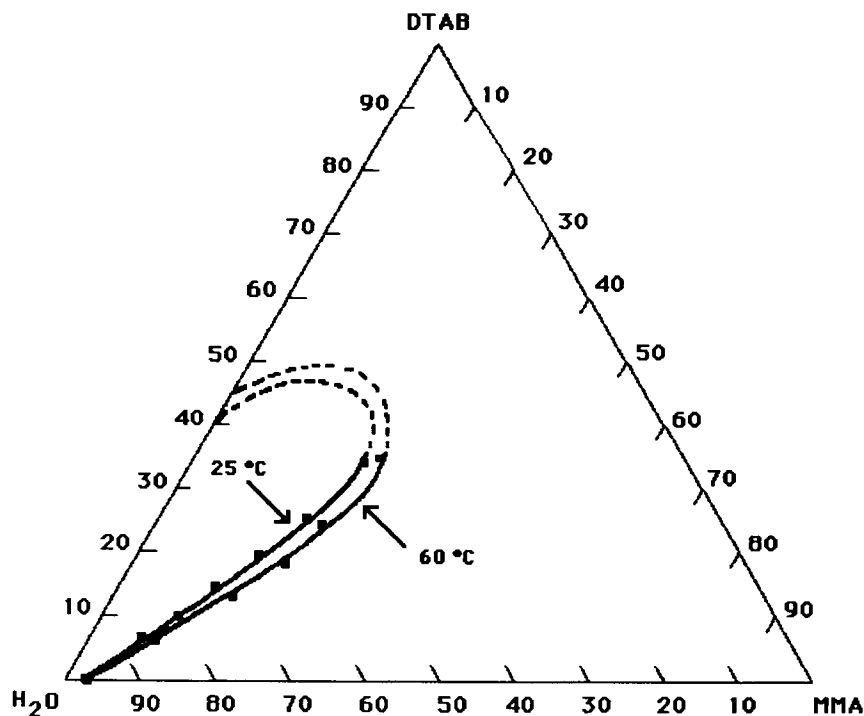


Figure 1 Extent of single-phase region in a partial-phase diagram of DTAB/MMA/water at 25 and 60°C. Samples at high surfactant concentration are viscous, and the boundaries were not determined exactly.

tion, but final conversions increase with the content of MMA in the microemulsions. Only two reaction rate intervals are observed (inset of Fig. 3): a nucleation interval in which the reaction rate increases followed by a decreasing reaction rate interval. Similar rate behavior has been documented elsewhere for microemulsion polymerization of other monomers.^{7,8,14,16} The reaction rate at the maximum (ca. 20% conversion) also increases with MMA concentration. The final latexes range from bluish to opaque depending on MMA concentration, and the latexes are more opaque as the MMA concentration increases. At higher DTAB concentrations (> 10 wt % DTAB), latexes are unstable at all MMA concentrations.

Figure 4 shows the effect of varying the concentration of a water-soluble initiator (KPS) on microemulsion polymerization of MMA. Again, overall reaction rates are fast and increase with KPS concentration. Final conversions are moderate (50–65% in 60 min) and increase with KPS concentration. Induction times are small and seem to be independent of KPS concentration. The overall reaction rate as a function of conversion does not exhibit a constant rate interval, but only an interval of increasing rate followed by one of decreasing rate (inset in

Fig. 4). Polymerization reaction rates are at a maximum at about 20% conversion for all KPS concentrations examined and increase with initiator concentration.

Faster overall reaction rates and higher conversions (ca. 80% in 60 min) are achieved with the oil-soluble initiator AIBN (Fig. 5). Final conversions are practically independent of AIBN concentration in the range examined. The induction period is longer for AIBN than for KPS, probably because the solubility of oxygen (and, hence, its concentration) in MMA is higher than in water. Again, only two rate intervals are detected (inset of Fig. 5). The maximum rate of polymerization occurs at higher conversions (ca. 30%) for AIBN than for KPS, and its magnitude increases with AIBN concentration.

Polymerization of MMA was also performed using a water-soluble initiator (V-50) that decomposes into cationic free radicals. Figure 6 reports the conversion of MMA using KPS, AIBN, and V-50 at identical concentrations (in moles/mole of MMA). Reaction rates are much faster and conversions are higher with V-50 than with AIBN or KPS.

The effect of temperature on MMA microemulsion polymerization initiated with KPS and with

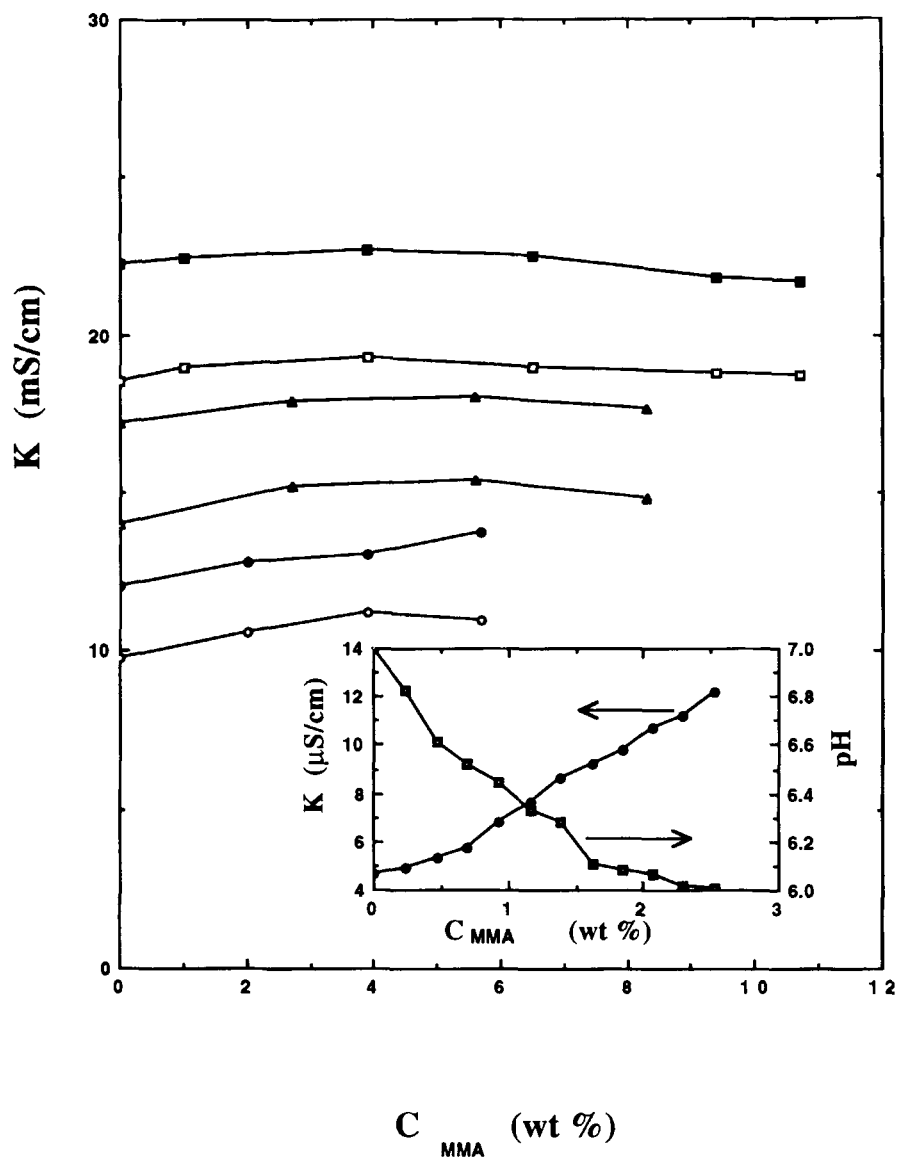


Figure 2 Electrical conductivities of DTAB/MMA/water microemulsions at 25 (open symbols) and 60°C (solid symbols) at various DTAB/water ratios: (■) 80/20; (▲) 85/15; (●) 90/10. Inset: Electrical conductivity and pH of aqueous solutions of MMA as a function of MMA content.

AIBN is shown in Figure 7. With both initiators, overall reaction rates and final conversions increase with increasing temperature. Two rate intervals are observed at all the temperatures examined with both initiators [insets of Fig. 7(A) and (B)]. Arrhenius plots (not shown) give activation energies of 13.4 and 10.3 kcal/mol for the polymerization of MMA with KPS and with AIBN, respectively.

Final latexes range from bluish-transparent to opaque-translucent depending on initiator concentration and temperature of reaction. Lower initiator

concentrations and lower temperatures yield more opaque samples. Final latex particle size and average molecular weights are reported in Table I. Particle-size increases as initiator (KPS or AIBN) concentration or temperature decrease. Independently of type and concentration of initiator and temperature, latexes with a narrow size distribution are obtained as inferred from QLS: The normalized intensity autocorrelation function of the dilute latexes are single-exponential decaying functions with small values of variances, $\nu \approx 0.1$, and the diffusion coefficients are

Table I Number Average Molecular Weight (M_n) and Polydispersity (M_w/M_n) of the Polymethylmethacrylate and Particle Size of Final Latexes as a Function of Potassium Persulfate or AIBN Concentration

[K ₂ S ₂ O ₈] wt %	$M_n \times 10^{-3}$	M_w/M_n	Diameter (nm)
0.25	1858	3.62	74.84
0.5	1740	3.92	63.0
0.75	1658	4.09	54.9
1.0	1303	4.05	52.7
[AIBN]			
wt %	$M_n \times 10^{-3}$	M_w/M_n	Diameter (nm)
0.25	2016	2.62	61.0
0.5	1883	3.21	59.4
0.75	1794	3.68	58.2
1.0	1671	3.16	55.2

independent of the scattering vector. Molecular weights are large ($> 10^6$) and increase as initiator concentration (KPS or AIBN) decreases. Log-log plots of the average molecular weight (\bar{M}_n) and of particle size (D_p) vs. initiator concentration for AIBN and KPS give straight lines.²¹ Least-square fitting gives the following correlations: $\bar{M}_n \propto [\text{KPS}]^{-0.22}$ (correlation coefficient of .996); $\bar{M}_n \propto [\text{AIBN}]^{-0.13}$ (correlation coefficient of .96); $D_p \propto [\text{KPS}]^{-0.26}$ (correlation coefficient of .99); and $D_p \propto [\text{AIBN}]^{-0.09}$ (correlation coefficient of .85). In all cases, molecular weight distributions are wide ($\bar{M}_w/\bar{M}_n > 3$). Latexes prepared with DTAB concentrations smaller than 10 wt % have remained stable for months. Above this concentration, latexes are unstable and flocculate rapidly.

DISCUSSION

Unpolymerized microemulsions of DTAB/MMA/water are optically transparent and have low viscosities (ca. < 10 cP) for DTAB concentrations smaller than 20 wt%. In contrast to DTAB/styrene/water microemulsions, the MMA/DTAB/water one-phase microemulsion region increases slightly with increasing temperature (Fig. 1) and it is larger than the one reported for DTAB/styrene/water microemulsions.¹³ This is probably because of the more hydrophilic character of MMA, which may allow it to act as a cosurfactant, and its high water solubility (1.5 wt % at 45°C)²². Addition of ionic initiators such as potassium persulfate tends to reduce one-phase microemulsion regions,^{4,5} because they behave as electrolytes in water, which,

when present in large amounts, change substantially one-phase microemulsion coexistence regions and induce formation of liquid crystalline regions.²³ Here, however, the phase boundaries at 25°C do not change upon addition of the small amounts of KPS of interest. Phase boundaries were not examined with KPS at 60°C because polymerization is induced even in the presence of inhibitor.

Electrical conductivities of the unpolymerized microemulsions are high (> 5 mS/cm), suggesting a water-continuous structure, and increase with temperature and DTAB concentration (Fig. 2). Also, microemulsion conductivity increases upon addition of MMA, and for higher DTAB concentrations, conductivity goes through a maximum and then decreases at higher MMA concentrations. One should expect that upon addition of a nonconductive substance, such as MMA, the conductivity should decrease. However, because MMA hydrolyzes in water to produce methanol and methacrylic acid, the latter being a weak acid that dissociates in water to produce H⁺ and methacrylate ions, the conductivity could, in fact, increase. To prove this hypothesis, we measured the conductivity and pH of MMA aqueous solutions as a function of MMA content. The conductivity increases and the pH decreases (consistently with the formation of methacrylic acid) as the concentration of MMA in water increases (inset in Fig. 2).

Polymerization of MMA microemulsions is rapid (Fig. 3) and faster than that reported for styrene/DTAB/water microemulsions.¹³ This is because the rate of polymerization (rate constant of propagation) of polar monomers is several times higher than those of nonpolar monomers due to the effect of conjugation of the double bond with a polar substituent.¹⁷ In particular, the rate constant of propagation of MMA at 60°C is 0.513 m³/mol s compared to 0.19 m³/mol s for styrene.²⁴ The transparent microemulsions become increasingly turbid as the reaction proceeds and the turbidity increases with increasing MMA content in the microemulsions. Reaction rates and final conversions also increase as MMA content in microemulsion increases (Fig. 3). This effect can be explained if the amount of monomer solubilized in the droplets increases or the number of reacting particles increases with total MMA concentration. In fact, we detected a large dependence on the maximum rate of polymerization with MMA concentration: $R_{p(\text{max})} \propto [\text{MMA}]^{1.3}$. Overall reaction rates and final conversions have also been shown to depend on overall monomer concentration for MMA and styrene microemulsion polymerization.^{7,9,10,13}

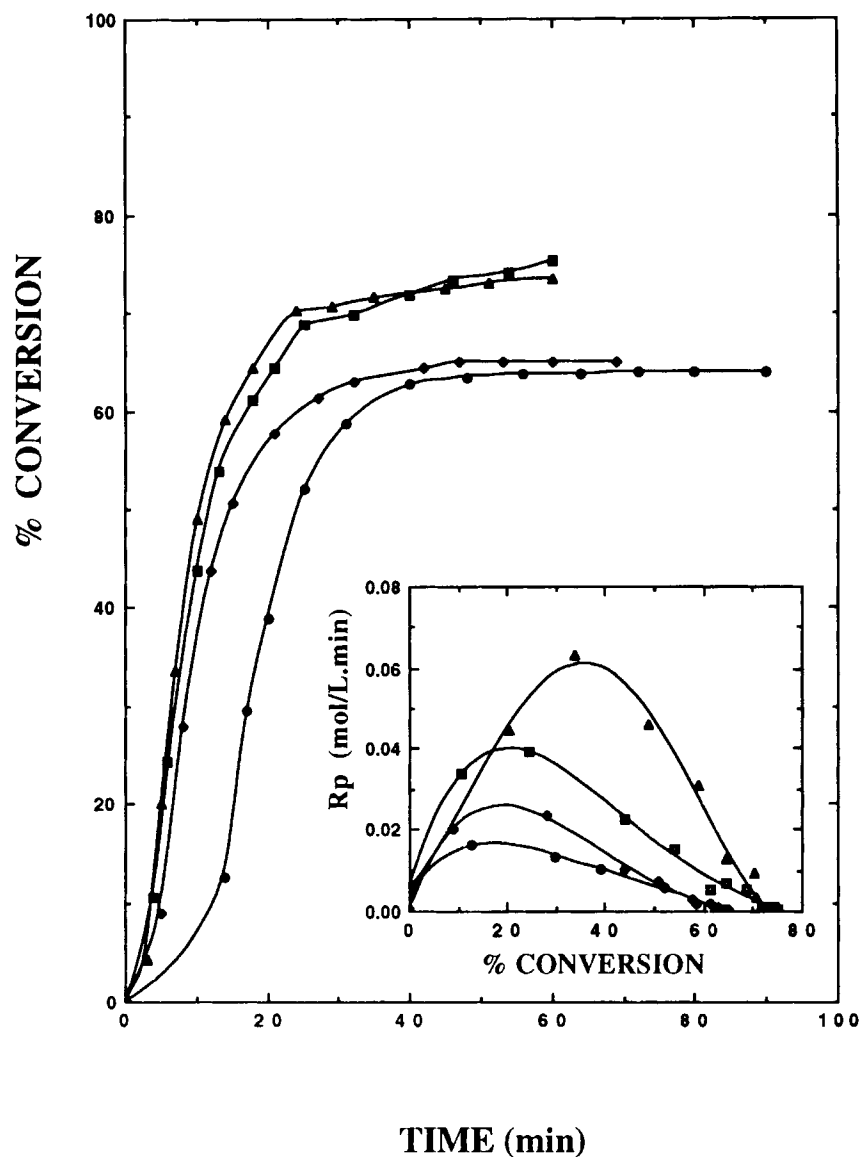


Figure 3 Conversion as a function of time for polymerization at 60°C using potassium persulfate of microemulsion made along constant DTAB/water line of 7/93 containing various MMA concentrations: (●) 3%; (◆) 4%; (■) 6%; (▲) 8%. Inset: Polymerization rate as a function of conversion for data shown in the figure.

Reaction rates and final conversions also increase with increasing amount of initiator, regardless of type of initiator (Figs. 4 and 5). Reaction rates are faster and final conversions are larger with AIBN than with KPS. Elsewhere we reported similar results for the polymerization of styrene in DTAB microemulsions¹⁴ and suggested that the SO_4^- free radicals from KPS, being negatively charged, are strongly bound to the positively charged DTAB microemulsion droplets. This effect reduces the rate of initiation and also decreases the concentration of free radicals from KPS molecules in the aqueous

phase.²⁵ Both effects, of course, tend to decrease the rate of polymerization. To test this hypothesis, we performed polymerizations using a water-soluble initiator (V-50) that decomposes into cationic free radicals. Here, since the free radicals and the droplets have similar charges, they repel each other and allow the initiator to react more effectively with dissolved MMA molecules in the aqueous phase to generate primary polymer particles there. Then, one should expect faster reaction rates and higher conversions with V-50 than with KPS. The polymerization of MMA at 60°C using KPS, V-50, and AIBN

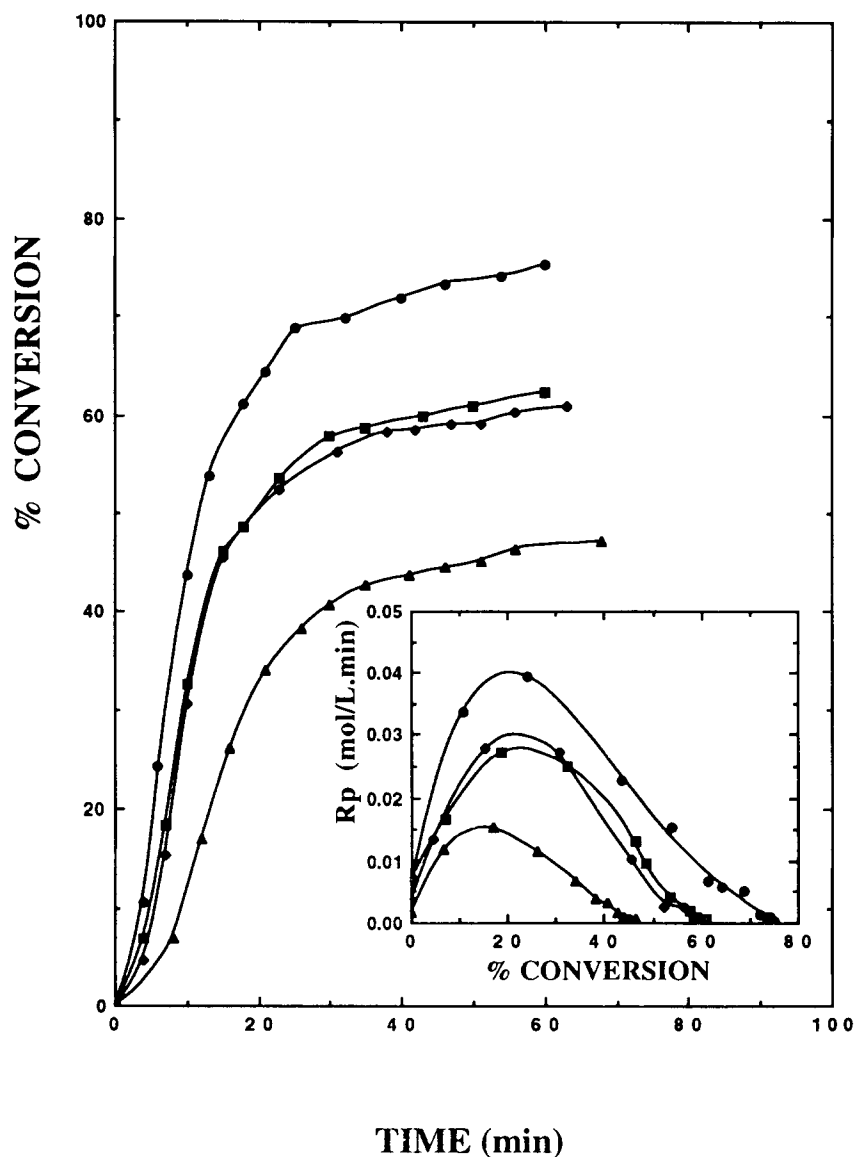


Figure 4 Conversion as a function of time for the polymerization at 60°C of 6.6% DTAB/87.4% water/6% MMA microemulsion using various concentrations of potassium persulfate: (▲) 0.25%; (■) 0.5%; (◆) 0.75%; (●) 1%. Inset: Polymerization rate as a function of conversion for data shown in the figure.

(Fig. 6) supports our argument since faster reaction rates and higher conversions are achieved with V-50 than with KPS (or AIBN). Polymerization of MMA in anionic microemulsions made with Aerosol OT shows the opposite effect, i.e., polymerization rates are faster and conversions are higher with KPS than with V-50.²¹

AIBN, on the other hand, decomposes within each populated microemulsion droplet to produce two free radicals, but the uncharged cyanoisopropyl radicals can diffuse out of the droplet and react in the aqueous phase with MMA molecules to produce pri-

mary reaction sites there. In these sites, the MMA present in the aqueous phase can react to generate a primary particle that can be stabilized with surfactant from the microemulsion droplets or the radicals can migrate to the microemulsion droplets and propagate the reaction. Termination reactions between the pair of free radicals from AIBN inside each microemulsion droplet must be rare as evidenced by the large molecular weights produced with this initiator (see Table I). That termination reactions within droplets probably occur mainly by chain transfer to monomer can be inferred from the

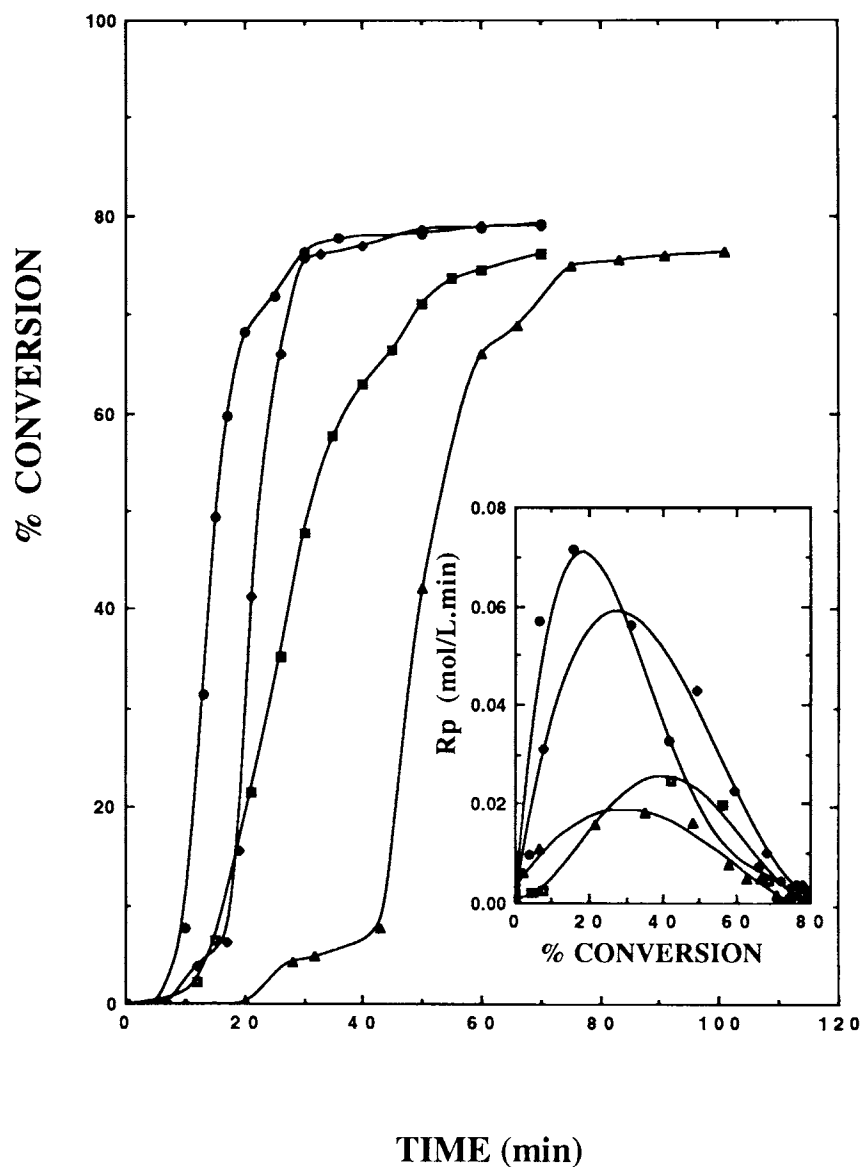


Figure 5 Conversion as a function of time for the polymerization at 60°C of 6.6% DTAB/87.4% water/6% MMA microemulsion using various concentrations of AIBN: (▲) 0.25%; (■) 0.5%; (◆) 0.75%; (●) 1%. Inset: Polymerization rate as a function of conversion for data shown in the figure.

large molecular weights obtained (see Table I). This can be demonstrated from the general expression for the polymer chain length with bimolecular termination and chain transfer to monomer²⁶:

$$\frac{1}{x_N} = \frac{R_T}{R_P} + \frac{k_{TM}}{k_P}$$

where R_T and R_P are the rate of bimolecular termination and propagation reactions; x_N , the polymer chain length; and k_{TM} and k_P the rate constants for

chain transfer to monomer and propagation reactions, respectively. If one assumes that bimolecular termination reaction is negligible, the maximum chain length that can be obtained from the reported value of k_{TM} ($0.18 \times 10^{-4} k_P$)²⁷ for MMA is 55,500, which is equivalent to a molecular weight of about 5,500,000. From the values of the molecular weights and the polydispersity obtained here (Table I), one must conclude that although termination by disproportionation can take place, termination within droplets indeed occurs mainly by chain transfer to

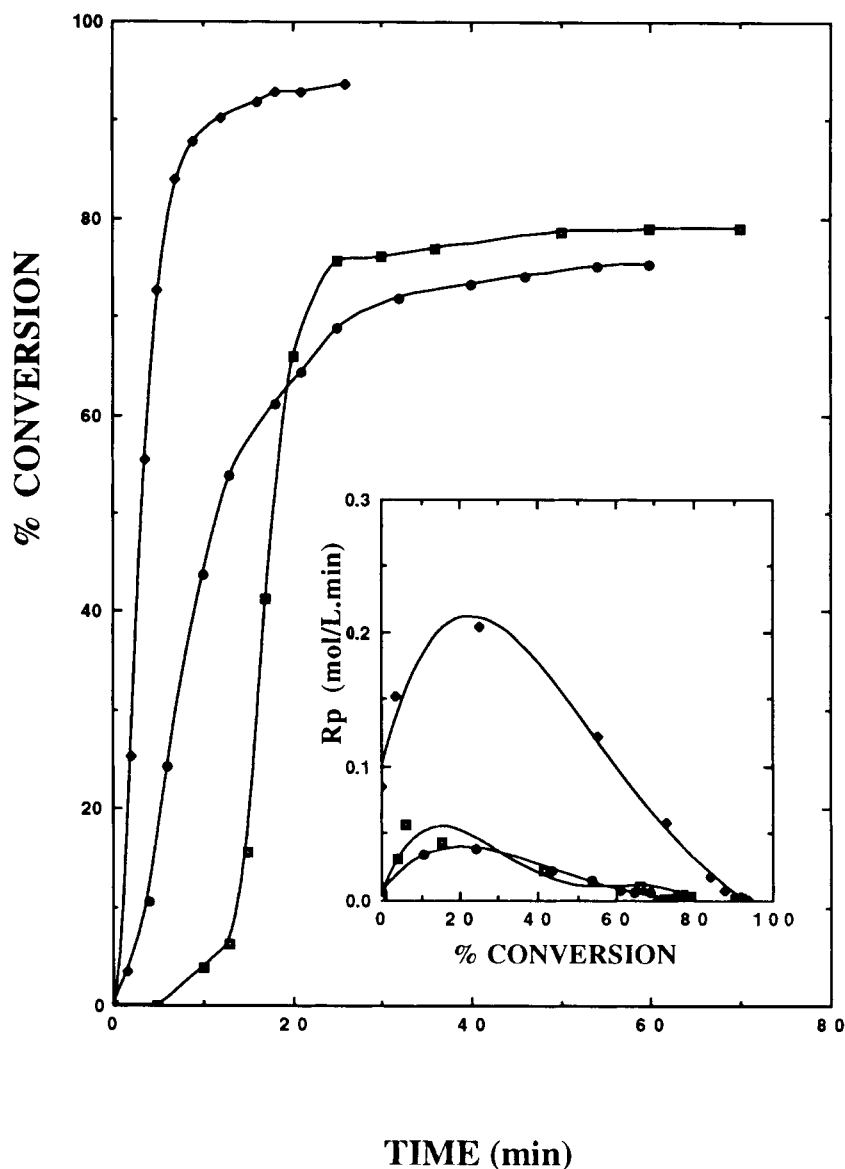


Figure 6 Conversion as a function of time for the polymerization at 60°C of 6.6% DTAB/87.4% water/6% MMA microemulsion using (●) 1% potassium persulfate, (◆) 1% V-50, or (■) 0.75% AIBN as initiator. Inset: Polymerization rate as a function of conversion for data shown in the figure.

monomer, giving a small radical that can easily migrate out of the droplet.

That induction times are consistently longer with AIBN than with KPS can be due to two effects: One is that the solubility of oxygen is higher in MMA than in water, so there is a higher oxygen concentration inside the droplets than in the aqueous phase. The second effect is that the effective concentration of AIBN (mol AIBN per mL of MMA) is much higher than that of KPS (mol KPS per mL of water), so the probability of encounters between an

oxygen molecule and a free radical is much higher for AIBN inside a droplet than it is for KPS in the aqueous phase.

As expected, reaction rates increase with temperature for both AIBN and KPS because the rate of initiator decomposition augments rapidly with temperature.²⁷ Conversions increase with temperature because the mobility of macromolecules increases with temperature, especially when the reaction temperature exceeds the glass transition of the polymer-monomer mixture in the reacting loci.

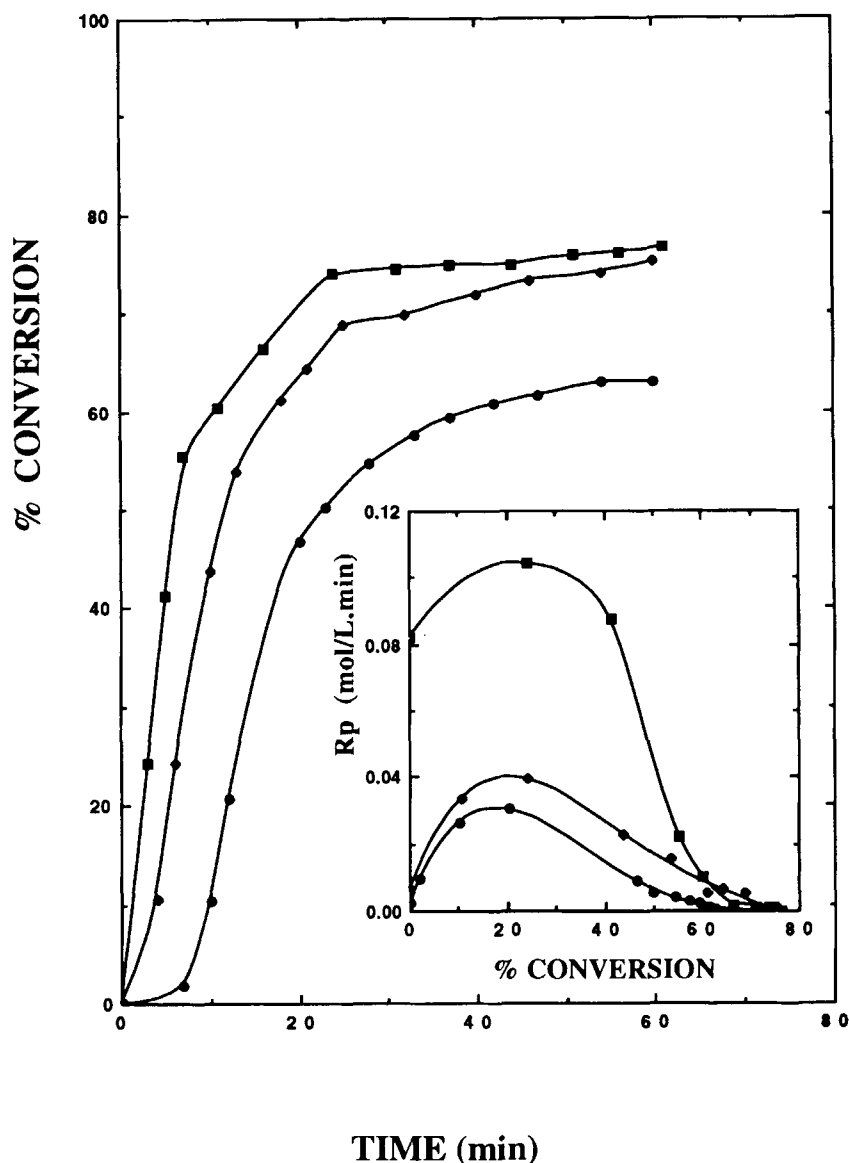


Figure 7 Conversion as a function of time for the polymerization at 60°C of 6.6% DTAB/87.4% water/6% MMA microemulsion at different temperatures using 1% potassium persulfate [Fig. 7(A)] or 1% AIBN [Fig. 7(B)]: (●) 50°C; (◆) 60°C; (■) 70°C. Inset: Polymerization rate as a function of conversion for data shown in the figure.

The activation energies obtained from Arrhenius plots (10.3 kcal/mol for AIBN and 13.4 kcal/mol for KPS) are smaller than that reported for bulk polymerization of MMA with AIBN (20 kcal/mol).²⁸

Regardless of type and concentration of initiator, initial concentration of MMA, or temperature, the reaction rate exhibits only two intervals: one in which the reaction rate increases monotonically with conversion followed by another in which the polymerization rate decreases steadily. It has been sug-

gested that the first interval corresponds to a nucleation rate interval that ends when all the non-initiated microemulsion droplets disappear.^{9,10,14} The second interval has been identified as a termination interval in which the concentration of monomer within each particle decreases steadily since there is no monomer reservoir to maintain the concentration constant. However, other authors have suggested that there is a continuous nucleation of particles during the entire reaction since there is enough surfactant to nucleate new particles as others

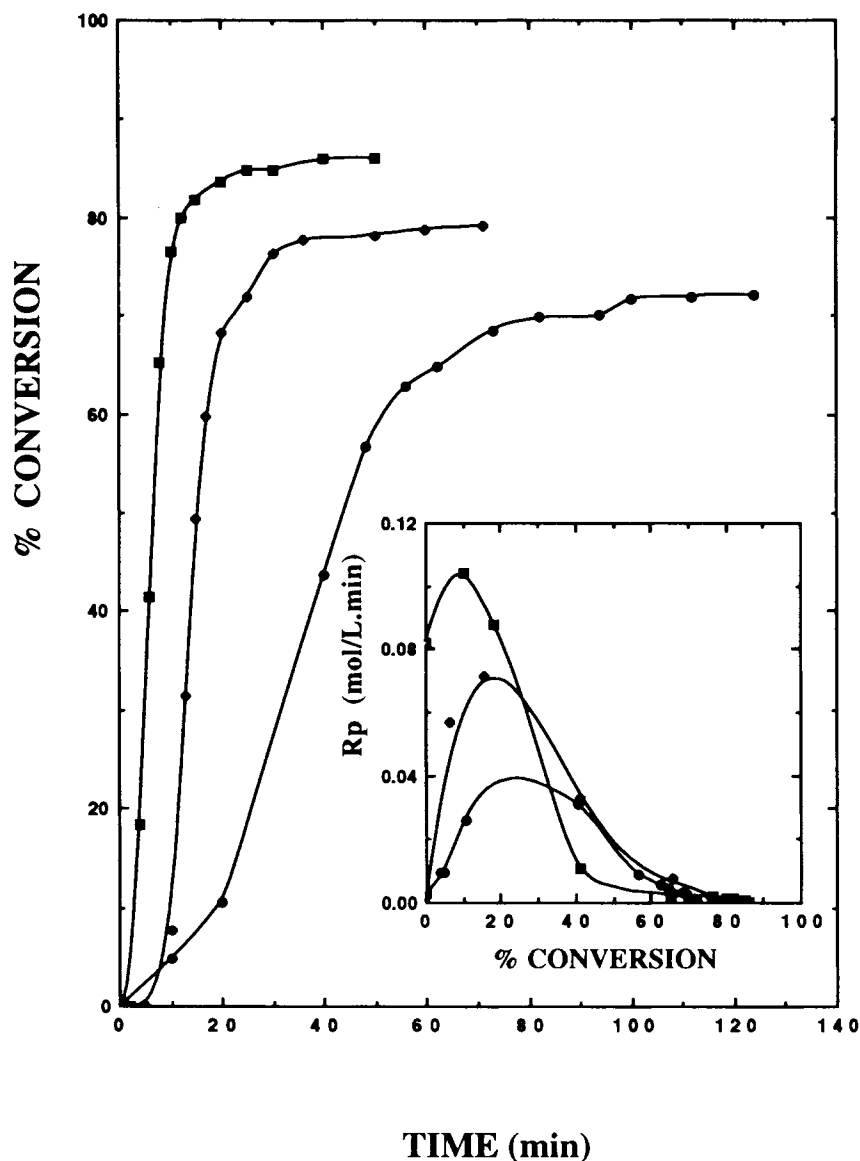


Figure 7 (Continued from the previous page)

grow.^{7,29,30} In this view, the observed maximum rate arises from a decrease in both the average number of free radicals per particle and the monomer concentration per particle and an increase in the number of particles.

Evidently, because of the larger solubility of MMA in water compared to that of styrene, there are significant differences in the microemulsion polymerization mechanisms between these two monomers. The evidence accumulated here suggests that because the high concentration of MMA molecules in water an initiation mechanism in the aqueous phase competes with initiation in microemulsion droplets. Also, it has been shown³¹ that the area

occupied by a molecule of emulsifier (sodium dodecylbenzenesulfonate) on a particle of MMA is 1.31 nm^2 , whereas that occupied at the surface of a polystyrene particle is only 0.50 nm^2 . Hence, as the reaction proceeds and particles grow, DTAB molecules become available, and they could stabilize new initiation sites. Thus, a continuous particle nucleation throughout the reaction is feasible. However, after the maximum in polymerization rate, the number of "new" particles must be small since most of the monomer is already inside the reacting particles and the particle-size distribution is relatively narrow. More systematic work is evidently needed using monomers with varying degrees of water solubility

to further understand the polymerization process in microemulsions and to determine the mechanism of initiation and particle growth.

This work was supported by the Secretaría de Educación Pública de México (C90-01-0521) and by the National Science Foundation through grants PYIA-8351179, INT-8801569, and INT-8996291. One of us (L.A.R.-G.) acknowledges the financial support of Industrias Resistol S.A.

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Received June 10, 1992

Accepted July 28, 1992