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S. E. Loh^a; L. M. Gan^a; C. H. Chew^a; S. C. Ng^b

^a Department of Chemistry, National University of Singapore, Republic of Singapore ^b Department of Physics, National University of Singapore, Republic of Singapore

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POLYMERIZATION OF METHYL METHACRYLATE IN WINSOR I-LIKE SYSTEM

S. E. LOH, L. M. GAN,* and C. H. CHEW

Department of Chemistry

S. C. NG

Department of Physics

National University of Singapore
Republic of Singapore

Key Words: Methyl methacrylate; Microemulsion polymerization; Winsor I-like system

ABSTRACT

Methyl methacrylate (MMA) was polymerized in a ternary Winsor I-like system (WL) which was comprised of two clear phases: a microemulsion phase containing a cationic surfactant and a bulk MMA phase. The polymerization of MMA proceeded only in the microemulsion phase at the expense of the bulk MMA phase. The method is suitable for producing high molecular weights of PMMA (10^6) with a relatively high weight ratio (8:1) of polymer to surfactant. Unlike styrene polymerization in a similar WL system, PMMA latex particles of nanosizes (30–60 nm in diameter) were rather polydispersed. Factors that affect the polydispersity of PMMA particles obtained by this WL method are discussed in conjunction with the nucleation mechanisms.

INTRODUCTION

Microemulsion polymerization has attracted much attention recently because of its ability to produce high molecular weight microparticles [1–9]. A drawback is that a high weight ratio of surfactant to monomer is required to stabilize the polymer particles whose sizes range from 20 to 60 nm in diameter. On the other hand, emulsifier-free polymerization has been studied for the production of monodisperse and clean polymer latexes [10–12]. However, their polymer contents and molecular weights are somewhat lower than those obtained from emulsifier-containing polymerization. Miniemulsion polymerization has been widely studied since 1970 [13–16]. Asua et al. obtained a high-solid content (60%) latex from miniemulsion terpolymerization of styrene, 2-ethylhexyl acrylate, and methacrylic acid using sodium lauryl sulfate and A103 (disodium salt of polyoxyethylenated nonyl phenol half ester of sulfosuccinic acid) surfactants [17]. However, the polymer particles were relatively large and had a broad particle size distribution. The use of the least amount of surfactant to produce a stable latex of small size with a relatively high polymer content remains a challenge.

A microemulsion phase can also coexist with other phases as described by Winsor in 1954 [18]. It is generally known that a Winsor I system consists of a microemulsion (lower phase) in equilibrium with an aqueous phase (upper phase). For a Winsor II system, a microemulsion (upper phase) is in equilibrium with an aqueous phase (lower phase). When a middle phase microemulsion coexists with an upper organic phase and a lower aqueous phase, it is known as a Winsor III system.

Work on styrene polymerization in a Winsor I-like system (WL) was first reported by Gan et al. [19]. The WL system consisted of an o/w microemulsion in the latex phase and was topped with an amount of monomer on the upper phase. The polystyrene particles produced were small (< 90 nm in diameter) with a rather narrow size distribution. Moreover, the polymer content of the stable latex could be as high as 10% polystyrene by using only about 1% of dodecyltrimethylammonium bromide (DTAB). In this study a more water-soluble (150 mM) methyl methacrylate (MMA) was polymerized in a similar ternary WL system at various conditions. A general comparison is made between the polymerization of styrene and MMA in the ternary WL system.

EXPERIMENTAL

Materials

MMA was vacuum-distilled at 2.5 torr (21 °C). Cetyltrimethylammonium bromide (CTAB) and potassium persulfate (KPS) were recrystallized from a distilled ethanol-acetone mixture (1:3 by volume) and distilled water, respectively. Hydroquinone was purified by recrystallization in distilled water. The above-mentioned chemicals were from Fluka. V-50 initiator was used as received.

Polymerization

The conversion of MMA to polymer (PMMA) in the WL system was obtained by gravimetry as a function of time at 60 ± 0.1 °C. Thirty screw-capped tubes, each containing an identical WL composition, were degassed for one cycle at 2.5 torr and

filled with nitrogen gas. They were then immersed in a water bath at $60 \pm 0.1^\circ\text{C}$ for polymerization. At different time intervals each polymerization was first terminated by adding hydroquinone before the latex was precipitated out from a large quantity of methanol. The polymer was washed repeatedly with methanol and water in order to remove the residual CTAB. The polymer conversion was calculated from the weight of the polymer obtained.

Molecular Weight Determination

Molecular weights of PMMA were determined by gel permeation chromatography (GPC) using a Waters 410 liquid chromatography system equipped with a Waters 410 differential refractometer. The columns used were Varian Micropak TSK 7000H and GMH 6 in series, and the eluent was degassed tetrahydrofuran (THF) which contained 0.025% 2,6-di-*tert*-butyl-*p*-cresol as a stabilizer. The flow rate was maintained at 0.8 mL/min. Polystyrene standards (0.2 mg/mL in THF) from Polysciences were used for calibration.

Particle Size Determination

Particle sizes of the latexes were measured by quasi-elastic light scattering (QLS) using a Malvern 4700 light-scattering spectrophotometer. Intensity correlation data were analyzed by the method of cumulants to provide the average delay rate. Prior to measurements, the latexes were diluted with distilled water until the volume fractions of particles were in the 0.01 to 0.1 range. The hydrodynamic radius of latex particles (R_h) was calculated from the intrinsic diffusion coefficient (D_0) using the Stokes-Einstein equation, i.e., $R_h = kT/6\pi\eta D_0$, where η is the viscosity of the continuous medium.

The latexes were also examined with a Jeol TEM-100CX electron microscope. One drop of a latex was thoroughly mixed with 2 mL of 0.2% phosphotungstic acid (PTA). A drop of the mixture was then placed on a copper grid coated with a thin layer of Formvar.

RESULTS

Phase Diagram

The partial phase diagram of the ternary system CTAB/MMA/water before and after polymerization at 30°C is presented in Fig. 1. The transparent o/w microemulsion region is denoted by ME, the turbid o/w emulsion region by E, and the liquid crystalline region by L. In the absence of agitation, o/w emulsions in region E tend to separate into two clear phases.

After polymerization, the composition region that produced stable transparent/translucent latexes shifted to the shaded area which has higher weight ratios of MMA to CTAB. It should be noted that the size of the shaded area depends on the methods of polymerization. For microemulsion polymerization of MMA, transparent latexes could only be obtained from those compositions under the shaded area in the microemulsion region ME. As the MMA content was increased up to the *ab* line, translucent but stable latexes could also be prepared by emulsion polymeriza-

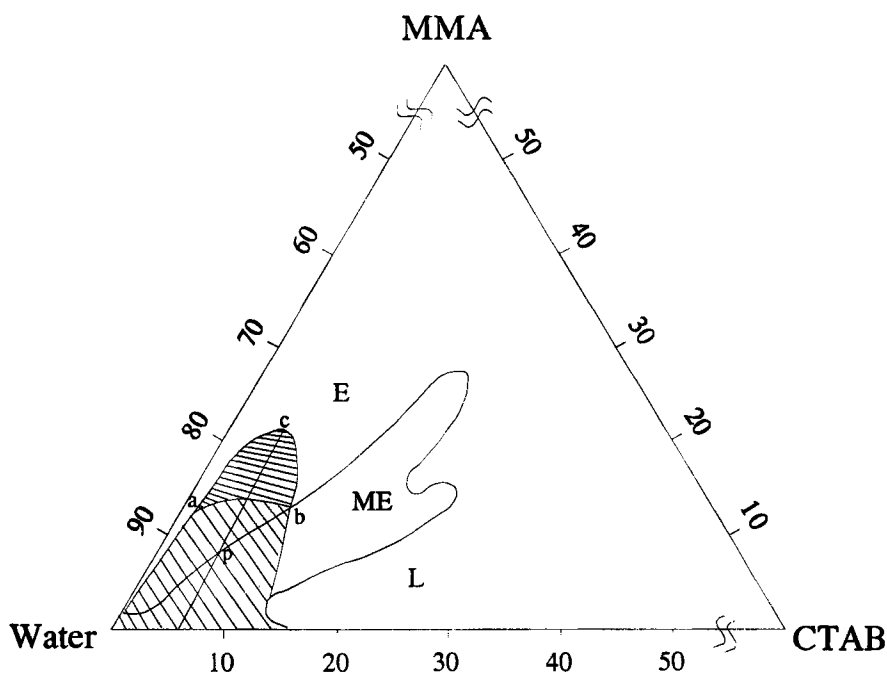


FIG. 1. Partial phase diagram of CTAB/water/MMA at 30°C. Before polymerization: E, turbid emulsion region; ME, transparent microemulsion region; L, liquid crystalline region. After polymerization: the transparent/translucent region shifted to lower CTAB concentrations as represented by the shaded area.

tion under a constant stirring condition. At even higher MMA concentrations up to the region *abc*, stable latexes could still be obtained but only by the WL polymerization method.

This shows that one can study MMA polymerization at various concentrations with a fixed weight ratio of CTAB/water (for example, along the *pc* line of Fig. 1) via microemulsion, emulsion, and WL polymerization. When microemulsion compositions below point *p* are used for polymerization, transparent/translucent PMMA latexes are produced. As more MMA is added to composition *p*, the new composition is shifted along the *pc* line toward the MMA apex. All turbid o/w emulsions beyond the line *ab* produce only an unstable latex by normal emulsion polymerization, i.e., under a constant stirring condition. But in the absence of agitation, each of those o/w emulsions eventually separate into two clear phases. They are the o/w microemulsion with the composition *p* in the lower phase, and the remaining MMA separates out together with a trace amount of water and CTAB in the upper phase. Such a two-phase system is known as a Winsor I (WI) system. Hence, a WI system can be transformed into an o/w emulsion by simple agitation, while it reverts back to a WI system in the absence of agitation. When the polymerization is carried out only in the o/w microemulsion (lower phase of WI) using a water-soluble initiator, the upper phase MMA will diffuse to the lower phase and a transparent/translucent but stable latex can still be produced within the *abc* region by the WI method of polymerization.

TABLE 1. Compositions of Winsor I-like System for Polymerization^a

Sample	Microemulsions			The upper MMA phase, wt%	Total MMA, wt%
	CTAB, wt%	MMA, wt%	Water, wt%		
WL-1	1.0	2.0	91.0	6.0	8.0
WL-2	3.0	3.0	89.0	5.0	8.0
WL-3	3.0	3.0	82.0	12.0	15.0
WL-4	5.7	5.0	79.3	10.0	15.0

^a[KPS] = 0.6 mM based on water; $T = 60^{\circ}\text{C}$.

Polymerization

Although Fig. 1 indicates that stable latexes of high PMMA contents can be prepared from WI systems in a certain concentration region, a long equilibrium time is usually required to attain a WI system. In this study we modified the WI system slightly by simply topping up an excess amount of MMA on an o/w microemulsion of any composition below point p along the pc line in Fig. 1. The two-phase system may not necessarily be in equilibrium, and it is thus referred as a "Winsor I-like" system (WL). Table 1 lists the compositions of four WL systems which had been polymerized by varying the concentrations of CTAB and MMA in both phases.

Figure 2 shows the polymerization curves for samples WL-2 and WL-4. The latter system contained a higher concentration of CTAB and MMA than the former.

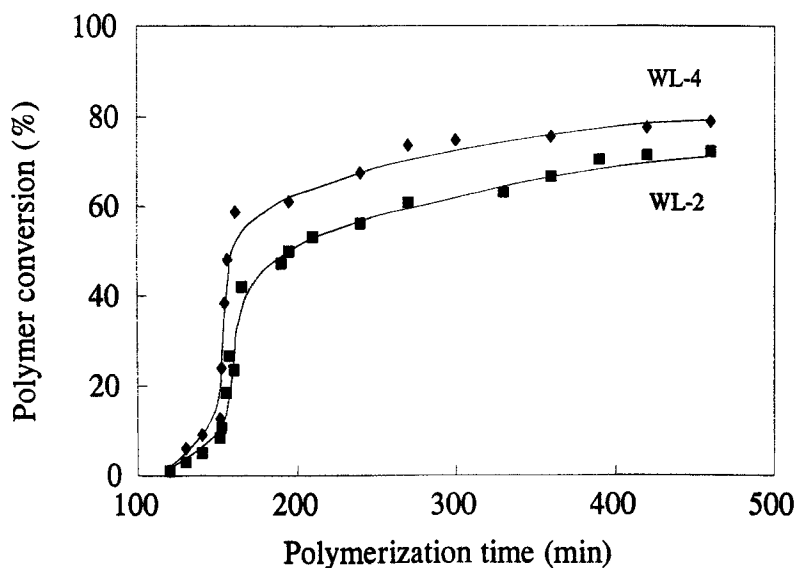


FIG. 2. Time-MMA conversion curves for samples WL-2 and WL-4.

Polymerization occurred only in the microemulsion phase using the water-soluble initiator KPS. The interfacial area (A_i) between oil and microemulsion phases was 3.8 cm^2 , which was the cross-sectional area of the reaction tube. The percentage of polymer conversion was calculated based only on the amount of MMA in the microemulsion phase at any particular time. This is the sum of the amount of MMA originally presented in the microemulsion and the amount of MMA diffused into the microemulsion phase up to a particular time during polymerization. A long induction period of about 2 hours was generally observed due to the difficulty of properly purging the WL samples. After the long induction period, the polymerization was fast within the next 50 minutes, i.e., about 60% MMA in the microemulsion phase could be converted to PMMA. As the polymerization continued, more and more MMA in the upper monomer phase diffused into the microemulsion phase until the monomer phase disappeared. It usually required about 12 hours of polymerization to achieve over 90% conversion of the total amount of MMA in sample WL-2 or sample WL-4. In any case, stable latexes were obtained.

Latexes

Since rather monodisperse nanoparticles of polystyrene had been successfully prepared by the WL method [19], the same technique was applied to the preparation of PMMA microlatexes in this study. Several factors that would affect the particle sizes of the microemulsion latexes have been investigated. The first is concerned with the interfacial area (A_i) between two phases, followed by the concentrations of the initiator and the surfactant in the microemulsion phase, and the amounts of monomer in the upper phase.

The A_i controls the diffusion rate of MMA from the upper phase to the lower microemulsion phase during polymerization. As shown in Table 2, the average hydrodynamic radius (R_h) of latex particles (sample WL-2) decreased with the use of a larger A_i indicating more latex particles per milliliter (N_d) were produced. The polydispersity index (PI) of particle sizes as measured by QLS became slightly larger. All the subsequent investigations in this study were conducted in reaction tubes with a cross-sectional area (A_i) of 3.8 cm^2 .

TABLE 2. The Effect of Various Interfacial Areas (A_i) between the Upper MMA Phase and the Lower Microemulsion Phase on Particle Sizes of Latex WL-2^a

Interfacial area $A_i, \text{ cm}^2$	$R_h, \text{ nm}$	$N_d,$ $10^{15}/\text{mL latex}$	PI
3.8	24.0	1.6	0.18
5.0	24.4	1.5	0.17
15.3	19.5	2.9	0.22
74.2	18.0	3.7	0.21

^a[KPS] = 0.6 mM; $T = 60^\circ\text{C}$. PI = Polydispersity index of particle sizes measured by QLS.

TABLE 3. Effect of KPS Concentration on Latex Particle Size of Sample WL-1^a

[I], mM	R_h , nm	N_d , $10^{15}/\text{mL latex}$	PI
0.24	23.1	1.5	0.27
0.42	22.7	1.6	0.27
0.60	21.9	1.7	0.26
1.00	21.0	2.0	0.28

^aThe interfacial area (A_i) of the reaction vessel was 3.8 cm^2 ; $T = 60^\circ\text{C}$.

The effect of KPS concentrations on the latex particle sizes of sample WL-1 is shown in Table 3. R_h only decreased slightly from 23.1 to 17.7 nm with a fourfold increase in KPS concentration. The high polydispersity of about 0.27 was not affected by varying the KPS concentration from 0.24 to 1.00 mM.

Table 4 shows the effect of various amounts of MMA in the upper phase on particle sizes of microemulsion latexes using the anionic initiator KPS and the cationic initiator V-50. Sample M-1 was a microemulsion and samples WL-5 to WL-7 were prepared by topping up different amounts of MMA on sample M-1. Both types of initiators produced microlatexes of about similar sizes and PI. R_h increased significantly from about 20 to 35 nm with an increase of MMA in the upper phase as from samples M-1 to WL-7. The PI also reduced from about 0.18 to 0.13.

The broad particle size distribution of PMMA latexes can be seen clearly from the transmission electron micrograph of Fig. 3. This means that the WL method did not produce a relatively narrow size distribution of PMMA particles as that for polystyrene latexes of $\text{PI} = 1.13$ [19]. This is due to the different solubilities of monomers in water and their nucleation mechanisms as will be discussed later.

TABLE 4. Effect of Various Amounts of MMA in the Upper Oil Phase on Particle Sizes of Microemulsion Latexes Using Two Types of Initiators

Sample	CTAB/MMA ₁ /MMA ₂ , ^a	[KPS] = 0.6 mM			[V-50] = 0.6 mM		
		R_h , nm	N_d , $10^{15}/\text{mL}$	PI	R_h , nm	N_d , $10^{15}/\text{mL}$	PI
M-1	3/3—	16.5	1.84	0.18	20.5	0.95	0.16
WL-5	3/3/2	24.8	0.81	0.14	22.9	1.00	0.14
WL-6	3/3/4	30.8	0.57	0.13	26.5	0.87	0.13
WL-7	3/3/7	36.3	0.48	0.13	33.5	0.64	0.13

^aMMA₁ and MMA₂ denote the weight percentage of MMA in the microemulsion and the upper oil phase, respectively. CTAB was kept constant at 3 wt% and the remaining wt% was made up with water.

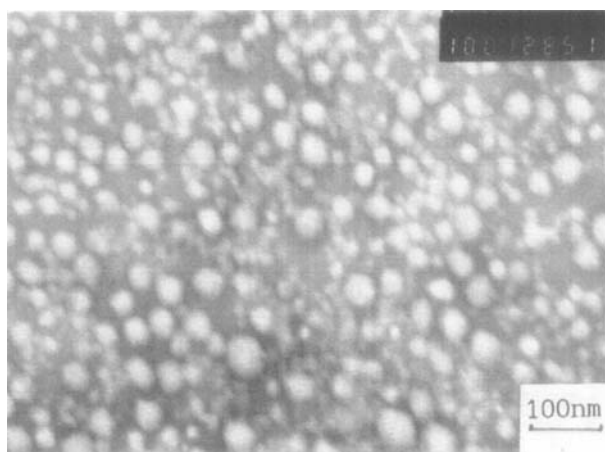


FIG. 3. Transmission electron micrograph of sample WL-7.

Figure 4 shows the growth of PMMA particles for samples WL-2 and WL-4 during polymerization. It was found that R_h increased very rapidly in the early stage of polymerization up to about 40% conversion of MMA in the microemulsion phase. Thereafter R_h increased rather slowly with a significant increase in R_h only toward the end of polymerization. Both latexes WL-2 and WL-4 exhibited good stability at 60°C after postpolymerization as shown in Fig. 5. Only latex WL-3 showed a significant particle coalescence on prolonged heating at about 60°C. It is noted that latex WL-1 was stable at 60°C for more than 1 month. This means that only 1 wt% CTAB was sufficient to effectively stabilize the latex containing 8 wt%

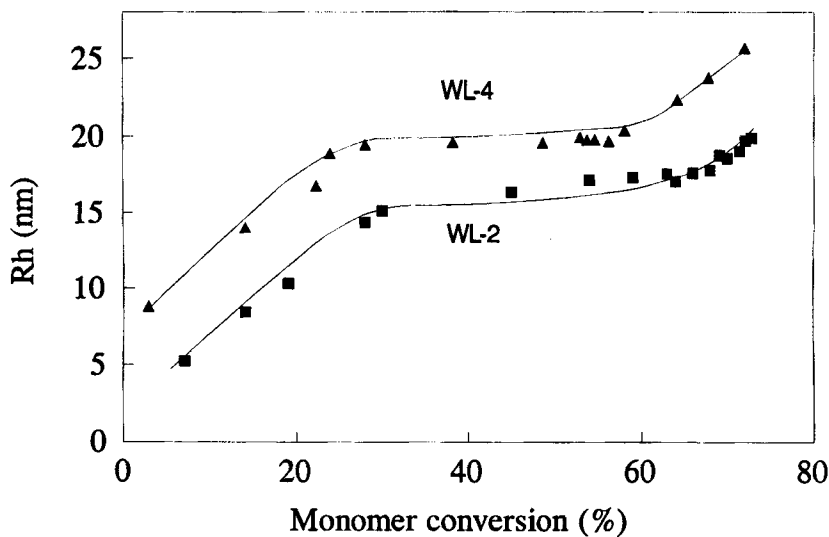


FIG. 4. Growth of latex particles during polymerization.

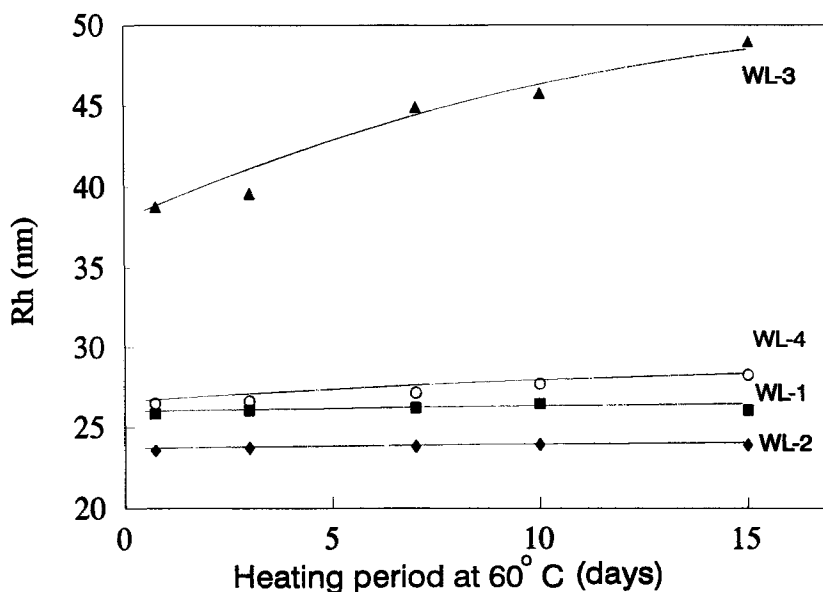


FIG. 5. The stabilities of PMMA latexes at 60°C.

PMMA. However, such a stable latex with the similar high weight ratio (8:1) of polymer to surfactant cannot be obtained by normal microemulsion polymerization. This is the advantage of using the WL method for preparing stable latexes with higher ratios of polymer to surfactant.

Molecular Weights of Poly(Methyl Methacrylate)

High average molecular weights of PMMA (M_w), ranging from about 4 to 7 $\times 10^6$, were generally obtained by WL-type polymerization. M_w decreased significantly with an increase of monomer conversion, especially above 70% conversion, as shown in Fig. 6. M_w of sample WL-4 at any stage of polymer formation was higher than that of sample WL-2 due to the double amount of MMA used in the former system. It is clearly shown by gel permeation chromatography (Fig. 7) that the monomodal distribution of PMMA molecular weights generally broadened with the emergence of a new broad peak at higher percentages of monomer conversion. This means that lower molecular weights of PMMA were produced during the later stage of polymerization.

DISCUSSION

Winsor I-like (WL) polymerization is considered to be a seed-and-feed polymerization in a single-step process which consists of an o/w microemulsion phase and a monomer phase. The polymer particles (seeds) are nucleated in situ only in the microemulsion phase. The monomer feed is constantly supplied by diffusion from the monomer phase to the polymerization loci in the microemulsion phase.

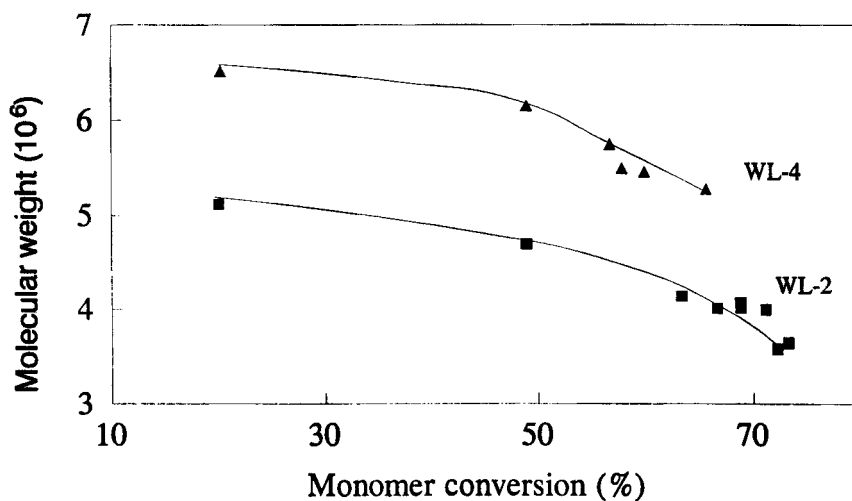


FIG. 6. Molecular weights of PMMA as a function of polymer formation.

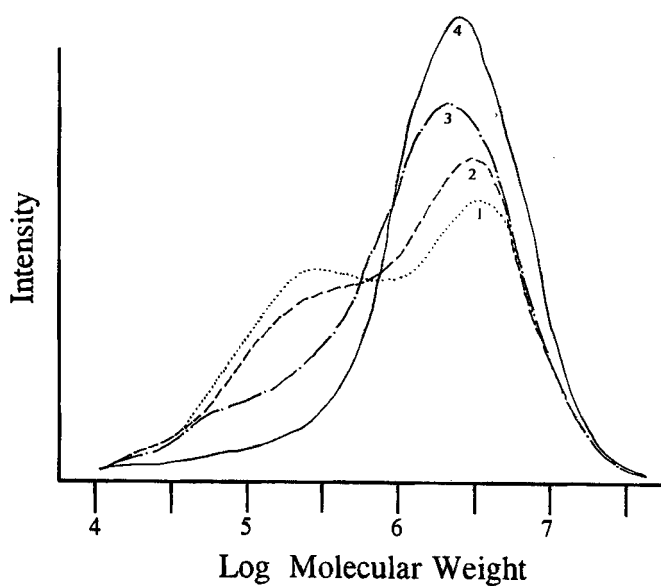


FIG. 7. The molecular weight distributions of sample WL-2 as a function of monomer conversion. (1) 80%, (2) 60%, (3) 30%, (4) 10%.

The oil phase only serves as a large monomer reservoir which slowly disappears during polymerization. The rate of disappearance of the monomer phase is governed by both the rate of polymerization and by the interfacial area (A_i) between the two phases, i.e., the cross-sectional area of a reaction tube. The hope is that the limited supply of monomer passing through the interface will be just sufficient for the growth of monomer-swollen polymer particles and thus reduce the possibility of continuous particle nucleation. If this ideal monomer-supply situation can be attained during polymerization, the WL method can be used to produce monodisperse polymer particles.

In fact, rather monodisperse polystyrene particles have been prepared by the WL method [19]. But why were polydisperse PMMA particles always obtained by using a similar method? Changes of the interfacial area (A_i), the concentrations of the surfactant and the initiator in the microemulsion phase, and the amount of the monomer reservoir did not seem to improve the polydispersity of PMMA particles significantly. This is attributed to the continuous homogeneous nucleation of PMMA particles in the WL system for two reasons. First, the MMA solubility in water (150 nM) is 30-fold higher than that of styrene. Second, the propagation rate of MMA polymerization in an aqueous phase is much faster than that of styrene [20]. Antonietti et al. [21] reported the inconsistency of PMMA particle sizes in their theoretical prediction for the polymerization of MMA in a cetyltrimethylammonium chloride/water microemulsion. They concluded that the irregularities were due to the higher solubility of MMA in water and to a lower interface energy between the oil and water phases.

In the case of a WL system containing styrene, it is believed that polystyrene only forms in the microemulsion droplets via micellar nucleation [19]. Once polystyrene is formed, droplets containing polymer swell very rapidly by absorbing more monomer and form highly monomer-swollen polymer particles [22]. The fast-growing polymer particles are then stabilized by adsorbing more surfactant from unpolymerized microemulsion droplets which diminish in number during polymerization. This minimizes the possibility of the continuous nucleation needed to produce new polymer particles, resulting in the formation of more uniform polymer particles. However, this is not the case for MMA polymerization in a WL system. Free radicals generated by KPS in the aqueous phase would react with the MMA solubilized in water to form oligomeric radicals. It is estimated [23] that oligomeric radicals with four or more MMA units correspond to species with a sufficient surface activity for the usual micellar entry to microemulsion droplets (micellar nucleation). When the oligomeric radicals grow to more than 10 units of MMA, the solubility limit causes them to precipitate. The precipitated oligomeric radicals then adsorb surfactant molecules to form new particles (homogeneous nucleation) which grow by recruiting more monomer and surfactant as do micellar particles. The number of polymer particles is thus governed by the entry of oligomeric radicals into micelles (micellar nucleation) and the rate of precipitated oligomeric radicals (homogeneous nucleation) to form particles. Both mechanisms seem to be operating in the WL system containing MMA. The continuous increase of PMMA particles during polymerization may be attributed to the persistent occurrence of homogeneous nucleation. Hence, only polydisperse PMMA particles were observed under the conditions studied.

It seems that the homogeneous nucleation of PMMA is inevitable as long as the MMA phase is present. This is because only a fraction of MMA molecules diffusing across the interface will be absorbed by monomer-swollen polymer particles near the interface. Since the system was not stirred during polymerization, the diffusion of the remaining MMA to all other polymerization loci might not be fast enough to compete with the precipitation of the growing oligomeric radicals as is needed for homogeneous nucleation to proceed. When mild stirring was applied to the microemulsion phase, the polydispersity index of the MMA latex particles produced was reduced from 0.18 to 0.12, but this PI is still far from a narrow size distribution.

The significance of the continuous nucleation of PMMA is also clearly reflected from seeding polymerization based on polymerized microemulsion samples (S_0) as shown in Table 5. The PI for sample S_0 was 0.13, but it increased to 0.15 and 0.17 for samples S2 and S7, respectively, after adding more feed to the seed sample S_0 . Once hydroquinone was added to samples S2H and S7H, their PI reduced to about 0.14, which is close to the seed of sample S_0 (0.13). Moreover, their numbers of latex particles per mL (N_d) were also drastically reduced from 11.0 to 8.2×10^{15} and from 16.0 to 9.2×10^{15} for samples S2 to S2H and S7 to S7H, respectively. The results show that the continuous homogeneous nucleation of PMMA did occur significantly even in the aqueous phase of the seeding polymerization system. Thus, there is no doubt that continuous homogeneous nucleation of PMMA occurs in the WL system.

For the WL polymerization of MMA, a relatively large amount of dissolved MMA is maintained in the aqueous phase because of the constant supply of MMA from the oil phase. It is thus inevitable that polydisperse latex particles and broader

TABLE 5. Compositions^a for Seeding Polymerization of MMA

Sample	Additional MMA, ^c wt%	R_n , nm	PI	N_d , 10^{15} /mL latex
S_0	0	24.9	0.13	7.9
S2	2	24.6	0.15	11.0
S2H ^b	2	27.0	0.14	8.2
S7	7	25.5	0.17	16.0
S7H ^b	7	30.5	0.14	9.2

^aMicroemulsion composition: 3 wt% MMA, 3 wt% CTAB, 94 wt% water, and [AIBN] = 0.45 mM based on water content; $T = 60^\circ\text{C}$.

^bHydroquinone inhibitor (0.1 mM) was also added to the prepolymerized microemulsion S_0 .

^cVarious amounts of additional MMA containing AIBN of the same concentration as in Footnote "a" were added to the prepolymerized microemulsion sample S_0 . The seeded latexes were thoroughly mixed with the additional MMA for 24 hours at an ice-cold temperature before they were subjected to a second polymerization sequence.

molecular weight distributions will be obtained due to continuous homogeneous nucleation. Unlike styrene, MMA is not suitable for WL polymerization if rather uniform particle sizes are to be obtained. On the contrary, WL polymerization of MMA usually produces latex particles with a broader particle size distribution than are obtained by microemulsion polymerization [8]. The increase of PI for latex particles with increasing A_i (Table 2) is also caused by continuous homogeneous nucleation. This is because more MMA can diffuse through the larger interface at a given time and be available in the aqueous phase for homogeneous nucleation. Similarly, the decrease of PMMA molecular weights during the later stage of polymerization was due to the continuous generation of polymer particles and an uneven distribution of monomer to the growing particles. This was especially so for those polymerization loci away from the interface because no stirring was applied to the WL polymerization and it was a diffusion control process. Consequently, the molecular weight distribution became broader with the emergence of a new broad peak of lower molecular-weight polymers arising from the deficient supply of monomer.

CONCLUSIONS

In contrast to styrene polymerization, polymerization of MMA by the Winsor I-like method produces only polydisperse latex particles ranging from about 30 to 60 nm in diameter. The continuous homogeneous nucleation of PMMA in the aqueous phase is responsible for the polydispersity in particle sizes. A relatively water-soluble monomer is thus not suitable for preparing polymer particles with a narrow size distribution by WL polymerization. However, it is a potential method for obtaining polymer latexes with higher weight ratios of polymer to surfactant. Although high molecular weights of PMMA (10^6) can easily be obtained, the molecular weight distribution is broader than that obtained by a similar o/w microemulsion polymerization.

REFERENCES

- [1] H. I. Tang and P. L. Thomas, and E. Gulari, *Polymer*, **25**, 1357 (1984).
- [2] P. L. Johnson and E. Gulari, *J. Polym. Sci., Polym. Chem. Ed.*, **22**, 3967 (1984).
- [3] C. K. Gratzel, M. Jirousek, and M. Gratzel, *Langmuir*, **2**, 292 (1986).
- [4] P. L. Kuo, W. J. Turro, C. M. Tseng, M. S. El-Aasser, and J. W. Vanderhoff, *Macromolecules*, **20**, 1216 (1987).
- [5] J. S. Guo, M. S. El-Aasser, and J. M. Vanderhoff, *J. Polym. Sci., Polym. Chem. Ed.*, **27**, 691 (1989).
- [6] L. M. Gan, C. H. Chew, and I. Lye, *Makromol. Chem.*, **193**, 1249 (1992).
- [7] L. M. Gan, C. H. Chew, S. C. Ng, and K. C. Lee, *Polymer*, **34**, 3064 (1993).
- [8] L. M. Gan, C. H. Chew, S. C. Ng, and S. E. Loh, *Langmuir*, **9**, 2799 (1993).
- [9] V. H. Perez-Luna, J. E. Puig, V. M. Castano, B. E. Rodriguez, A. K. Murthy, and E. W. Kaler, *Ibid.*, **6**, 1040 (1990).

- [10] E. Song and G. W. Poerhlein, *J. Polym. Sci., Polym. Chem. Ed.*, **28**, 2359 (1990).
- [11] J. W. Goodwin, J. Hearn, C. C. Ho, and R. H. Ottewill, *Br. Polym. J.*, **5**, 347 (1973).
- [12] Y. C. Li, J. W. Goodwin, and R. H. Ottewill, *Progr. Colloid Polym. Sci.*, **60**, 163 (1976).
- [13] J. Ugelstad, F. K. Hansen, and S. Lange, *Makromol. Chem.*, **175**, 507 (1974).
- [14] F. K. Hansen and J. Ugelstad, *J. Polym. Sci., Polym. Chem. Ed.*, **17**, 3069 (1979).
- [15] J. Ugelstad, M. S. El-Aasser, and J. W. Vanderhoff, *J. Polym. Sci., Polym. Lett. Ed.*, **11**, 503 (1973).
- [16] Y. T. Choi, M. S. El-Aasser, E. D. Sudol, and J. W. Vanderhoff, *J. Polym. Chem., Polym. Chem. Ed.*, **23**, 2973 (1985).
- [17] J. M. Asua and L. Lopez de Arbina, *Polymer*, **33**, 4832 (1992).
- [18] P. Winsor, *Solvent Properties of Amphiphilic Compounds*, Butterworths, London, 1954.
- [19] L. M. Gan, N. Lian, C. H. Chew, and G. Z. Li, *Langmuir*, **10**, 2197 (1994).
- [20] B. S. Hawkett, D. H. Napper, and R. G. Gilbert, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 3173 (1981).
- [21] M. Antonietti, W. Bremser, D. Muschenborn, C. Rosenauer, B. Schupp, and M. Schmidt, *Macromolecules*, **24**, 6636 (1991).
- [22] J. S. Guo, E. D. Sudol, J. W. Vanderhoff, and M. S. El-Aasser, *J. Polym. Sci., Polym. Chem. Ed.*, **30**, 691, 703 (1992).
- [23] A. I. Maxwell, B. R. Morrison, D. H. Napper, and R. G. Gilbert, *Macromolecules*, **24**, 1629 (1991).

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