Photoinitiated Copolymerization of Acrylamide and Styrene in Oil-in-Water Microemulsion

LIPING ZHANG,[1] ZHAOHUA ZENG,[1] YONGLIE CHEN,[1] CHI WU,[2] JUN GAO[2]

[1] Institute of Polymer Science, Zhongshan University, Guangzhou 510275, China

[2] Department of Chemistry, Hong Kong Chinese University, Shatin, Hong Kong

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ABSTRACT: This article describes the copolymerization of acrylamide with styrene in oil-in-water microemulsion, using dodecyl betaine as emulsifier and α-hydroxy-α,α-dimethyl acetophenone or α,α-dimethoxy-phenyl acetophenone as photoinitiator. Results indicated that the photoinitiation of polymerization occurs at the interface between the oil phase and the water phase and that the polymerization occurs in the microemulsion droplet. Particle size increased with increasing polymerization time. The copolymer chain consisted of isolated acrylamide units randomly distributed among styrene groups. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **66:** 2543–2549, 1997

Key words: photoinitiated copolymerization; acrylamide; styrene; oil-in-water microemulsion; particle size

INTRODUCTION

Heterogeneous copolymerization in microemulsion systems has recently been investigated.[1–3] This allows copolymerization of comonomers with different polarity and with different solubility in water. Rodriguez and Kaler[1] studied the copolymerization of styrene (St) and acrylic acid in a cationic microemulsion made with dodecyltrimethylammounium bromide. It was found that the resulting latex was a monodisperse dispersion of spherical particles of 21 nm in radius. The copolymer backbone consists of isolated acrylic acid units randomly distributed among polystyrene blocks. The initial stages of the copolymerization of acrylamide (AAm) with methyl methacrylate or St in water-in-oil microemulsion initiated by radical initiators with different solubility in water were investigated by Vaskova et al.[2] They found that the initial rate of copolymerization depends on the mole fraction of AAm in the comonomer mixture and was independent of the solubility of the radical initiator in water. The monomer reactivity ratios of St-acrylonitrile copolymerization in oil-in-water microemulsion was studied recently.[3] It was found that the monomer reactivity ratios of monomer pairs were not necessarily constant but depended on the actual molar ratio of the monomers in the microenvironment of the polymerization loci. The copolymerization loci were found to be the microemulsion droplets. Photoinitiated copolymerization of water- and oil-soluble monomers in oil-in-water microemulsion has not been investigated in detail, as was seen from the available literature. The change of particle size has not been investigated in the copolymerization with a thermal initiator. The aim of this article was to study the influence of photoinitiators, monomer feed on copolymer composition, and the sizes of microemulsion droplets before and after polymerization.

EXPERIMENTAL

Chemicals

Chemically pure AAm was recrystallized twice from chloroform. Chemically pure St was distilled

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Correspondence to: L. Zhang.

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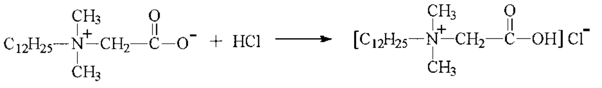
at reduced pressure before use. α-Hydroxy-α,α-dimethyl acetophenone (HMAP) (product of Merck) and α,α-dimethoxy-phenyl acetophenone (DMPA) (product of Aldrich) were used without purification. Dodecyl betaine (DB) aqueous solution was an industry product which contained approximately 8–9% NaCl and 30% DB and was purified by first being transformed into dodecyl betaine hydrochloride (DBH) according to the following reaction.



$$C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_2-\overset{O}{\overset{\|}{C}}-O^- + HCl \longrightarrow [C_{12}H_{25}-\overset{CH_3}{\underset{CH_3}{\overset{|}{\underset{|}{N^+}}}}-CH_2-\overset{O}{\overset{\|}{C}}-OH]Cl^-$$

(dodecyl betaine) (dodecyl betaine hydrochloride)

The precipitated DBH was recrystallized from distilled water, and purified DB was obtained as an aqueous solution by passing the DBH aqueous solution through an alkaline anion-exchange resin.

Procedures

The oil-in-water microemulsion was prepared with stirring on a JB-3 electrical magnetic stirrer by adding St to the mixture of DB, water, and AAm. The stirring speed was 1500 rpm. After being stirred for 20–30 minutes, it became transparent. Phase separating was not observed after 9 months of storage at room temperature. The polymerization was carried out at 25°C by irradiation from a medium-pressure Hg lamp.

The products were washed with hot water and then with toluene to remove DB and any homopolymers of AAm and St that might have formed during the reaction.[1] The material that did not dissolve in these solvents was dried and weighed to calculate percent conversion of monomers. The particle size of microemulsion droplets before and after polymerization was characterized at 25°C with a commercial laser light-scattering spectrometer (ALV-5000, Langen in Hessen, Germany) with an argon ion laser (Coherent INNOVA 90, operated at 488 nm and 100 mW) as the light source. The composition of the products was characterized by using ^{1}H nuclear magnetic resonance (NMR) (Bruker dp × 400) and Fourier transform infrared (Nicolet 205 FTIR). Glass transition temperature (T_g) of the copolymer was measured with a Perkin Elmer DSC 7 differential scanning calorimeter at a heating rate of 20°C/minute.

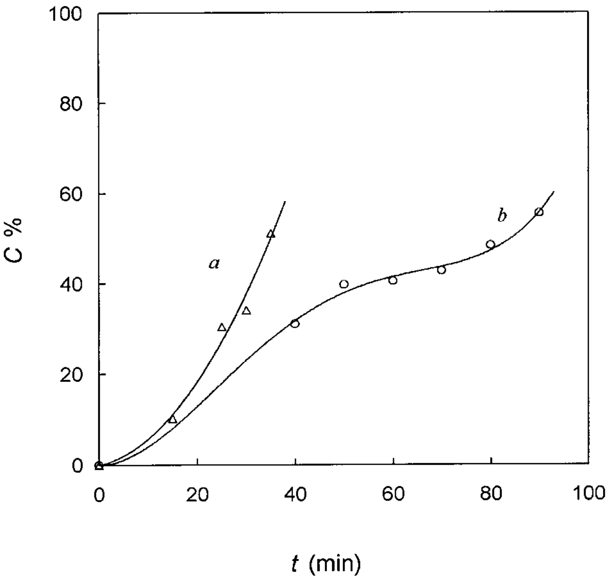


Figure 1 $C\%$ versus t for microemulsion copolymerization of AAm and St with (a) HMAP and (b) DMPA (7.62×10^{-3} mol/mol of St) as photoinitiator; AAm/St = 0.577.

RESULTS AND DISCUSSION

Copolymerization

Figure 1 is the curve of conversion of monomers (C %) versus copolymerization time t. The composition of the microemulsion here is St (4.5 wt %), AAm (2.1 wt %), DB (7.6 wt %), and H_2O (85.8 wt %). Figure 1 shows that HMAP has a higher initiating efficiency than DMPA.

Figure 2 shows the ultraviolet (UV) spectra of HMAP and DMPA. There is only one band (I) for both photoinitiators when recorded in St. A new band was found at around 310 nm (II) and 300 nm (II′) for HMAP and DMPA, respectively, when recorded in oil-in-water microemulsion and is much narrower than (I). The extinction coefficients of these two bands are about 10^2, which suggests that they may be attributed to $n \rightarrow \pi^*$ transition. Because HMAP and DMPA are oil-soluble photoinitiators, the similarity of bands (I) in St and in microemulsion for both photoinitiators implies that (I) arises from photoinitiators located in the oil phase. It is well known that for the $n \rightarrow \pi^*$ transition, a blue shift occurs when the medium polarity increases. It is possible that (II) and (II′) are the blue shift of (I) resulting from photoinitiators located at the interface between the oil phase and the water phase. The regular arrangement of the emulsifier molecules at

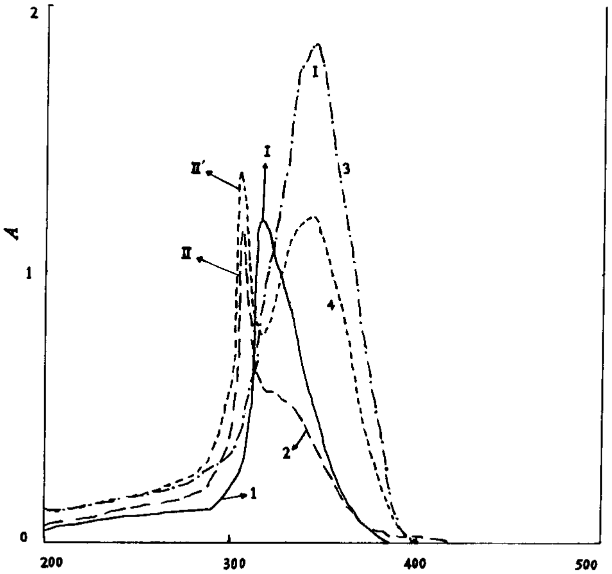
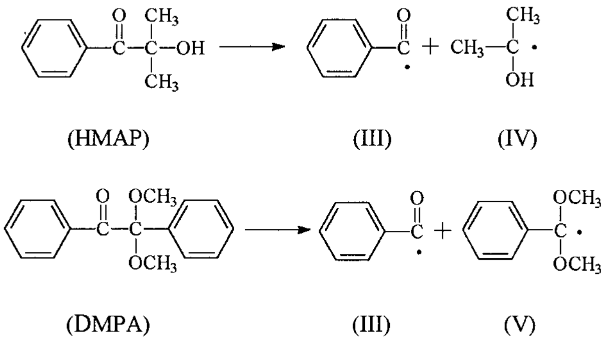


Figure 2 UV spectra of HMAP and DMPA in different media. (1) HMAP in St, (2) HMAP in oil-in-water microemulsion; (3) DMPA in St, (4) DMPA in oil-in-water microemulsion.

this interface, and hence the rather regular assembly of photoinitiator molecules, explains the sharp absorption of (II) and (II′). (II) and (II′) are not ascribed to the interaction between photoinitiators and AAm or water since the UV spectra recorded in pure water or in AAm aqueous solution showed only one band, that is, 247 nm for HMAP and 253 nm for DMPA. It can be shown that HMAP was concentrated relatively on the interface compared with DMPA. From the relative strength of II and I and of II′ and I of the UV spectrum, this is reasonable considering the higher polarity of HMAP.

It is well documented that the photofragmentation of the two photoinitiators occurs according to the following schemes:



(HMAP) (III) (IV)

(DMPA) (III) (V)

Benzoyl radical (III) is the main radical that is responsible for the initiation. There is a serious "cage effect" in the oil phase of the microemulsion droplet for nascent radical pairs generated by photofragmentation. Only those which are near or at the interface between the water and oil phases can diffuse into water phase [one of the radicals (IV or V)] and leave behind another radical (III) to initiate copolymerization. UV absorption of two photoinitiators has suggested that some photoinitiators do locate at the interface. The larger polarity of HMAP than DMPA may have two consequences: first, more HMAP molecules are located at the interface, and second, radical (IV) can diffuse more efficiently into the water phase than radical (V) because of the larger polarity of (IV). Therefore, the higher copolymerization rate by using HMAP is attributable to these consequences.

Composition of Copolymers

Copolymer formation is confirmed by ^{1}H NMR and FTIR. The two bands in Figure 3 at 6.55 and 7.05 ppm in ^{1}H NMR spectrum suggest that the St units are grouped in blocks.[4] Two amide peaks are of equal area and width and appear at 2.17 and 3.30 ppm. This is attributed to the relatively slow reorientation rate of the polymer segments, permitting effective coupling of the electric quadrupole moment of the ^{14}N nucleus to the motions of the molecular framework.[5] Two bands in Figure 4 at 3388 and 699 cm^{-1} are found in the FTIR spectrum, which were assigned to N—H absorption in AAm units and C—H absorption in St units. Quantitative analysis of these two bands shows a copolymer unit ratio of AAm to St ($P_{\mathrm{AAm}}/P_{\mathrm{St}}$) that increases with increasing polymerization time t (Fig. 5). Because AAm is water soluble

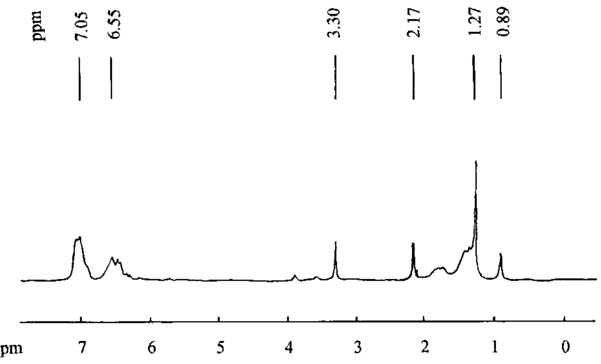


Figure 3 ^{1}H NMR spectrum of copolymer of AAm and St.

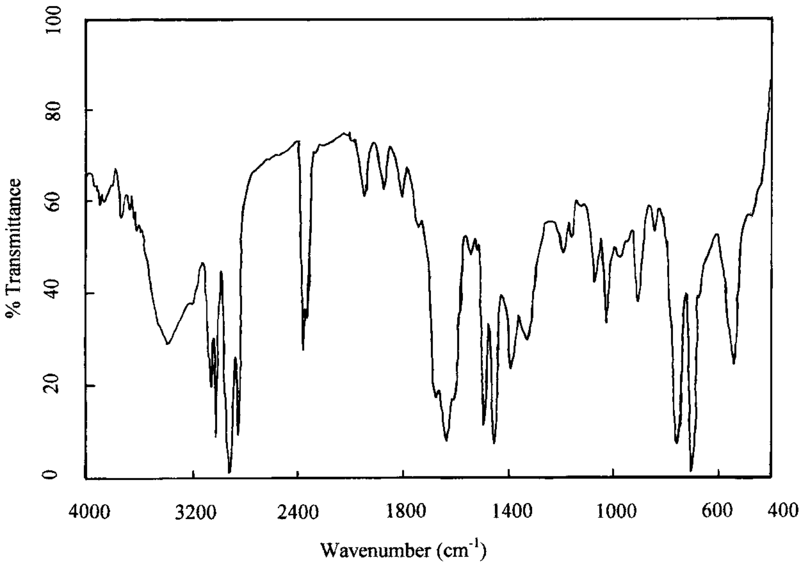


Figure 4 FTIR spectrum of copolymer of AAm and St.

and St is oil soluble, they come into contact at the interface between the oil phase and the water phase. AAm is dissolved in a large continuous medium, while pure St forms the microemulsion droplet. The concentration of St in the microemulsion droplet is much higher than the concentration of AAm in water phase. At the first stage of copolymerization, St is much easier to add to the propagation chain than AAm. The concentration of St in oil phase decreased with the increasing copolymerization time, while more and more AAm in water phase gathered at the interface and was added to the propagation chain gradually. This explains why $P_{\mathrm{AAm}}/P_{\mathrm{St}}$ increases with increasing t. Figure 6 shows the plots of the AAm unit ratio in copolymer (F_1) versus the AAm monomer feed ratio (f_1). The results show that F_1 increases linearly with increasing f_1 up to $f_1 \cong 0.5$, whether

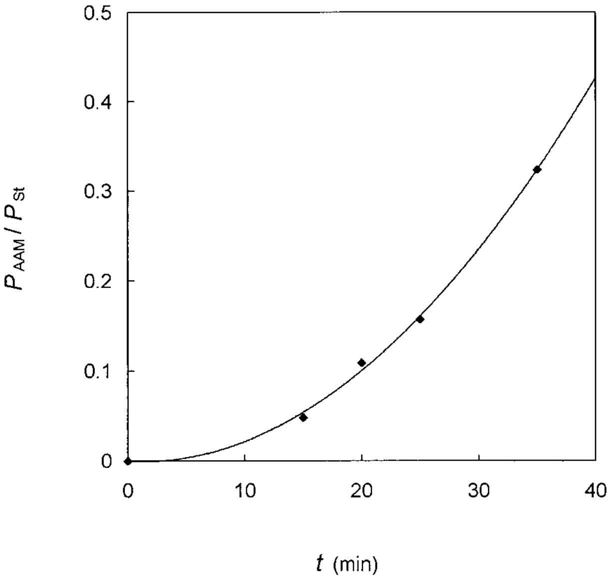


Figure 5 $P_{\mathrm{AAm}}/P_{\mathrm{St}}$ versus t for microemulsion copolymerization of AAm and St with HMAP (7.62×10^{-3} mol/mol of St) as photoinitiator; AAm/St = 0.44.

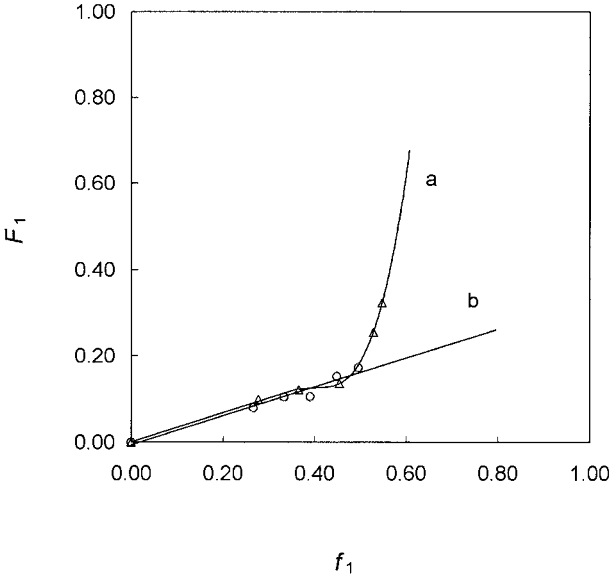


Figure 6 f_1 versus F_1 for microemulsion copolymerization of AAm and St with (a) HMAP and (b) DMPA (7.62×10^{-3} mol/mol of St) as photoinitiator.

Table I Medium Effects on Copolymerization of AAm (M_1) and St (M_2)[7]

Medium	r_1	r_2
Dioxane	0.40	0.96
Tetrahydrofuran	0.34	1.27
Dimethyl formamide	0.26	1.60
Dimethyl sulfoxide	0.20	2.00
Acetic Acid	0.25	1.85

DMPA or HMAP is used as the photoinitiator. The conversion of AAm is lower than that of St within the experimental range, that is, $f_1 \leq 0.6$.

The reactivity ratios of the two monomers were estimated according to eq. (1).[6]

$$\frac{f_1(1-2F_1)}{(1-f_1)F_1} = r_2 + \frac{f_1^2(F_1-1)}{(1-f_1)^2F_1} r_1 \qquad (1)$$

The reactivity ratio of AAm (r_1) is approximately 0.04 and that of St (r_2) is approximately 3.9. r_2 is almost 90 times greater than r_1. Table I[7] shows that in solution copolymerization, the maximum value of r_2/r_1 is 10, while it is 90 in the microemulsion system. This apparently higher reactivity of St is a consequence of much higher St concentration within the droplets as discussed above.

Table II shows T_g values of the copolymers. There are two glass transition temperatures of copolymer, each of which is lower than the glass transition temperature of the corresponding homopolymer. It is well known that T_g increases with increasing molecular weight in some range of molecular weight. Fedors[8] put forward an equation to relate the T_g at infinite molecular weight $T_g(\infty)$ with T_g at molecular weight M

$$T_g = T_g(\infty) - A/(M + B) \qquad (2)$$

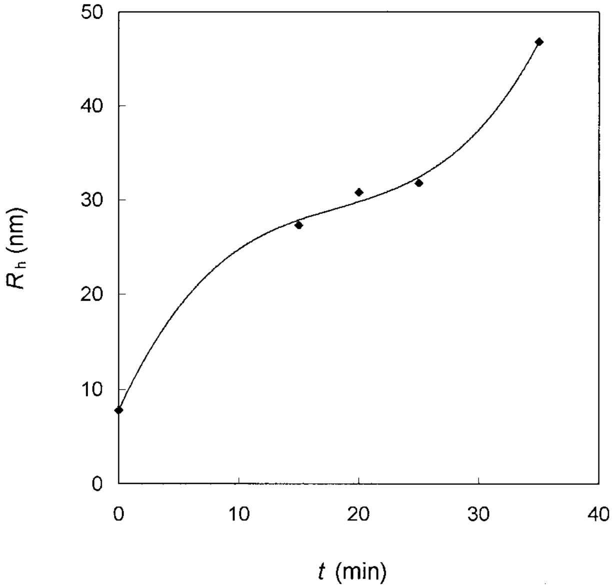


Figure 7 R_h versus t for microemulsion copolymerization of AAm and St with HMAP (7.62×10^{-3} mol/mol of St) as photoinitiator; AAm/St = 0.577.

where $T_g(\infty)$ is the limiting glass transition temperature of the polymer of infinite molecular weight and A and B are parameters the values of which depend on the chemical structures of the polymer. Table II shows that T_{g1} is very close to the T_g of polystyrene, which suggests that St units are grouped in rather long blocks. For polystyrene, A is 100,000 g/mol and B is 378 g/mol.[8] According to this equation, M_{PSt} is 2.46×10^4 for copolymer k6-1. On the other hand, T_{g2} is much smaller than T_g of polyacrylamide. AAm units are separated by St groups, and the amount of AAm units is much less than that of St units, according to Fedors' equation. This agrees with the result of NMR analysis and is very similar to the result obtained for thermally initiated systems.[1]

Table II The Glass Transition Temperature of Copolymer of AAm and St, with HMAP as Photoinitiator (7.62×10^{-3} mol/mol of St)

No.	AAm/St	P_{AAm}/P_{St}	T_{g1} (°C)	T_{g2} (°C)
K3-1	0.385	0.109	89	136
K4-1	0.577	0.138	97	143
K5-1	0.832	0.157	97	145
K6-1	1.12	0.342	96	148
PSt			100[8]	
PAAm			168[9]	

Table III Particle Sizes (R_h) Before and After Various Times (t) of Copolymerization of AAm and St in Oil-in-Water Microemulsion, with HMPP as Photoinitiator (7.62 × 10^{-3} mol/mol of St)

No.	t (min)	AAm/St	$P_{\mathrm{AAm}}/P_{\mathrm{St}}$	R_h (nm)	V_{cell} (10^5 nm^3)	$V_{\mathrm{cell}} - V_{\mathrm{PAAM}}$ (10^5 nm^3)
K 0-2	0	0.577	0	7.8	0.018	0.018
K 0-4-1	0	0.832		16.8		
K 0-5-1	0	1.12		12.6		
K 0-6-1	0	1.21		10.3		
K 1-2	15	0.577	0.048	27.3	0.854	0.832
K 2-2	20	0.577	0.109	30.8	1.225	1.156
K 3-2	25	0.577	0.157	31.7	1.344	1.238
K 4-2	35	0.577	0.324	46.8	4.307	3.656

Particle Sizes of Microemulsion Droplet

The oil-in-water microemulsion studied here (4.5 wt % St, 2.1 wt % AAM, 7.6 wt % DB, and 85.8 wt % water) was transparent and stable, and no phase separation was detected after 9 months of storage at room temperature. Figure 7 shows that particle size increases with the increasing of copolymerization time t. The microemulsion droplet may be composed of copolymer and St which has not polymerized. We suppose that the volume of copolymer can be separated into two parts, that is, the volume of St units (V_{PSt}) and the volume of AAm units (V_{PAAm}). The density of polystyrene is 1.04–1.065 (the average value is 1.05); the density of AAm is 1.302.[7]

$$V = m/\rho = nM/\rho$$

$$\frac{V_{\mathrm{PAAm}}}{V_{\mathrm{PSt}}} = \frac{n_{\mathrm{PAAm}}}{n_{\mathrm{PSt}}} \cdot \frac{\rho_{\mathrm{PSt}}}{\rho_{\mathrm{PAAm}}} \cdot \frac{M_{\mathrm{PAAm}}}{M_{\mathrm{PSt}}}$$

$$= \frac{P_{\mathrm{AAm}}}{P_{\mathrm{St}}} \cdot \frac{1.05}{1.30} \cdot \frac{71}{104}$$

$$= 0.551\, \frac{P_{\mathrm{AAm}}}{P_{\mathrm{St}}}$$

$$V_{\mathrm{cell}} = V_{\mathrm{PAAm}} + V_{\mathrm{PSt}} + V_{\mathrm{St}}$$

$$= V_{\mathrm{PAAm}} + V_{\mathrm{PSt}} + V_0(1 - C'\,\%)$$

$$C'\,\% = \frac{n_{\mathrm{PSt}}}{n_{\mathrm{St}}} \cdot 100\%$$

$$= \frac{1 - F_1}{1 - f_1} \cdot C\,\%$$

$$V_{\mathrm{PMMm}} = \frac{V_{\mathrm{cell}} - V_0(1 - C\,'\%)}{1 + (0.551 \cdot P_{\mathrm{AAm}}/P_{\mathrm{St}})^{-1}} \qquad (3)$$

where V_{cell} is the volume of the whole microemulsion droplet, V_{PAAm} is the volume of all AAm units in copolymer, V_{PSt} is the volume of all St units in copolymer, $C\%$ is the conversion of copolymerization, $C'\%$ is the conversion of St, and V_0 is the volume of droplet before polymerization. Results are presented in Table III.

Table III shows that $V_{\mathrm{cell}} - V_{\mathrm{PAAM}}$ increases with increasing copolymerization time t; this means that St was transferred from other uninitiated (unnucleated) droplets acting as the monomer reservoir. There are two factors that result in the increase of particle size. First, AAm in continuous medium copolymerizes into nucleated droplets continuously. Second, St from the monomer reservoir may also diffuse into the nucleated droplet.

CONCLUSION

The oil-in-water microemulsion of St and AAm using DB as emulsifier was stable, transparent, and light blue after polymerization. HMAP has higher initiating efficiency than DMPA. The UV spectra of the two photoinitiators show that the photoinitiators were located at the interface between the oil phase and the water phase. The copolymer unit ratio ($P_{\mathrm{AAm}}/P_{\mathrm{St}}$) increases with increasing monomer feed ratio and polymerization time. The reactivity ratio of St is much higher than that of AAm compared with solution polymerization. The copolymer backbone consists of isolated AAm units randomly distributed among polystyrene blocks. The particle size increases with increasing polymerization time. These results suggest that the photoinitiation of polymerization occurs at the interface between oil phase and water phase and that the polymerization occurs in the microemulsion droplet.

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