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ORIGINAL CONTRIBUTION

Microemulsion polymerization of styrene using a polymerizable nonionic surfactant and a cationic surfactant

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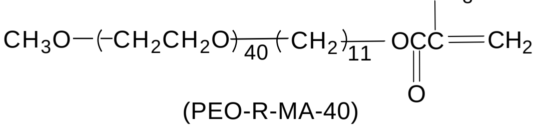
Abstract High polymer/surfactant weight ratios (up to about 15:1) of polystyrene microlatexes have been successfully produced by microemulsion polymerization using a small amount of polymerizable surfactant, ω-methoxypoly(ethylene oxide)$_{40}$ undecyl α-methacrylate macromonomer (PEO-R-MA-40), and cetyltrimethylammonium bromide (CTAB). After generating "seeding particles" in a ternary microemulsion containing only 0.2 wt% CTAB and 0.1 wt% styrene, the additional styrene containing less than 1 wt% PEO-R-MA-40 was added dropwise to the polymerized microemulsion for a period of about 4 h at room temperature. PEO-R-MA-40 copolymerized readily with styrene. The stable microlatexes were bluish-transparent at a lower polymer content and became bluish-opaque at a higher polymer content. Nearly monodisperse latex particles with diameters ranging from 50 to 80 nm and their molar masses ranging from 0.6 to 1.6×10^6 g/mol could be obtained by varying the polymerization conditions. The dependence of the number of particles per milliliter of microlatex, the latex particle size and the copolymer molar mass on the polymerization time is discussed in conjunction with the effect of the macromonomer concentration.

Key words Microemulsion polymerization · Styrene · Polymerizable nonionic surfactant · Macromonomer

Introduction

Various polymerization methods have been used to produce rather monodisperse polymer particles. These include seeding emulsion polymerizations [1], emulsion polymerizations using steric stabilizers [2], emulsifier-free methods [3], and dispersion [4, 5, 6, 7], emulsion [8, 9, 10] or microemulsion [11] polymerizations using a polymerizable surfactant. Polymerizable surfactants have an advantage over nonpolymerizable surfactants since the templating effect of the amphiphilic interface may be better preserved during polymerization. Polymerizations using a polymerizable surfactant have been studied in many systems [4, 5, 6, 7, 8, 9, 10, 11]. Among various polymerizable surfactants, poly(ethylene oxide) (PEO) macromonomers have recently received particular attention owing to their special amphiphilic nature [12].

In 1997, Liu et al. [13] synthesized an amphiphilic PEO macromonomer, ω-methoxypoly(ethylene oxide)$_{40}$ undecyl α-methacrylate (PEO-R-MA-40), having the following surfactant structure:



$$\mathrm{CH_3O{-}(CH_2CH_2O)_{40}{-}(CH_2)_{11}{-}O\overset{\displaystyle O}{\underset{}{C}}C(CH_3){=}CH_2}$$

(PEO-R-MA-40)

It was successfully used as a polymerizable stabilizer in the dispersion polymerization of styrene (St) [4, 5] and very stable monodisperse polystyrene (PS) microlatexes with particle sizes over than 200 nm were obtained. It is estimated that the weight ratio of polymer to polymerizable stabilizer was about 6:1. In another study [8], nearly monodisperse PS microlatexes with diameters ranging from about 30 to 90 nm were also obtained by emulsion polymerization using PEO-R-MA-40. The weight ratios of PS to PEO-R-MA-40 of the stable latexes produced from the emulsion systems were less than 10:1. Capek et al. [6] also studied the dispersion copolymerization of St and methacryloyl-terminated PEO or *p*-vinylbenzyl-terminated PEO macromonomers using water-soluble and/or oil-soluble initiators. PS microlatexes with monodisperse particle sizes of over 50 nm were produced. In 1998, Búcsi et al. [9] produced monodisperse core–shell latex particles of PS functionalized with surface groups that were indroduced by macromonomers via a two-step emulsion polymerization. The macromonomers were constituted of a PEO hydrophilic block and a hydrophobic portion with a vinyl group.

This article describes the synthesis of nearly monodisperse PS microlatexes stabilized by a small amount of a copolymerizable PEO macromonomer and cationic surfactant cetyltrimethylammonium bromide (CTAB). The study employed the microemulsion polymerization technique by the dropwise-addition of a mixture of St and PEO-R-MA-40 to the polymerizing microemulsion system.

Experimental

Materials

PEO-R-MA-40 was synthesized as described previously [13]. St from Fluka was distilled at 10 mmHg (26 °C) to remove inhibitor and was stored at 4 °C. CTAB from Fluka was recrystallized from a mixture of ethanol–acetone (1:3 by volume). Ammonium persulfate (APS) and *N*,*N*,*N′*,*N′*-tetramethylethylenediamine (TMEDA) from Aldrich was used without further purification. Deionized water was used.

Microemulsion polymerization process

A typical transparent ternary microemulsion with a composition of 0.2 g CTAB, 0.1 g St and 85.9 g water was added into a flask with stirring and nitrogen bubbling for 10 min. A redox initiator consisting of 0.0232 g TMEDA and 0.0456 g APS in 5 g water was then introduced into the microemulsion. After about 15 min, a mixture of 8.0 g St and 0.8 g PEO-R-MA-40 in an addition funnel was added dropwise into the polymerizing microemulsion for a period of about 4 h at 28 °C. During the monomer addition, nitrogen was continuously bubbled into the system with stirring at about 400 rpm. After the completion of St addition, the polymerization system was further stirred for another 1 h.

A syringe was used to withdraw the polymerized microemulsion through a rubber septum at different polymerization intervals. A small amount of hydroquinone was mixed with each drawn sample to terminate the polymerization. The latex sample was used directly for the determination of the particle size by transmission electron microscopy (TEM). The dried latex–polymer was washed with water until it was free of surfactant CTAB and the unreacted PEO macromonomer. The purified polymer sample was used for characterization by X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), ^{1}H NMR, and gel permeation chromatography (GPC).

Particle size determination

The particle sizes of the PS microlatexes were determined using a JEOL JEM-100CX electron microscope. One drop of each latex was premixed with 1–10 drops of a solution containing 6 wt% sodium dodecyl sulfate, to which a drop of 2 wt% phosphotungstic acid was then added. After mixing thoroughly, a drop of this mixture was put on a copper grid coated with a thin layer of Formvar. It should be noted that it is not easy to get a reasonably good TEM image from this system. The diameters of the particles were measured directly from each transmission electron micrograph. The number-average diameter (D_n) and the weight-average diameter (D_w) were calculated from the simple equations

$$D_\mathrm{n} = \sum N_i D_i \Big/ \sum N_i \, , \tag{1}$$

$$D_\mathrm{W} = \sum N_i D_i^4 \Big/ \sum N_i D_i^3 \, . \tag{2}$$

Particle surface analysis by XPS

The purified polymer powders were further vacuum dried for 2 days before they were analyzed by XPS. The surface analysis of each copolymer was carried out using a VG ESCALAB Mk II spectrometer with a Mg Kα X-ray source (1253.6 eV) and with an energy analyzer set at a constant retarded ratio of 40. The X-ray source was run at a reduced power of 120 W (12 kV and 10 mA). The powder sample was mounted on standard sample studs by means of double-sided adhesive tape. The pressure in the analysis chamber during the measurements was maintained at or lower than 10^{-8} mbar. To compensate for surface charging effects, all binding energy were referred to the C(1*s*) neutral carbon peak at 284.6 eV. The peak areas for the calculation of the oxygen and carbon compositions were corrected by experimentally determined instrumental sensitivity factors. The fraction (*F*) of PEO-R-MA-40 on the particle surface of PS, based on the pure macromonomer (also measured by XPS), can be calculated from the following equation [14]:

$$F = \mathrm{O\ in\ particle\ surface(\%)/O\ in\ PEO\text{-}R\text{-}MA\text{-}40(\%)}. \tag{3}$$

FTIR and ^{1}H NMR measurements on polymers

The FTIR measurement of each purified polymer was performed using a Bio-Rad FTS 165 FTIR spectrophotometer; 16 scans were signal-averaged at a resolution of 1 cm^{-1}. The samples were prepared by mixing the polymer with KBr and pressing the mixture into a compact pellet.

The ^{1}H NMR spectrum of each polymer was recorded with a Bruker ACF 300 (300 MHz) spectrometer using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard. The experiment was run by accumulating 32 scans for the average composition analysis of the polymers.

Molar mass determination

The molar masses of the polymers were determined by GPC using a Waters 410 differential refractometer detector. The eluant was high-performance liquid chromatograpy grade tetrahydrofuran which contained 0.0025% 2,6-di-*tert*-butyl-*p*-cresol as a stabilizer. The flow rate was maintained at 0.8 ml/min. PS standards were used for the calibration.

Calculation of N_d

The number of latex particles per milliliter of microlatex (N_d) can be calculated from the following equations [15],

$$N_d = 6\omega(\pi d_p D_w^3), \qquad (4)$$

where ω refers to the weight of polymer per milliliter of microlatex, d_p is the density [16] of PS microlatex particles, about 0.92 g/cm^3, and D_w the weight-average diameter of the particles.

Results

A small amount of PEO-R-MA-40 was used not only as a surfactant but it also participated as a comonomer in the modified microemulsion polymerization of St using APS/TMEDA redox initiator. The initial composition of 0.2 wt% CTAB, 0.1 wt% St and about 91 wt% water is within the small oil-in-water microemulsion region as shown in Fig. 1. The seeding PS particles formed in the initial microemulsion containing various concentrations of equimolar APS/TMEDA ranged from about 10 to 20 nm in diameter. Additional St containing a small amount of PEO-R-MA-40 was continuously added dropwise to the polymerizing microemulsion with stirring at 400 rpm. As the polymerization proceeded, the microemulsion systems changed from bluish-transparent to bluish-opaque depending on the polymer contents in the systems. However, the bluish-opaque ones become bluish-transparent upon dilution with H_2O. All these latexes have been stable for 1 year.

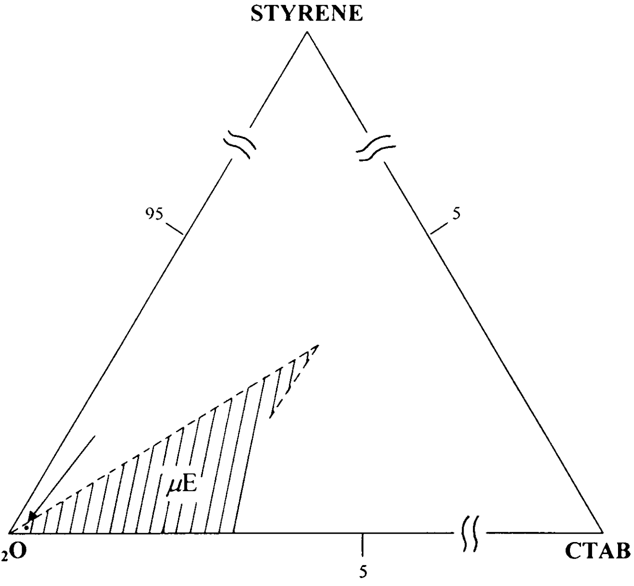


Fig. 1 The partial phase diagram of the oil-in-water microemulsions (μE) containing styrene, water and cetyltrimethylammonium bromide (*CTAB*) at 30 °C. The *arrow* indicates the composition point for the present study

Microlatexes

The concentration effect of PEO-R-MA-40 on the characteristics of the final microlatexes is summarized in Table 1. For the system containing 0.2 wt% CTAB with additional 8.0 wt% St (samples 3–7), D_w decreased from about 68 to 51 nm as the content of PEO-R-MA-40 was increased from 0.4 to 1.5 wt%; however, N_d increased sharply from about 0.6 to 1.5×10^{15} with a slight decrease in M_w from 0.94 to 0.64×10^6 g/mol. However, the microlatex obtained from a similar microemulsion system, but without additional PEO-R-MA-40, was unstable. On the other hand, stable microlatexes can be obtained from microemulsion systems containing 0.6 wt% PEO-R-MA-40 without CTAB or containing 0.6 wt% CTAB without PEO-R-MA-40 as for samples 1 and 2 respectively. Four TEM micrographs for latex particles obtained from the systems shown in Table 1 are displayed in Fig. 2.

The concentration effect of additional St on the characteristics of the microlatexes is shown in Table 2. The system contained a common mixture of 0.2 wt% CTAB and 0.8 wt% PEO-R-MA-40. D_w of the stable

Table 1 Effect of additional ω-methoxypoly(ethylene oxide)$_{40}$ undecyl α-methacrylate (*PEO-R-MA-40*) on the microlatexes. Equimolar (4 mM) ammonium persulfate (*APS*)/*N*,*N*,*N′*,*N′*-tetramethylethylenediamine (*TMEDA*) based on the total weight of each initial microemulsion was used and all polymerizations were carried out at 28 °C for 5 h. Cetyltrimethyl ammonium bromide (*CTAB*)

Microemulsion systems	1	2	3	4	5	6	7
Initial composition							
Styrene (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1
CTAB (g)	0	0.6	0.2	0.2	0.2	0.2	0.2
PEO-R-MA-40 (g)	0.6	0	0	0	0	0	0
Water (g)	91.3	91.3	91.3	91.1	90.9	90.7	90.2
Additional components							
Styrene (g)	8.0	8.0	8.0	8.0	8.0	8.0	8.0
PEO-R-MA-40 (g)	0	0	0.4	0.6	0.8	1.0	1.5
Microlatex characteristics							
D_w (nm)	64.7	60.5	68.2	62.4	59.3	55.8	51.0
M_w (10^6 g/mol)	1.02	1.60	0.94	0.86	0.80	0.74	0.64
M_w/M_n	3.4	4.1	3.3	3.5	3.9	3.6	4.5
N_d (10^{15})	0.67	0.75	0.55	0.74	0.88	1.08	1.47

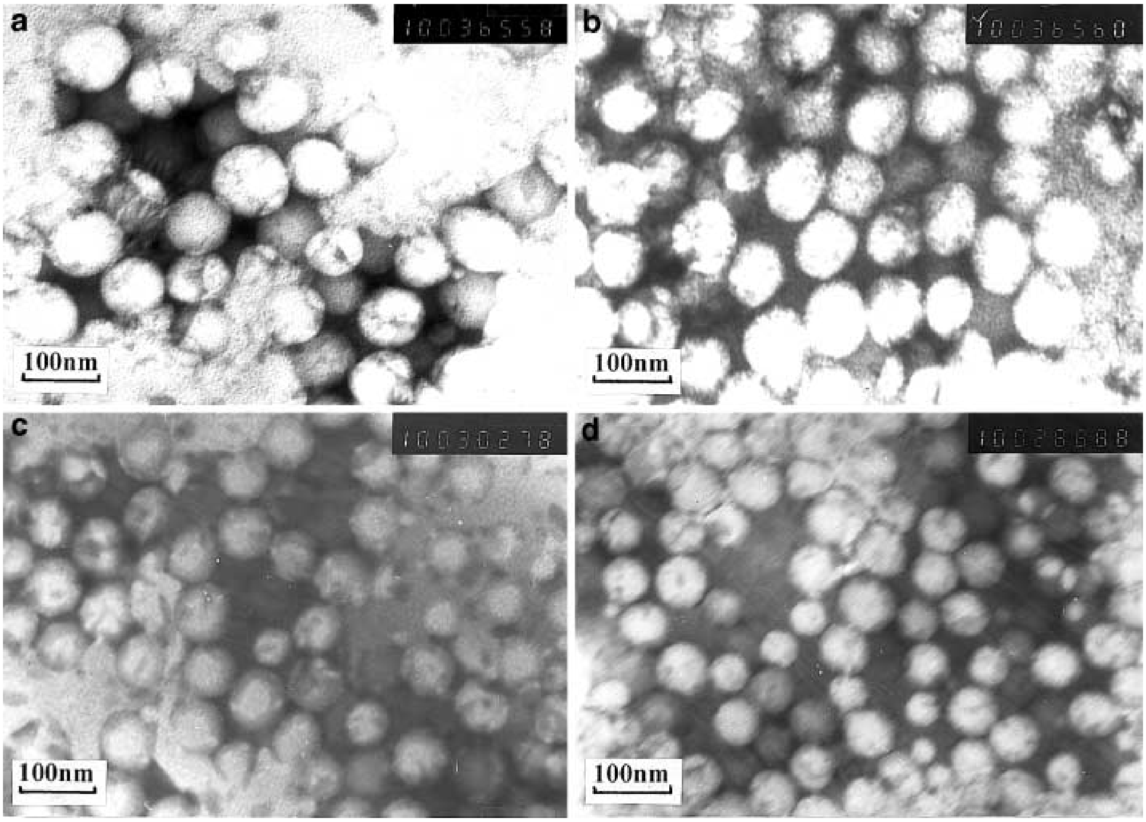


Fig. 2 Transmission electron micrographs (*TEMs*) of polystyrene (*PS*) latexes with different additional ω-methoxypoly(ethylene oxide)$_{40}$ undecyl α-methacrylate (*PEO-R-MA-40*) contents obtained from the systems shown in Table 1: **a** sample 1 with 0.6 wt% PEO-R-MA-40; **b** sample 3 with 0.4 wt% PEO and 0.2 wt% CTAB; **c** sample 4 with 0.6 wt% PEO and 0.2 wt% CTAB; **d** sample 6 with 1.0 wt% PEO and 0.2 wt% CTAB

Table 2 Effect of additional styrene on the microlatexes. Equimolar (4 mM) ammonium persulfate (*APS*)/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (*TMEDA*) based on the total weight of each initial microemulsion was used and all polymerizations were carried out at 28 °C for 5 h

Microemulsion systems	1	2	3	4
Initial composition				
Styrene (g)	0.1	0.1	0.1	0.1
CTAB (g)	0.2	0.2	0.2	0.2
Water (g)	90.9	88.9	85.9	83.9
Additional components				
Styrene (g)	8.0	10.0	13.0	15.0
PEO-R-MA-40 (g)	0.8	0.8	0.8	0.8
Microlatex characteristics				
Polymer/surfactant weight ratio	8.0:1	10.0:1	13.0:1	15.0:1
D_w (nm)	59.3	63.6	69.6	78.2
M_w (10^6 g/mol)	0.80	0.93	1.12	1.16
M_w/M_n	3.9	5.7	5.1	5.8

microlatex increased from about 59 to 78 nm as the addition of St to the polymerizing microemulsion system was increased from 8 to 15 wt%, but M_w only increased slightly from 0.80 to 1.16×10^6 g/mol. Thus, the maximum polymer/surfactant weight ratio for a stable latex reached to about 15:1. Two TEM micrographs for latex particles with polymer/surfactant weight ratios of about 10 and 15 are shown in Fig. 3.

Microlatexes during the polymerization

The effect of PEO-R-MA-40 concentration on the increase in D_w and the change in N_d during the modified microemulsion polymerization is shown in Figs. 4 and 5, respectively. As expected, D_w increased with the polymerization time and it was larger for the system containing a smaller amount of PEO-R-MA-40 (0.4 versus 0.6, 1.0 or 1.5 wt%); however, this trend was not obvious for the first 40 min of polymerization, during which, D_w was about 27 nm for all four systems. The systems were distinctively different after 1 h of polymerization. At 5 h of polymerization, D_w was about 68, 62, 56 and 51 nm for the systems containing 0.4, 0.6, 1.0 and 1.5 wt% PEO-R-MA-40, respectively.

Throughout the same period of polymerization as shown in Fig. 5, N_d remained rather constant at about 0.6×10^{15} for the system containing 0.4 wt% PEO-R-MA-40; however, N_d increased significantly from about 0.6×10^{15} to 0.8×10^{15}, 1.1×10^{15} or 1.5×10^{15} for the

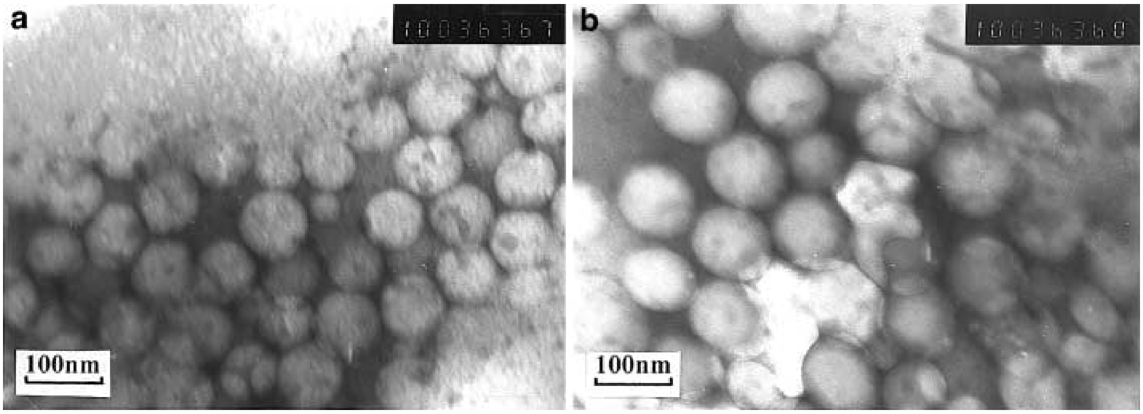


Fig. 3 TEMs of PS latexes from the systems shown in Table 2: **a** sample 2 with a polymer/surfactant weight ratio of about 10; **b** sample 4 with a polymer/surfactant weight ratio of about 15 for both systems containing 0.8 wt% PEO-R-MA-40 and 0.2 wt% CTAB

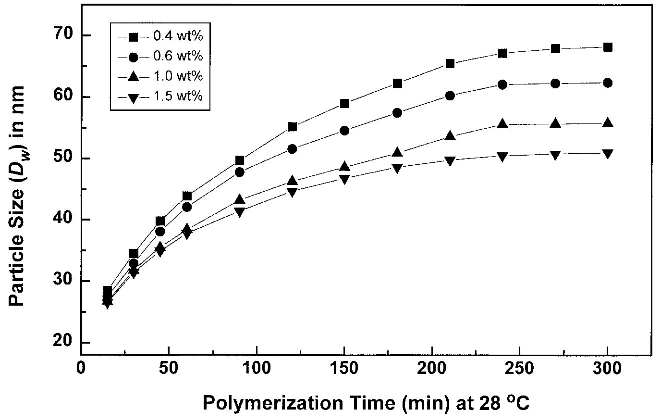


Fig. 4 The effect of PEO-R-MA-40 concentration from 0.4 to 1.5 wt% on the increase in polymer latex particle size (D_w) during the microemulsion polymerization. Their compositions are as listed in Table 1 for samples 3, 4, 6 and 7

systems containing 0.6, 1.0 or 1.5 wt% PEO-R-MA-40, respectively. The increase in N_d was almost linearly dependent on D_w for the systems containing 0.6 or 1.0 wt% PEO-R-MA-40 as depicted in Fig. 6. At 1.5 wt% PEO-R-MA-40, the linear relationship between N_d and D_w deviated beyond $D_w > 45$ nm. On the other hand, N_d seems to be rather independent of D_w for the system containing 0.4 wt% PEO-R-MA-40. As to the molar masses of the polymers from the four systems, they all decreased with the increase in D_w as shown in Fig. 7.

Characterization of polymers

An X-ray photoelectron spectrometer was used to analyze the particle surface of the copolymer powders.

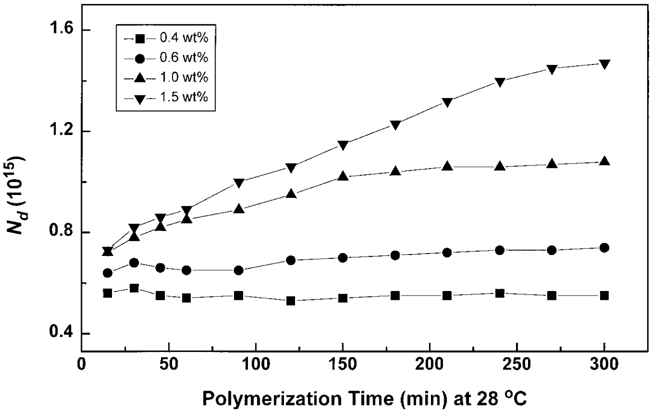


Fig. 5 The effect of PEO-R-MA-40 concentration from 0.4 to 1.5 wt% on the number of polymer particles per milliliter of latex (N_d) during the microemulsion polymerization. Their compositions are as listed in Table 1 for samples 3, 4, 6 and 7

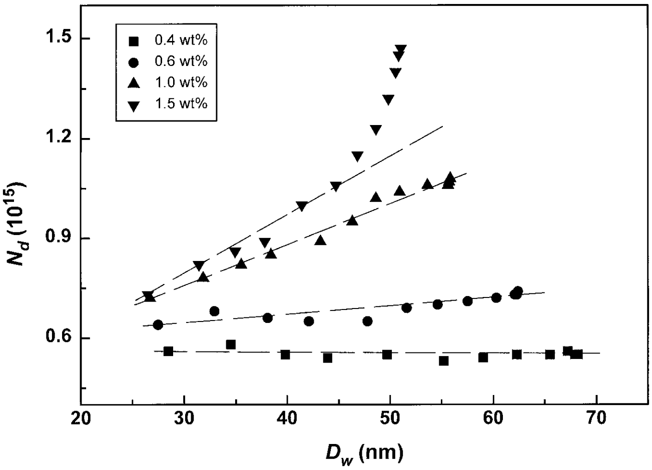


Fig. 6 The relationship between N_d and D_w for the same systems as in Fig. 4

The presence of abundant carbon and oxygen on the particle surface of each sample is revealed by two strong peaks C(1*s*) and O(1*s*), as shown in Fig. 8. Some results

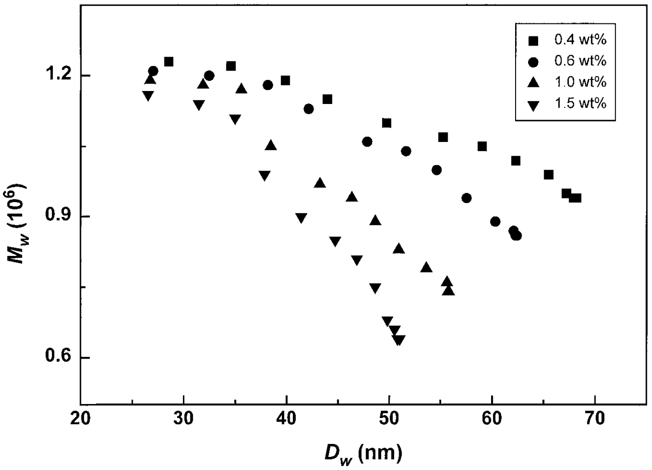


Fig. 7 The effect of D_w on the molar mass (M_w) of the polymer for the same systems as in Fig. 4

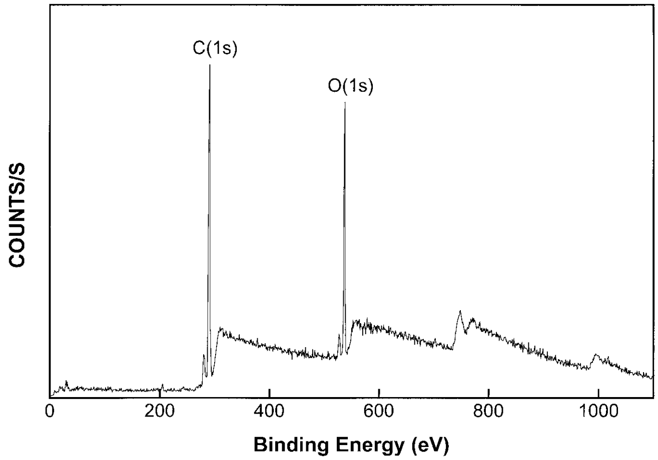


Fig. 8 X-ray photoelectron spectrum (wide scan) of the copolymer particles obtained from sample 7 as shown in Table 1

Table 3 Characteristics of the latex (sample 7 in Table 1) particle surface at different polymerization times

Polymerization time (h)	Fraction of PEO-R-MA-40 on the particle surface (%)
0.5	26.8
1.0	37.6
2.0	46.5
3.0	58.2
4.0	69.4

from XPS analysis of the particle surface are shown in Table 3. It is found that PEO-R-MA-40 was increasingly enriched on the particle surface of the microlatexes as the polymerization proceeded.

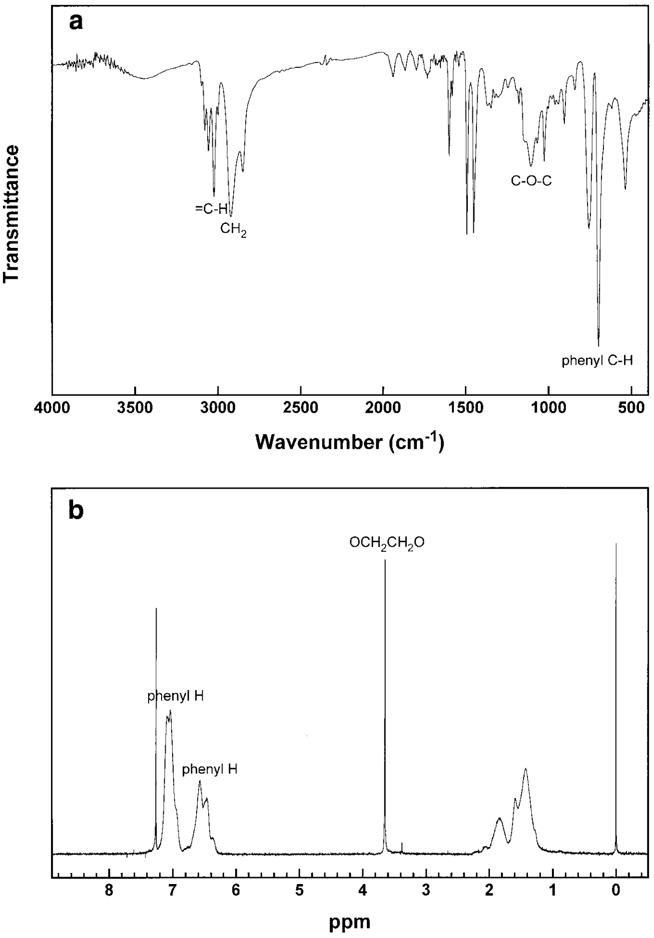


Fig. 9 Fourier transform IR spectrum of the polymer. **b** ^{1}H NMR spectrum of the polymer. This is sample 6 in Table 1

The FTIR spectrum of the polymer which was prepared using 8.1 wt% St, 1.0 wt% PEO-R-MA-40, 0.2 wt% CTAB, 90.7 wt% H_2O and 4 mM APS/TMEDA at 28 °C is shown in Fig. 9a. The strong peak, at 1107 cm^{-1}, due to the asymmetrical stretching of C–O–C is clearly observed, indicating that the PEO-R-MA-40 macromonomer coexisted as a copolymer. The peaks observed at 753 and 696 cm^{-1} were caused by the deformation of five adjacent hydrogen atoms in the benzene ring from St and the stretching of aromatic C–H and CH_2 at 3028 and 2923 cm^{-1}.

The ^{1}H NMR spectrum for the same copolymer is shown in Fig. 9b. On the basis of the areas of the peaks of the phenyl protons and the oxyethylene protons [17, 18], the St/PEO weight ratio (R) can be calculated using the following equation:

$$R = (A_p M_{St}/5)(A_o M_{PEO}/160), \qquad (5)$$

where A_p and A_o refer to the areas of the peaks of the phenyl protons and the oxyethylene protons, respectively, while M_{St} and M_{PEO} are the respective molar masses of St and PEO-R-MA-40. The experimental St/PEO weight ratio from the peaks is 8.2:1.0, which is in good agreement with the feed ratio of 8.1:1.0 for sample 6 (Table 1). On the other hand, the experimental St/PEO weight ratio for sample 4 at lower PEO content is 15.1:1 compared to its feed ratio of 13.5:1.0. At a higher content of PEO, as in sample 7, the experimental St/PEO weight ratio is 6.5:1.0 compared to its feed ratio of 5.4:1.0. This indicates that the experimental St/PEO weight ratios are slightly higher than those of the feed ones, indicating that St is slightly more reactive than PEO-R-MA-40. However, the monomer reactivity ratios for St and PEO-R-MA-40 copolymerization in benzene solution have been estimated [19] to be about 0.94 for St and about 1.06 for the PEO macromonomer. This slight discrepancy is probably due to the inaccuracy of the relative reactivities as it is difficult to determine r_1 and r_2 accurately for a conventional monomer (M_1) and a macromonomer (M_2), respectively [19].

Discussion

The ternary microemulsion system initially consisted of St-swollen micelles, some dissolved St and CTAB in the aqueous phase. Once the APS/TMEDA initiator decomposes, the primary radicals formed are captured directly by St-swollen micelles and/or react with St monomer dissolved in the aqueous phase to form oligomeric radicals of increasing hydrophobicity. The hydrophobic nature of these oligomeric radicals favors their entry into St-swollen micelles for further polymerization.

After the primary PS particles form in the microemulsion system, the controlled addition of St and with a small amount of PEO-R-MA-40 causes St to diffuse into the seeded PS particles for further growth and with some copolymerization of PEO-R-MA-40 on the surface of the PS particles. It is seen that the St monomers added are rapidly transported into the growing polymer particles to maintain the dynamic equilibrium of St in the system. Since long-chain PEO groups of PEO-R-MA-40 are water-soluble, they tend to distribute on the surface of the growing polymer particles. With further addition of mixed monomers (St and PEO macromonomer), more and more PEO groups of PEO-R-MA-40 are enriched on the surface of the polymer particles. Thus, the latex particles become very stable owing to the steric stabilization exerted by long-chain PEO groups. The XPS analysis results have shown that PEO-R-MA-40 macromonomers were gradually enriched on the surface of the latex particles with increasing polymerization time (Table 3); thus, it is very likely that homopolystyrene may be formed near the core of the latex particles, especially towards the final state of the polymerization [11].

In another study, it was found that N_d remained almost constant for the modified microemulsion polymerization of St via hollow-fiber feeding monomer. However, the formation of new secondary particles (via homogeneous nucleation) may be inevitable owing to the good solubility of polymerizable PEO-R-MA-40 in water for the present system. For the lower content of 0.4 wt% PEO-R-MA-40, the effect of the homogeneous nucleation is insignificant. This is reflected in N_d remaining almost constant throughout the polymerization as shown in Figs. 5 and 6. As the PEO-R-MA-40 content was increased to 0.6–1.5 wt%, the homogeneous nucleation became significant and N_d slowly increased throughout the polymerization (Fig. 5) or with the increase in D_w (Fig. 6).

It has been reported [20, 21] that chain transfer to the monomer is the controlling termination mechanism for most oil-in-water microemulsion polymerizations. Owing to the termination by chain transfer reactions to the monomer, the molar masses of polymers often do not change significantly. However, the present systems consisted of a comonomer of PEO-R-MA-40. Since PEO-R-MA-40 contains more active hydrogen atoms, it can contribute to the higher rate of chain transfer termination. As a result, M_w slowly decreased as more mixed monomers were introduced into the system for the particle growth to larger D_w. The effect of PEO-R-MA-40 concentration from 0.4 to 1.5 wt% on lowering M_w is clearly shown in Fig. 7. On the other hand, it is also possible that the decrease in M_w may arise from the less stable latex particles formed with PEO-R-MA-40 as exemplified by samples 1 and 2 in Table 1. This indicates that sample 2 stabilized by cationic CTAB produced PS of higher M_w (1.60×10^6 g/mol) than that (1.02×10^6 g/mol) stabilized by nonionic PEO-R-MA-40. According to recent literature [22], the highest M_w are found in microemulsion polymerization when the polymerizing droplets are most effectively stabilized during the entire reaction process.

Conclusions

Nearly monodisperse microlatexes stabilized by CTAB and a polymerizable surfactant PEO-R-MA-40 can be readily produced by the microemulsion copolymerization of St and a lower content of PEO-R-MA-40 (below 0.6 wt%) at room temperature. The maximum weight ratio of polymer/surfactant for the microlatexes obtained from this modified method was up to about 15:1. By changing the polymerization conditions, latex particles with diameters ranging from 50 to 80 nm and copolymer molar masses ranging from 0.6 to 1.6×10^6 g/mol were obtained. The major effect of a higher amount (above 0.6 wt%) of macromonomer PEO-R-MA-40 on the microemulsion polymerization of St is twofold. It reduces M_w of the polymer, but it increases N_d of the latex particles. A

PEO-R-MA-40 concentration below 0.6 wt% may be used to produce larger D_w without significantly sacrificing M_w.

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References

1. Vanderhoff JW, Vitkuske JF, Bradford EB, Alfrey T Jr (1956) J Polym Sci 20:225
2. Everett DH, Stageman J (1978) Faraday Discuss Chem Soc 65:230
3. Goodwin JW, Hearn J, Ho CC, Ottewill RH (1974) Colloid Polym Sci 252:464
4. Liu J, Chew CH, Wong SY, Gan LM, Lin J, Tan KL (1998) Polymer 39:283
5. Liu J, Gan LM, Chew CH, Gong H, Gan LH (1997) J Polym Sci Polym Chem 35:3575
6. Capek I, Riza M, Akashi M (1997) J Polym Sci Polym Chem 35:3131
7. Chen M, Serizawa T, Kishida A, Akashi M (1999) J Polym Sci Polym Chem 37:2155
8. Liu J, Chew CH, Gan LM, Teo WK, Gan LH (1997) Langmuir 13:4988
9. Búcsi A, Forcada J, Gibanel S, Héroguez V, Fontanille M, Gnanou Y (1998) Macromolecules 31:2087
10. Ishizu K, Yamashita M, Ichimura A (1997) Polymer 38:5471
11. Dreja M, Pyckhout-Hintzen W, Tieke B (1998) Macromolecules 31:272
12. Ito K (1994) In: Mishra MK (ed) Macromolecular design. Frontiers, New York, pp 129–160
13. Liu J, Chew CH, Gan LM (1996) J Macromol Sci Chem Ed A 33:337
14. Deslandes Y, Mitchell DF, Paine AJ (1993) Langmuir 9:1468
15. Ming W, Zhao J, Lu X, Wang C, Fu SK (1996) Macromolecules 29:7678
16. Wu C, Chan KK (1995) J Polym Sci Polym Phys Ed 33:919
17. Ito K, Yokoyama S, Arakawa F (1986) Polym Bull 16:345
18. Ito K, Tsuchida H, Hayashi A, Kitano T, Yamada E, Matsumoto T (1985) Polym J 17:827
19. Liu J, Chew CH, Wong SY, Gan LM (1996) J Macromol Sci Pure Appl Chem A 33:1181
20. López RG, Treviño ME, Salazar LV, Peralta RD, Becerra F, Puig JE, Mendizábal E (1997) Polym Bull 38:411
21. Morgan J, Kaler EW (1998) Macromolecules 31:3197
22. Dreja M, Tieke B (1998) Langmuir 14:800