Fine Polystyrene Latexes with Reactive Poly(ethylene oxide)–Poly(propylene oxide)–Poly(ethylene oxide) Triblock Macrosurfactants in Modified Miniemulsion Polymerization

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ABSTRACT: Polystyrene latexes were produced via a newly accessible miniemulsion polymerization where reactive poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) triblock macrosurfactants were used to impart the interfacial activity during the emulsification and the reactivity in the polymerization. Through atomic force microscopy studies, it was found that the polystyrene latexes produced were extremely small to about 50 nm in a proper experimental condition, and covered richly with poly(ethylene oxide) groups. The polystyrene latexes were expected to have great applicability in the production of structured latex films. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 328–332, 2002

Key words: macrosurfactants; miniemulsion polymerization; atomic force microscopy (AFM)

INTRODUCTION

Miniemulsion polymerization is a process where relatively stable monomer droplets emulsified in the presence of a surfactant and cosurfactant (or hydrophobe) are polymerized carefully with retaining their initial size in the range of 50–500 nm.[1,2] Basically, the surfactant provides initial droplet stability against droplets coalescence, while the cosurfactant retards Ostwald ripening.

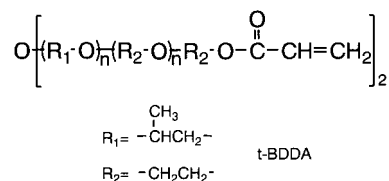Conventional surfactant systems employed in the miniemulsion polymerization is composed of a hydrophilic low molecular weight main surfactant and hydrophobic cosurfactant such as a long-chain alkane (i.e., hexadecane[3,4]) or a long-chain alcohol (i.e., cetyl alcohol[5,6]). Here, one important thing is that the presence of cosurfactants themselves in the final latex causes a serious problem in final applications. Therefore, in recent studies, the enhancement of emulsion stability has been achieved by using an oligomeric surfactant like sodium lauryl sulfate[7,8] or sodium hexadecyl sulfate.[9] Nonionic surfactants were also found to enhance the stability by forming the steric hindrance at the oil/water interface.[7,8,10] Incorporation of a diblock copolymer and a chain transfer agent into the surfactant system was another accessible methodology to improve the stability of emulsion droplets.[8,11] However, to obtain potentially applicable polymer latexes, there is a need for another useful surfactant system.

In the present study, we are releasing an effective surfactant system in the miniemulsion poly-

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$$O\left[(R_1\text{-}O)_{\overline{n}}(R_2\text{-}O)_{\overline{n}}R_2\text{-}O\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH{=}CH_2\right]_2$$

$$R_1 = -\underset{\underset{\displaystyle CH_3}{|}}{CH}CH_2-$$

$$R_2 = -CH_2CH_2-$$ *t*-BDDA

Scheme 1   A schematic molecular structure of macrosurfactants.

EXPERIMENTAL

Poly(ethylene oxide)–poly(propylene oxide)–poly-(ethylene oxide) (PEO-PPO-PEO) triblock diols (M_w = 1.1 × 10^3, 2.0 × 10^3, 2.8 × 10^3 gmol^{-1}, Aldrich Chemical Co.) were dried under vacuum at 80°C for 3 h. Acrylol chloride (AC, Acros Organics), triethylamine (TEA, Aldrich), and benzoyl peroxide (BPO, Junsei Chemical Co.) were of reagent grade. The inhibitor in styrene (St. Junsei) was removed using a removing column (Aldrich).

Reactive macrosurfactants (*t*-BDDA) shown in Scheme 1 were synthesized by the reaction of a PEO–PPO–PEO triblock diol with AC.[12] The triblock diol (1 mol) dissolved in tetrahydrofuran was poured into a 500-mL round-bottomed flask and cooled to 0°C. TEA (2 mol) and AC (2 mol) were added into the reactor and reacted at 70°C for 5 h under vigorous stirring. Then, the reaction mixture was filtered to remove the salt, triethanolamine hydrochloride, and evaporated completely. After trapping the moisture, the solution was evaporated until a viscous liquid was recovered. The molecular weight of *t*-BDDA was measured with a model 410 GPC. The surface tensions were measured changing the concentration of *t*-BDDA in water with Surface Tensiometer (Krüss GmbH, K12 Mk6) at 10°C.

The miniemulsion polymerization was carried out as follows. St, BPO, and *t*-BDDA were weighed into a cylindrical bottle and dissolved fully. Then, distilled deionized water containing 0.25 g/dL SLS (sodium lauryl sulfate) was added stirring with a magnetic bar into the monomer mixture until a fine dispersion appears. The monomer dispersion was then ultrasonic homogenized for 5 min in an iced water bath and transferred to the four-necked glass reactor equipped with a stirrer, a reflux condenser, and thermocouples. After deaerating by purging the nitrogen gas for 10 min, the reactor was submerged into a thermostated water bath and polymerized with the rotation speed of 100 rpm at 70 ± 0.1°C for 10 h. The reaction recipe is summarized in Table I. The topography of the latexes produced was observed with atomic force microscopy (AFM) using a Nanoscope III from Digital Instrument working in the tapping mode. The particle size of PS nanolatexes was determined with the surface roughness that was obtained from the Nanoscope III software.[14] In determination of particle size, three scans were carried out along the linear latex array, then the distance between top points was measured against about 50 particles.

RESULTS AND DISCUSSION

The macrosurfactants (*t*-BDDA) synthesized in this study have a hydrophilic/hydrophobic/hydrophilic triblock structure. One interesting thing in the molecular system of *t*-BDDA is that the hydrophilic block is PEO. It has been generally known that the PEO-based molecule has a temperature-dependent phase behavior in water, because of the selective hydrogen bonding of EO units with water molecules.[15,16] The *t*-BDDA used in this study showed a lower critical solution tem-

Table I   Standard Recipe for the Miniemulsion Polymerization[a]

Ingredient	Weight (g)
St	7.89
t-BDDA2[b]	2.11[variable]
BPO	0.10
DDI water[c]	89.9

[a] 80°C; 10 h; 100 rpm.
[b] Abbreviation of poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) tri-block diol diacrylate. The concentration of *t*-BDDA in latexes was varied against total monomer weights.
[c] Distilled deionized water containing 0.25 g/dL SLS.

Table II   Molecular Characteristics of Macrosurfactants

Sample	Type[a]	M_n ($\times 10^3$ gmol^{-1})	M_w ($\times 10^3$ gmol^{-1})	PDI[b] (M_w/M_n)	CP[c] (°C)
	Triblock Diols				
t-BDDA1	PEO-PPO-PEO	1.10	1.19	1.10	15.0
t-BDDA2	PEO-PPO-PEO	2.00	2.11	1.09	16.0
t-BDDA3	PEO-PPO-PEO	2.80	3.01	1.18	15.5

[a] PEO: polyethylene oxide, PPO: polypropylene oxide.
[b] PDI: polydispersity index.
[c] Cloud point measured with a thermooptical microscope at 0.5 g/dL t-BDDA concentration in water.

perature, LCST in water around 15°C at the concentration of 0.1–3 wt % (Table II).[13] Therefore, to achieve an acceptable surface activity, the emulsifying process should be carried out below the cloud point. Figure 1 shows the change of surface tensions with the concentration of t-BDDA in water at 10°C. One can easily find that the t-BDDA have critical micelle concentrations (CMC) in water at around 0.02 mmol %, which is attributed to their amphiphilic triblock molecular structure. This result implies obviously that the t-BDDA has a high surface activity in water. In this observation, the CMC was not so dependent on the molecular weight of t-BDDA. It appears that the similar ratio in the block lengths does not cause any significant change in the molecular assembly at the air/water interface.

After obtaining fine St emulsions by ultrasonic homogenization, they were polymerized carefully. Figure 2 shows AFM images of PS nanolatexes synthesized with changing the concentration of
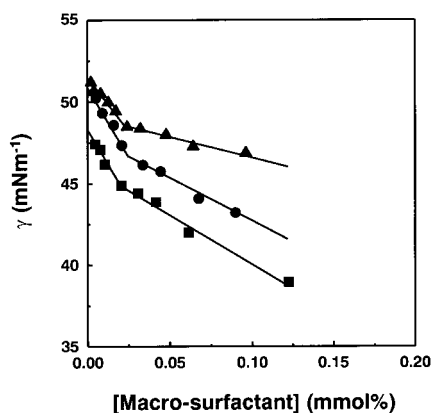
t-BDDA. In the absence of t-BDDA, many large particles were detected in the micrometer-size range. However, as the concentration of t-BDDA increased, the large particles disappeared gradually. From the concentration of 1 mmol, fine PS nanolatexes were obtained with narrow size distribution. This result elucidates directly that the t-BDDA has an ability to emulsify the St monomers in the nano-sized range, and stabilize the emulsions until the polymerization is completed. The effect of t-BDDA molecular weights on the latex surface morphology was observed at the same concentration of t-BDDA and shown in Figure 3. At higher molecular weight of t-BDDA, the
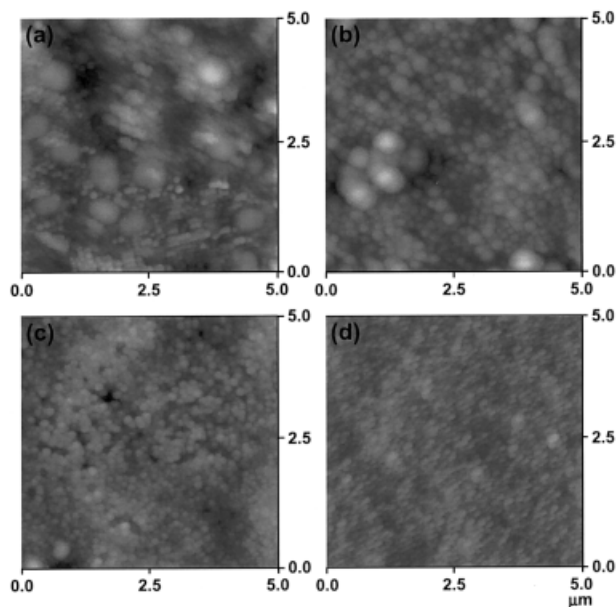

Figure 2 AFM images of PS latex particles with the concentration of macrosurfactants: 0 mmol (a), 0.5 mmol (b), 1 mmol (c), and 1.5 mmol (d). t-BDDA2 was selected as a macrosurfactant in this observation.

Figure 1 Critical micelle concentrations of macrosurfactants determined from the measurement of surface tensions: t-BDDA1 (■), t-BDDA2 (●), and t-BDDA3 (▲).

size reduction of PS latexes produced was more significant. Even though there was not a significant difference in CMC owing to the similar ratio in block lengths, the long hydrophilic PEO chains seems to conform effectively at the monomer/water interface. The average latex size and size deviation of PS nanolatexes were determined from the AFM images and shown in Figure 4. It can be deduced from the size characterization that higher concentration and molecular weight of *t*-BDDA are required preferentially for the synthesis of fine PS latexes. At a proper surfactant composition, the PS nanolatexes were very small to about 50 nm and narrow in size distribution.

In the AFM images, it was of interest that the PS latexes were totally adhered together at the high concentration (above 1.5 mmol) and high molecular weight (*t*-BDDA3 sample) of *t*-BDDA. Actually, those latexes formed films right after air drying. Relative to such observation, it may be said that the autohesion phenomenon happens by means of the large surface area of the latexes.[17,18] Considered on the basis of our previous studies,[12,13] however, it is reasonable to think that the PS nanolatexes have the morphology of PS core and PEO-rich shell. Therefore, the soft PEO shells contact favorably together in the interstice and form a latex film as the water in the interstitial space evaporates. This structured latex mor-
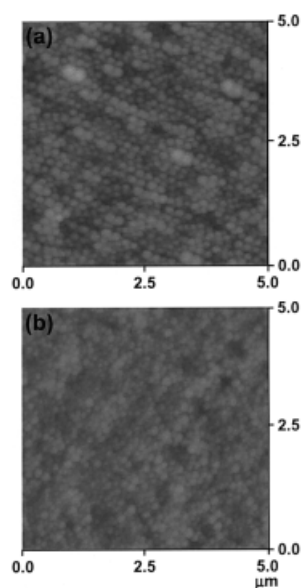

Figure 4 Particle size (Dn) and standard deviation (SD) of PS nanolatexes with the concentration of macrosurfactants: *t*-BDDA1 (■, □), *t*-BDDA2 (●, ○), and *t*-BDDA3 (▲, △).

phology is meaningful in the aspect that they are applicable in producing the latex films having advanced functionality and two-phase morphology simultaneously.

CONCLUSIONS

Here in this study, we are proposing a useful macrosurfactant, *t*-BDDA for the synthesis of PS latexes in the miniemulsion polymerization. The *t*-BDDA showed an excellent capability in emulsifying the St monomer at a low temperature, which is due mainly to its hydrophilic/hydrophobic/hydrophilic triblock molecular structure. The PS latexes polymerized in a proper surfactant condition displayed not only a small size but also a structured morphology. Especially, the EO units on the surface of final latexes were believed to find a great applicability in producing advanced latex films in further studies.

Figure 3 AFM images of PS nanolatex particles with the molecular weight of macrosurfactants: *t*-BDDA1 (a) and *t*-BDDA3 (b). The concentration of macrosurfactants was 1 mmol in this observation.
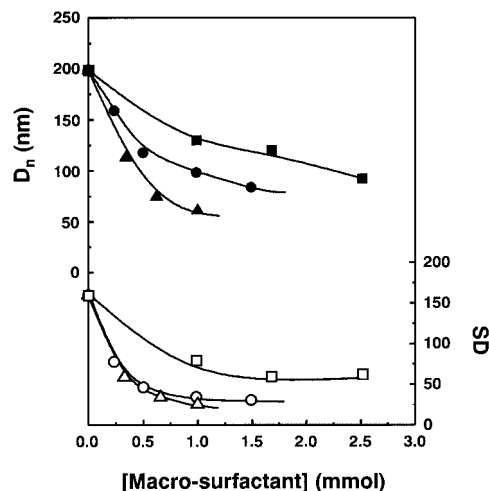
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