Amphiphilic ABA Triblock Copolymer as Surfactant in Syntheses of Microlatexes Bearing Cationic Groups

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ABSTRACT: Polystyrene microlatexes have been prepared by conventional emulsion polymerization with a novel amphiphilic water-soluble ABA triblock copolymer, poly[2-(dimethylamino)ethyl methacrylate]15-b-poly(propylene oxide)36-b-poly[2-(dimethyl-amino)ethyl methacrylate]15 (PDMAEMA15-PPO36-PDMAEMA15), as a polycationic emulsifier under acidic or neutral conditions. The ABA triblock copolymer was developed by oxyanion-initiated polymerization in our laboratory. In this study, it acted well both as a polycationic polymeric surfactant to form block copolymeric micelles for emulsion polymerization and as a stabilizer to be anchored into the polystyrene microlatex or adsorbed onto its surface. The results obtained with various copolymer concentrations and different pH media showed that microlatex diameters decreased remarkably with increased concentration of this ABA triblock copolymeric emulsifier, but were not as much affected by the pH of media within the experimental range of 3.4–7.0. The observed difference of the particle sizes from transmission electron microscopy and dynamic light scattering measurements is discussed in terms of the effect of the absorbed surfactants and their electrical double layers. This difference has led to the formation of a cationic polyelectrolyte fringe on the surface of microspheres. The final microlatexes were characterized with respect to total conversion, particle diameter, and particle size distribution as well as colloidal stability. © 2002 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 40: 3734–3742, 2002

Keywords: ABA triblock copolymer; emulsion polymerization; polycationic surfactant; block copolymers; surfactant

INTRODUCTION

There has been substantial interest in the preparation of amphiphilic block copolymers that can be used as dispersants, emulsifiers, wetting agents, flocculants, and demulsifiers in many industrial and pharmaceutical preparations. Amphiphilic block copolymers composed of hydrophilic and hydrophobic segments can form a micellar structure.1–3 These micelles have a hydrophobic compact inner core and a hydrophilic swollen outer shell in an aqueous medium. In contrast with micelles formed from low-molecular-weight surfactants, block copolymeric micelles exhibit a better structural stability, slower dissociation into free polymeric chains, and a lower critical micelle concentration (cmc) than low-molecular-weight surfactants.4–6 This system enables easy control of the particle size and solubilization of hydrophobic compounds.7

Well-defined block copolymers containing 2-(dimethylamino)ethyl methacrylate (DMAEMA) polymer segments have been obtained from living anionic polymerization8 or group-transfer polymer-
ization techniques. Baines et al. demonstrated that poly[2-(dimethylamino)ethyl methacrylate-b-alkyl methacrylate] copolymers were effective steric stabilizers for the dispersion polymerization of styrene. They found that a variation of the DMAEMA content in the copolymers produced relatively little change in the latex particle size. As the concentration of block copolymer stabilizer was increased, the latex particle size decreased slightly.

Several research groups have investigated the possibility of using water-soluble diblock copolymers in place of conventional small-molecule surfactants for latex syntheses via emulsion polymerization. However, there has been little research describing the use of near-monodisperse (or narrow-distribution), well-defined block copolymer containing cationic polyelectrolyte (e.g., DMAEMA polymer) as a surfactant in emulsion polymerization, especially in the preparation of surface-functional particles. Riess reported the use of polystyrene-poly(ethylene oxide) (PEO) di- and triblock copolymers for the preparation of microlatexes or microgels. The block copolymer offered the possibility to prepare ‘hairy’ latexes, for example, latex particles having a fringe of PEO or poly(acrylic acid) (PAA) on their surface.

The properties of polymeric microlatex, including surface properties, particle size, size distribution, and colloid stability, are particularly important in biomedical applications. The surface of polymeric microlatex should be changed easily for the incorporation of proper biological ligands. Tuncel et al. achieved the synthesis of monosize polystyrene latexes carrying functional groups on their surfaces. The polystyrene latexes prepared with PAA as a steric stabilizer were used as the seed latex, and styrene/acylate monomers, such as DMAEMA, were copolymerized onto the polystyrene latex particles. Clinically, the polystyrene latex carrying DMAEMA (labeled with 99mTc) has been used as a radionuclide for viewing the human gastrointestinal system by gamma scintigraphy. Therefore, the research has potential importance for latexes bearing poly(DMAEMA) on their surfaces.

Very recently, we synthesized and characterized a novel near-monodisperse ABA triblock copolymer via oxanion-initiated polymerization. The hydrophilic blocks were poly(DMAEMA), whereas the hydrophobic segment was poly(propylene oxide) (PPO) above ambient temperature.

The purpose of this article is to report on the classical batch emulsion polymerization of styrene with poly[2-(dimethylamino)ethyl methacrylate]15-b-poly(propylene oxide)36-b-poly[2-(dimethylamino)ethyl methacrylate]15 (PDMAEMA15-PPO36-PDMAEMA15) triblock copolymer alone as an emulsifier. The ABA triblock copolymer was highly surface-active in acidic or neutral aqueous media. We discuss the effect of the ABA triblock copolymer on the control of the emulsion-polymerization process of styrene, including particle size and particle size distribution at different pH media. Also, the best condition leading to uniform, stable colloidal particles is proposed.

EXPERIMENTAL

Materials

The synthesis and characterization of PDMAEMA15-PPO36-PDMAEMA15 triblock copolymer has been described in our latest report. It was synthesized by a typical oxanion-initiated polymerization and used as a polymeric surfactant in this study. Commercially available styrene (Shanghai Chemical Reagent Co., China) was cleaned and distilled under reduced pressure before use. 2,2’-Azobis(2-amidinopropane) hydrochloride (V50, Aldrich) and hydroquinone (Wuxi Min-feng Reagent Co., China) were of reagent grade and used as received. Cetyltrimethylammonium bromide (CTAB) with a purity of 99% (Aldrich) was used as received. Deionized water was used throughout this work.

Determination of Surface Tension

Surface-tension measurements were carried out with a JYW-200A automatic surface tensiometer equipped with an electrical torsion balance and platinum ring (Chengde Experimental Instrument Co., China). The triblock copolymer sample was dissolved in an aqueous solution and adjusted its pH to 3.0 with hydrochloric acid. All measurements were carried out at room temperature (ca. 20 °C), and the obtained values were corrected according to the surface tension of the deionized water (72–73 mN/m).

Emulsion-Polymerization Procedure

The batch-emulsion polymerization of styrene with PDMAEMA15-PPO36-PDMAEMA15 triblock copolymer as an emulsifier was examined and compared with an emulsifier-free emulsion polymerization. All emulsion polymerizations were carried out at different pH aqueous solutions.
marked Series A (pH 3.4), Series B (pH 5.0), and Series C (pH 7.0), respectively.

The reaction vessel was a 100-mL three-necked glass flask equipped with a reflux condenser, a nitrogen inlet, and a thermometer. The PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$ triblock copolymer was first dissolved in 50 mL of water and then adjusted by solution with hydrochloric acid to the required pH value. To the solution was added styrene monomer and V50 initiator. The mixture was heated at 35 °C under stirring by a magnetic bar to yield an emulsion. The emulsion was deoxygenated by bubbling nitrogen at 35 °C for 30 min, and then the emulsion was heated to a polymerization temperature and maintained in a thermostated bath at 70 °C for 24 h. Agitation speed was kept constant at about 400 rpm throughout the polymerization. For the kinetic experiments, the microlatex samples were taken from the reactor during the polymerization, immediately quenched with a preweighed amount of hydroquinone, and cooled by an ice–water bath.

The monomer conversions were determined by the gravimetric method. A typical recipe for the emulsion polymerization is presented in Table 1.

In another control experiment, a cationic emulsifier with low-molecular-weight CTAB was used to replace the ABA triblock copolymer in the emulsion polymerization of styrene.

### Table 1. Recipe for the Emulsion Polymerization with ABA Triblock Copolymer as an Emulsifier

<table>
<thead>
<tr>
<th>Ingredients</th>
<th>Quantities (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Styrene</td>
<td>1.0</td>
</tr>
<tr>
<td>PDMAEMA$<em>{15}$-PPO$</em>{36}$-PDMAEMA$_{15}$</td>
<td>0.005–0.100</td>
</tr>
<tr>
<td>V50</td>
<td>0.02</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>50.0</td>
</tr>
</tbody>
</table>

### RESULTS AND DISCUSSION

#### Amphiphilic Triblock Polyelectrolyte Emulsifier

Figure 1 determines the chemical structure of PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$ triblock copolymer that was synthesized by oxyanion-initiated polymerization in our laboratory. Poly(propylene glycol) [number-average molecular weight ($M_n$): 2100, polydispersity ($M_w/M_n$): 1.09, measured by gel permeation chromatography (GPC)] was first reacted with KH in tetrahydrofuran medium and generated a telechelic-type potassium alcoholete. The latter was able to initiate DMAEMA monomer and allowed the formation of well-defined, highly-diluted polymer particles.

#### Colloidal Stability

Colloidal stability of the microlatexes was evaluated by two methods. The first method observed by TEM whether the microlatexes flocculated after keeping them at ambient temperature for 8 months. The second method determined the turbidity variation in a 721B spectrophotometer instrument (Shanghai Analysis Apparatus Co.) at 500 nm wavelength after adding NaCl or KCl solution with a series of predetermined concentrations from 0.001 to 3.0 mol/L. The polymer particles were highly diluted in aqueous HCl solution (pH 3) at 20 °C.

#### Determination of Microlatex Particle Size and Size Distribution

The average particle diameters of the microlatexes were obtained from a dynamic light scattering (DLS) spectrometer (Malvern Autosizer 4700) at 25 °C. The microlatex samples were diluted by HCl aqueous solution with the same pH as that of the original emulsion-polymerization system. The cumulant method was chosen for measuring the $z$-average hydrodynamic diameter ($D_z$) and polydispersity. In addition, particle sizes were determined by transmission electron microscopy (TEM) (Hitachi H-600). The parameter $D_n$ was the number-average diameter of microlatex particles. At least 300 microlatex particles were counted for each sample in the particle size measurement.

### Figure 1. Structure of PDMAEMA-PPO-PDMAEMA triblock copolymer prepared via oxyanion-initiated polymerization.
near-mono-dispersity ABA triblock copolymer. GPC analysis of the purified ABA triblock copolymer indicated that the polymer had a relatively narrow polydispersity ($M_w/M_n = 1.10$). $^1$H NMR in CDCl$_3$ was used to determine the molecular weight of the ABA triblock copolymer by the comparison of peak integrals obtained from PPO (oxymethylene signal at $\delta$ 3.4–3.5 ppm) with those associated with DMAEMA (dimethylamino proton signal at $\delta$ 2.2–2.3 ppm). The results of $^1$H NMR and GPC confirmed that the ABA triblock copolymer had been successfully prepared in our recent study.

Above ambient temperature, the copolymer exhibited amphiphilic properties. Poly(DMAEMA) blocks were used as the cationic polyelectrolyte segments displaying pH-dependent ionization in acidic or neutral media, whereas PPO moiety was the hydrophobic middle block at higher temperature ($\text{RT} = 15^\circ$C). The surface activity of the triblock copolymer at an air/water interface was evaluated by determining surface tension under the conditions at pH 3.0. The cmc could be obtained by a distinct change in the curve of surface tension versus concentration of copolymer at 20 $^\circ$C. Figure 2 depicts the relationship between the surface tension and the concentration of the ABA triblock copolymer. It indicates that the surface tension decreases rapidly with increasing copolymer concentration up to 0.1 g/L at pH 3.0. Above these concentrations, a significantly higher limiting surface tension is approximately 40 mN m$^{-1}$ for PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$ triblock copolymer. This result reasonably agrees with the observation by Paz Banez et al. They presented the limiting surface tension of the DMAEMA homopolymer (degree of polymerization: 66) as 43 mN m$^{-1}$ at pH 9.5 and 52 mN m$^{-1}$ at pH 6.0. The surface-active property of the ABA triblock copolymer suggests that such a triblock copolymer has interesting applications as a novel surfactant or emulsifier in preparation of surface-clean and functional latexes.

Acidic or neutral media were chosen in our emulsion-polymerization process because the tertiary amine of poly(DMAEMA) moiety was protonated at acidic conditions to give cationic polyelectrolyte.

**Emulsion Polymerization**

To investigate the influence of the amphiphilic triblock polyelectrolyte on the formation of the polymer particles in the radical emulsion polymerization, we devised a series of polymerization conditions in the range of pH 3.4–7.0. V50 was used as an excellent radical initiator in emulsion polymerization and yielded two positively charged radicals in acidic or neutral aqueous media.

The prerequisite for ABA triblock copolymer as a surfactant was that the A blocks should be swollen by the diluent and extend away from the particle surface, whereas the B blocks were entangled with each other to form micelles in aqueous solution. The efficient fixation of the polymeric emulsifier onto the particle surface (see Fig. 3) mainly depended on the molecular structure and its amphiphilic property as well as the concentration of the ABA triblock copolymer in solution. The cationic polyelectrolyte layer with A block provided a protective barrier against flocculation. The triblock copolymer was adsorbed onto the particle surface or jointed into the particle surface.

![Figure 2. Variation of the surface tension with the PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$ triblock copolymer concentration in an aqueous solution at pH 3.0.](image1)

![Figure 3. Representation of a polystyrene microlatex stabilized by adsorption or anchor of PDMAEMA-PPO-PDMAEMA triblock copolymer onto the surface.](image2)
Figure 4 describes the conversion versus reaction-time curves for these emulsion polymerizations both in the presence of the polycationic triblock copolymer surfactant (2.0 g/L) at pH 3.4 and in the absence of any emulsifier. The water-soluble initiator V50 was used for both systems. The significant differences in the polymerization behavior can be observed. The curve (a) shows a very rapid polymerization of styrene with PDMAEMA-PPO-PDMAEMA as a surfactant. The polymerization of styrene reaches a high conversion value in the initial 60 min. After 5 h, the conversion of the monomer in this system is practically above 93%. In contrast, the curve (b) of conversion versus reaction time, on which the polymerization was performed without any surfactant, represents a slow slope during the polymerization process and a low conversion value within the experiment range. This difference may be attributed to the effect of micellization of the triblock copolymer in aqueous solution.

A consistent explanation of these behaviors can be given when we consider the nucleation mechanisms for particle formation in emulsion polymerization, that is, micellar and homogeneous nucleation. In the ABA triblock copolymer system (above cmc), the particle nucleation takes place with a combination of micellar and homogeneous nucleation mechanisms, whereas in the case of surfactant-free emulsion polymerization, the primary nucleation mechanism should be homogeneous nucleation because styrene has relatively low water solubility, and little micellization results in the very low polymerization rate.

The ABA triblock copolymer presents a low but measurable cmc that means there is still an equilibrium between micelles and free surfactant in the aqueous phase. Thus, the copolymer behaves like a conventional low-molar-mass surfactant (homogeneous nucleation plus micellar nucleation, possible secondary nucleation, etc.). The values of the slope $\alpha$ (in $N_p = K[C_{copol}]^\alpha$) for various compositions of the copolymer would have allowed us to determine the range of hydrophilicity corresponding either to a ‘surfactant exchange’ ($\alpha < 1$) or to a ‘frozen’ micelle situation ($\alpha$ close to 1), that is, a complete (or largely predominant) micellization of the surfactant leading to a number of monodisperse latex particles close to the number of initial micelles. For Series A, the log-log plot of the number of latex particles ($N_p$) versus the copolymer concentration is portrayed in Figure 5. The fact that slope $\alpha < 1$ suggests there are homogeneous nucleations and micellar nucleations in the ABA triblock copolymer system.

**Effect of Triblock Copolymer Concentration on Particle Size**

The influence of triblock copolymer concentration on the particle size of microlatexes has been investigated by the analyses of TEM and dynamic light scattering (DLS). In all cases, the particle size decreased when the amount of copolymer stabilizer increased. For Series A system, typical values are given in Table 2 for microlatexes prepared in the presence of the ABA triblock copolymer, suggesting that particles of low polydispersity can be obtained when the concentration of copolymer is over cmc.

Figure 6(a–c) show TEM micrographs of the particles of emulsion polymerization corresponding to the PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$
triblock copolymer concentrations at 0, 0.1, and 2.0 g/L, respectively.

Because of the domination of homogeneous nucleation in emulsifier-free emulsion polymerization, the resulting particle diameter ($D_n$) was about 130 nm as shown in Figure 6(a), larger than that in all cases of the ABA triblock copolymer. For the ABA triblock copolymer system with the concentration of 2.0 g/L, for example, No. 0724, the particle diameter ($D_n$) was about 35 nm as shown in Figure 6(c). Lower emulsifier concentration, however, resulted in a larger particle size and wider particle size distribution. Figure 6(b) shows the microlatexes in which the concentration of the ABA triblock copolymer was 0.1 g/L, just reaching the lowest limit of the cmc. The particle size is not uniform. This result can also be attributed to the presence of two major mechanisms, that is, micellar nucleation and homogeneous nucleation.

The particle sizes ($D_n$) obtained by TEM are systematically smaller than those of ($D_n$) from DLS measurement. This is evidence of the PDMAEMA fringe on the particle surface, as DLS leads to the hydrodynamic radius of the microlatex including the surface layer of poly(DMAEMA), whereas in TEM experiments this fringe is collapsed, and the particles are in the dry state. For example, the hydrodynamic diameter ($z$ average) as measured by DLS was 76 nm for sample No. 0724 in Table 2 (2.0 g/L of triblock copolymer). For the same sample, as compared with the average hard-core diameter as measured from the TEM micrograph of about 35 nm in size, the adsorbed poly(DMAEMA) layer thickness was approximately 20 nm. The observation agreed with the results obtained by other researchers. This fact has been mentioned in the literature as an effect of the absorbed surfactants and the electrical double layers that may become significant for small particle sizes because of the shrinkage of the dried particles in the electron beam. It is obvious that the highly effective, steric barriers

Table 2. Summary of the PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$ Concentration, Particle Size of Microlatexes and Particle Size Distribution in Series A

<table>
<thead>
<tr>
<th>Experiment Number</th>
<th>$W_{ABA}$ (g)</th>
<th>[ABA] (g/L)</th>
<th>Particle Size$^a$ (nm)</th>
<th>Polydispersity$^b$</th>
<th>pH (before Reaction)</th>
<th>pH (after Reaction)</th>
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<tr>
<td>0725</td>
<td>0</td>
<td>0</td>
<td>351</td>
<td>0.20</td>
<td>3.40</td>
<td>3.65</td>
</tr>
<tr>
<td>0721</td>
<td>0.005</td>
<td>0.1</td>
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<td>3.42</td>
<td>3.62</td>
</tr>
<tr>
<td>0723</td>
<td>0.025</td>
<td>0.5</td>
<td>91</td>
<td>0.11</td>
<td>3.38</td>
<td>3.74</td>
</tr>
<tr>
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<td>3.40</td>
<td>3.64</td>
</tr>
<tr>
<td>0724</td>
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<td>2.0</td>
<td>76</td>
<td>0.06</td>
<td>3.42</td>
<td>3.61</td>
</tr>
</tbody>
</table>

$^a$ Particle diameters ($z$ average) were measured by a dynamic light scattering instrument (Malvern Autosizer 4700).

$^b$ The particle size distribution was expressed as polydispersity, which was a model-independent estimate of the width of the size distribution.

Figure 6. TEM micrographs of polystyrene latex synthesized by: (a) emulsifier-free emulsion polymerization, (b) emulsion polymerization with 0.1 g/L of PDMAEMA-PPO-PDMAEMA triblock copolymer, and (c) emulsion polymerization with 2.0 g/L of the triblock copolymer. These polymerizations were carried out at pH = 3.4 media.
can be generated by these adsorbed hydrophilic blocks.

**pH Effect of the Aqueous Solution Medium on Particle Size and Particle Size Distribution**

To get a better understanding of the stabilization of PDMAEMA-PPO-PDMAEMA for emulsion polymerization in a definite pH scope, three series of pH values were chosen. At the same solid content, all reactions were carried out at 70 °C in aqueous solution with a definite pH value. Series A, B, and C were designated for the emulsion polymerization systems at pH 3.4, 5.0, and 7.0, respectively. After emulsion polymerization, the pH values of these systems were accurately determined with a pH meter and exhibited the same as that of initiate solution before reaction. Table 2 lists the pH value of Series A before and after the reaction. Figure 7 displays the plots of particle diameter ($\bar{z}$-average) vs concentration and polydispersity concentration of the block copolymer at different vs pH media. In all cases, microlatex particle diameters decreased with increased PDMAEMA$_{15}$-PPO$_{36}$-PDMAEMA$_{15}$ concentration. Figure 7(a) gives the variation of particle size emulsifier concentration and size distribution emulsifier concentration at pH 3.4. With the same concentration of copolymeric surfactant, the decreasing tendencies of particle diameter were interestingly similar to each other in the scope of pH 5.0–7.0 as shown in Figure 7(b,c), indicating that microlatex particles were not largely influenced by pH media alone. Furthermore, the particle size distribution as expressed with polydispersity becomes narrower with increasing concentration of the ABA triblock copolymer.

An additional increase of the amount of the ABA triblock copolymer (4.0 g/L) led to much smaller microlatex particles as illustrated in Figure 8(a,b). The former microlatexes were prepared at pH 3.4, and the latter were prepared at pH 7.0. Although the emulsion polymerization processed at pH 7.0, smaller microlatexes with better dispersities were still obtained. It was attributed to the swelling of the hydrophilic segments of poly(DMAEMA) in acidic conditions and to their shrinking at neutral aqueous solutions, which led to the larger microlatex size in acidic conditions than that of particles in neutral media.

**Stability of Microlatexes**

Because such hydrophilic microlatexes bearing cationic groups on their surface are likely to be used in biological applications involving high ionic strength, it was also valuable to evaluate their stability behavior against electrolyte, for example, KCl and NaCl aqueous solution. This study was performed through a turbidimetric method or observation of the microlatex particles from TEM microscopy. These results exhibited that all polystyrene microlatexes with the ABA triblock copolymer as an emulsifier were stable.
against KCl or NaCl solutions up to the concentration of salts at 2.5 mol/L. This evidence implies that these microlatexes stabilized by the polymeric surfactant were remarkable resistance against flocculation.

Figure 9 illustrates the microlatex particles prepared at pH 3.4 and 2.0 g/L of ABA triblock copolymer. The sample had been kept at ambient temperature for 8 months before it was run TEM. No coagulation appeared in this system, indicating that the polystyrene particles carrying cationic “hairy” groups have excellent colloidal stability.

In a control experiment when the concentration of NaCl was only at 0.5 g/L, the obvious flocculation occurred for the microlatex particles, which was prepared with 2.0 g/L of CTAB as a cationic surfactant to substitute the ABA triblock in emulsion polymerization. This fact confirms that PDMAEMA\textsubscript{15}-PPO\textsubscript{36}-PDMAEMA\textsubscript{15} is a more efficient polymeric surfactant.

The effect of length of the hydrophilic block on the preparation of microlatex will be researched further and reported elsewhere in detail.

CONCLUSIONS

The use of PDMAEMA\textsubscript{15}-PPO\textsubscript{36}-PDMAEMA\textsubscript{15} triblock copolymer as the polymeric surfactant in the radical emulsion polymerization of styrene allowed the preparation of very fine and stable microlatex particles bearing cationic groups on their surface. The particle sizes were below 100 nm. Polymerization of styrene exhibited different characteristics in the presence of the triblock copolymer and without any surfactant. A fast emulsion-polymerization speed was observed from the curve of conversion versus time for the copolymeric surfactant system. The adsorbing poly (DMAEMA) moiety at the particle surface was confirmed by the difference of particle diameters between DLS measurement and TEM analysis. The
thickness of the hydrophilic fringe, poly (DMAEMA) block, can be considered to be about 20 nm in aqueous solution at pH 3.4. The best condition yielding uniform and stable colloidal particles should ascertain that pH media may be at a broad range from 3.4 to 7.0 and the concentration of triblock copolymer over cmc (0.1 g/L). TEM measurement clearly indicated that the microlatexes were still stable after 8 months at ambient temperature. The results of the turbidimetric method confirmed that the microlatexes obtained from ABA triblock copolymer were more stable than those from CTAB to dilution in the presence of electrolyte.

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REFERENCES AND NOTES