

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/7736948>

Miniemulsion Polymerization of Styrene Using a pH-Responsive Cationic Diblock Macromonomer and Its Nonreactive Diblock Copolymer Counterpart as Stabilizers

ARTICLE in LANGMUIR · AUGUST 2005

Impact Factor: 4.46 · DOI: 10.1021/la050495b · Source: PubMed

CITATIONS

31

READS

39

6 AUTHORS, INCLUDING:



[Maud Save](#)

Université de Pau et des Pays de l'Adour

59 PUBLICATIONS 1,862 CITATIONS

[SEE PROFILE](#)



[Bernadette Charleux](#)

Claude Bernard University Lyon 1

190 PUBLICATIONS 7,630 CITATIONS

[SEE PROFILE](#)



[Yuting Li](#)

University of Washington Seattle

42 PUBLICATIONS 2,102 CITATIONS

[SEE PROFILE](#)



[Steven P Armes](#)

The University of Sheffield

612 PUBLICATIONS 27,648 CITATIONS

[SEE PROFILE](#)

Miniemulsion Polymerization of Styrene Using a pH-Responsive Cationic Diblock Macromonomer and Its Nonreactive Diblock Copolymer Counterpart as Stabilizers

Lisa Houillot, Julien Nicolas, Maud Save,* and Bernadette Charleux

Laboratoire de Chimie des Polymères, CNRS UMR 7610, Université Pierre et Marie Curie, Case 185, 75252 Paris Cedex 05, France

Yuting Li and Steven P. Armes

Department of Chemistry, University of Sheffield, Brook Hill, Sheffield, South Yorkshire, S37HF United Kingdom

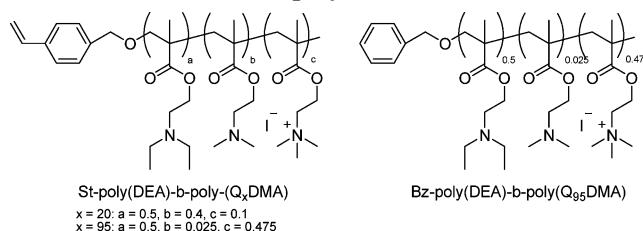
Received February 24, 2005. In Final Form: May 30, 2005

The miniemulsion polymerization of styrene has been carried out using two pH-responsive cationic diblock macromonomers as reactive stabilizers. As a comparison, the analogous nonpolymerizable cationic diblock copolymer was also investigated. Each of these three stabilizers based on 2-(diethylaminoethyl)-methacrylate and quaternized 2-(dimethylaminoethyl)methacrylate residues were prepared via oxyanionic polymerization and had relatively low polydispersities. It was found that all three copolymers were grafted to the polystyrene latex particles, as judged by X-ray photoelectron spectroscopy, aqueous electrophoresis and FTIR spectroscopy studies. Kinetics studies and colloidal characteristics indicated poorer stabilization properties of the partially quaternized diblock macromonomer and electron microscopy confirmed that the latexes invariably had relatively broad particle size distributions.

Introduction

The nucleation mechanism for miniemulsion polymerization is much more straightforward than emulsion polymerization since monomer droplets act as nanoreactors for the polymerization.^{1–3} Indeed, droplet nucleation is enhanced by the large number of droplets created during the high shear step. In the ideal case, there is no competition between micellar and droplet nucleation since the surfactant molecules stabilize the high monomer/water interface and its concentration in the aqueous phase is below the critical micelle concentration (cmc). Consequently, if Ostwald ripening is avoided by the addition of a cosurfactant, monomer transport in the aqueous phase is very limited.² Miniemulsion polymerization is much less exploited than emulsion polymerization in industrial processes because the high shear step is energy-intensive and the use of hydrophobic additives, which are typically volatile organic compounds, is not encouraged. Nevertheless, miniemulsion polymerization has some unique features that allow specific applications such as the efficient encapsulation of inorganic particles (titanium dioxide,⁴ calcium carbonate,⁵ carbon black,⁶ and magnetic nanoparticles⁷) or organic molecules (e.g., oil-soluble dye,⁸ photochromophore,⁹ or a capping agent for “controlled/living” radical polymerizations¹⁰).

Scheme 1. Chemical Structures of the St-poly(DEA)-b-poly(Q_xDMA) Diblock Macromonomer and the Bz-poly(DEA)-b-poly(Q_xDMA) Diblock Copolymer^a



^a *x* is the degree of quaternization, and *a*, *b*, and *c* are the relative proportions of each monomer residue.

Amphiphilic copolymers, particularly polyelectrolytes, have proved to be interesting steric or “electrosteric” stabilizers for the polymerization in aqueous dispersed media¹¹ but there are relatively few publications describing their use in miniemulsion polymerization.^{12–15} In the work presented here, a pH-responsive cationic diblock copolymer (Scheme 1) is used as an electrosteric stabilizer for the miniemulsion polymerization of styrene. Such copolymers can be dissolved molecularly in aqueous solution without using cosolvents simply by lowering the solution pH, whereas *in situ* micellization can be induced by adjusting the pH to approximately pH 8. On the other hand, the

* To whom correspondence should be addressed. Phone: 33 (0)1 44 27 55 73. Fax: 33 (0)1 44 27 70 89. E-mail address: save@crr.jussieu.fr.

(1) Schork, F. J.; Poehlein, G. W.; Wang, S.; Reimers, J.; Rodrigues, J.; Samer, C. *Colloids and Surfaces A: Physicochem. Eng. Aspects* **1999**, *153*, 39.

(2) Landfester, K. *Macromol. Rapid. Commun.* **2001**, *22*(12), 896.

(3) Asua, J. M. *Prog. Polym. Sci.* **2002**, *27*, 1283.

(4) Erdem, B.; Sudol, E. D.; Dimonie, V. L.; El-Aasser, M. S. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 4431.

(5) Bechtold, N.; Tiarks, F.; Willert, M.; Landfester, M.; Antonietti, M. *Macromol. Symp.* **2000**, *151*, 549.

(6) Tiarks, F.; Landfester, M.; Antonietti, M. *Macromol. Chem. Phys.* **2001**, *202*, 51.

(7) Liu, X.; Guan, Y.; Ma, Z.; Liu, H. *Langmuir* **2004**, *20*, 10278.

(8) Takasu, M.; Shiroya, T.; Takeshita, K.; Sakamoto, M.; Kawaguchi, H. *Colloid. Polym. Sci.* **2003**, *282*, 119.

(9) Han, M.; Lee, E.; Kim, E. *Opt. Mater.* **2003**, *21*, 579.

(10) (a) Nicolas, J.; Charleux, B.; Guerret, O.; Magnet, S. *Macromolecules* **2004**, *37*, 4453. (b) Lansalot, M.; Davis, T. P.; Heuts, J. P. A. *Macromolecules* **2002**, *35*, 7582.

(11) Riess, G.; Labbe, C. Block Copolymers in Emulsion and Dispersion polymerization. *Macromol. Rapid. Commun.* **2004**, *25*, 401.

(12) Pham, B. T. T.; Nguyen, D.; Ferguson, C. J.; Hawkett, B. S.; Serelis, A. K.; Such, C. H. *Macromolecules* **2003**, *36*, 8907.

(13) Durand, A.; Marie, E.; Rotureau, E.; Leonard, M.; Dellacherie, E. *Langmuir* **2004**, *20*, 6956.

(14) Baskar, G.; Landfester, K.; Antonietti, M. *Macromolecules* **2000**, *33*, 9228.

(15) (a) Lim, M. S.; Chen, H. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *38*, 1818. (b) Ou, J. L.; Lim, M. S.; Chen, H. *J. Appl. Polym. Sci.* **2003**, *87*, 2230.

pH-responsive character of the copolymer could be a drawback if the stabilizer desorption occurs at low pH inducing the latex destabilization. Thus, the reactive cationic diblock copolymer (referred to as diblock macromonomer) was used as stabilizer to lead to a covalent grafting of the cationic polymeric shell to the surface of the latex particles. Numerous studies highlighted the use of reactive surfactant monomers known as “surfmers” in both emulsion^{16,17} and miniemulsion¹⁸ polymerizations. Macromonomers composed of a hydrophilic homopolymer^{19,20} or an amphiphilic block copolymer²¹ served as stabilizers for the polymerization in aqueous dispersed media but, as far as we are aware, there is only one example concerning their use in miniemulsion polymerization.²² In the case of “surfactant-free” emulsion or dispersion polymerization, the hydrophilic polymeric shell is created in situ by the copolymerization of the macromonomer with the hydrophobic monomer, whereas for “surfactant-free” miniemulsion polymerization, the macromonomer must be surface-active to stabilize the initial miniemulsion droplets.

In 1997, Nagasaki and co-workers reported²³ the homopolymerization of 2-(diethylamino)ethyl methacrylate (DEA) using potassium ethoxide in THF at or above ambient temperature. It was also shown that using a potassium 4-vinylbenzyl alcoholate initiator led to formation of well-defined, styrene-capped, DEA-based macromonomers ($M_w/M_n = 1.1–1.3$): such selectivity is not possible using classical anionic polymerization. Recently, these macromonomer syntheses were extended to include other tertiary amine methacrylates, such as 2-(dimethylamino)ethyl methacrylate (DMA), 2-(*N*-morpholino)ethyl methacrylate (MEMA), and 2-(diisopropylamino)ethyl methacrylate (DPA).¹⁹ In particular, styrene-capped DMA macromonomers have been used as reactive polymeric stabilizers for the synthesis of polystyrene latexes²⁴ and pH-responsive microgels.²⁵ The living character of oxyanionic polymerization was demonstrated by synthesizing reasonably well-defined diblock or triblock copolymers.²⁶

The purpose of the present study was to investigate the efficiency of novel cationic diblock macromonomers as reactive stabilizers for the miniemulsion polymerization of styrene. First, oxyanionic polymerization is employed to synthesize a novel styrene-capped St-poly(DEA)-*b*-poly(DMA) diblock macromonomer. Then selective quaternization of the DMA residues produces a permanently cationic block. The nonquaternized DEA block is known to be pH-responsive: in its deprotonated form, the DEA

block is hydrophobic, leading to micellization of the amphiphilic copolymer above approximately pH 7.²⁷ The “electro-steric” stabilization performance of the following three cationic diblock copolymers has been studied: (1) a benzyl-terminated, selectively quaternized Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (mean degree of quaternization of the DMA block = 95%); (2) a styryl-terminated, selectively quaternized St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (mean degree of quaternization of the DMA block = 95%); (3) a styryl-terminated, selectively quaternized St-poly(DEA)-*b*-poly(Q₂₀DMA) diblock copolymer (mean degree of quaternization of the DMA block = 20%) (Scheme 1). The main objective was the synthesis of electrosterically stabilized polystyrene nanoparticles with cationic polyelectrolyte shells by miniemulsion polymerization. The cationic quaternary ammonium salts are known to be bactericidal compounds, and for instance, they can be used in the formulation of bactericide varnish or as stabilizer to recover cationic latexes which were designed for high performance, waterbased stain blocking paints.²⁸

Experimental Section

Materials. Styrene (St, Aldrich, 99%) was distilled under reduced pressure before use. Azobis(isobutyronitrile) (AIBN, Acros, 98%), sodium hydrogen carbonate buffer (NaHCO₃, Prolabo > 99%), and *n*-hexadecane (Aldrich, 99%) were used as received. 2-(Dimethylamino)ethyl methacrylate (DMA), 2-(diethylamino)ethyl methacrylate (DEA), benzyl alcohol, and potassium *t*-butoxide (1.0 M in THF) were purchased from Aldrich. THF was dried over sodium wire for 3 days and subsequently refluxed in the presence of sodium. It was distilled under nitrogen just prior to use. All monomers were passed through basic alumina columns, stirred over calcium hydride for 24 h, stored at −9 °C, and distilled immediately prior to use. All other reagents were used as received.

Analytical Techniques. The number- and weight-average molar masses (M_n and M_w) and the polydispersity (M_w/M_n) of the copolymers were obtained by size exclusion chromatography (SEC) in THF with a flow rate of 1.0 mL min^{−1}. The apparatus comprised three linear columns (Polymer Laboratories, two Mixed-C, 5 μ m columns and one linear column, 100 Å, 5 μ m) thermostated at 40 °C. The copolymer concentrations were 15 g/L. The triple detector system (Viscotek TriSEC model 302) comprising a refractive index detector, a viscometer (intrinsic viscosity measured online) and a light scattering detector ($\lambda = 670$ nm, 3 mW, 90° scattering angle) in THF was used. The refractive index increment values, dn/dc have been measured with the Viscotek TriSEC model 302 and the average dn/dc value for a poly(DEA)-*b*-poly(DMA) diblock copolymer was equal to 0.070. All ¹H NMR spectra were recorded using a 300 MHz Bruker Avance DPX300 spectrometer in either CDCl₃ or CD₃OD. The ¹H NMR spectra of the two diblock copolymer precursors and the corresponding quaternized diblock macromonomers and the diblock copolymer are reported in the Supporting Information.

Synthesis of the St-poly(DEA)-*b*-poly(DMA) Diblock Macromonomer. The styrene-functionalized DEA-DMA diblock macromonomer was synthesized via sequential monomer addition using oxyanionic polymerization. The typical polymerization protocol was as follows: All glassware was dried overnight at 150 °C, assembled hot under a nitrogen purge, and then flamed out under dynamic vacuum to remove any residual surface moisture. Polymerizations were carried out at 50 °C. The initiator precursor, 4-vinylbenzyl alcohol (4.0 mL of a 0.50 M solution in THF), was added to the polymerization flask containing 150 mL of anhydrous THF. To this solvent was added potassium *tert*-butoxide (2.0 mL of a 1.0 M THF solution, Aldrich), and the reaction mixture was stirred for approximately 30 min at 50 °C.

(27) Lee, A. S.; Gast, A. P.; Bütün, V.; Armes, S. P. *Macromolecules* **1999**, *32*, 4302.

(28) (a) Rush, T. E.; Pritchett, E. A.; Smith, R. A.; Arbir, F. W. *Modern Paint Coatings* **1978**, *68*(2), 53. (b) Umemura, Y.; Ozaki, Y.; Kawaide, A. *Eur. Pat. Appl.* **1989** EP 318258 (c) Jiang, S.; Luisi, I.; Clement, S. *PCT Int. Appl.* **2003** WO 2003047349.

(16) (a) Guyot, A.; Tauer, K. *Adv. Polym. Sci.* **1994**, *111*, 43. (b) Guyot, A. *Macromol. Symp.* **2002**, *179*, 105.

(17) (a) Aramedia, E.; Malléol, J.; Jeynes, C. Barandiaran, M. J.; Keddie, J. L.; Asua, J. M. *Langmuir* **2003**, *19*, 3212. (b) Unzué, M. J.; Schoonbrood, H. A. S.; Asua, J. M.; Montoya Goni, A.; Sherrington, D. C.; Stähler, K.; Goebel, K. H.; Tauer, K.; Sjöberg, M.; Holmberg, K. *J. Appl. Polym. Sci.* **1997**, *66*, 1803.

(18) Guyot, A.; Graillat, C.; Favero, C. C. *R. Chimie* **2003**, *6*, 1319.

(19) Lascelles, S. F.; Malet, F.; Raouf, M.; Billingham, N. C.; Armes, S. P. *Macromolecules* **1999**, *32*, 2462.

(20) Basinska, T.; Slomkowski, S.; Dworak, A.; Panchev, I.; Chehimi, M. M. *Colloid. Polym. Sci.* **2001**, *279*, 916.

(21) Gibanel, S.; Forcada, J.; Heroguez, V.; Schappacher, M.; Gnanou, Y. *Macromolecules* **2001**, *34*, 4451.

(22) Kim, J. W.; Ko, J. Y.; Park, J. G.; Jun, J. B.; Chang, I. S.; Suh, K. D. *J. Appl. Polym. Sci.* **2002**, *85*, 328.

(23) Nagasaki, Y.; Sato, Y.; Kato, M. *Macromol. Rapid Commun.* **1997**, *18*, 827.

(24) Amalvy, J. I.; Unali, G.-F.; Li, Y.; Granger-Bevan, S.; Armes, S. P.; Binks, B. P.; Rodrigues, J. A.; Whitby, C. P. *Langmuir* **2004**, *20*, 4345.

(25) Amalvy, J. I.; Wanless, E. J.; Li, Y.; Michailidou, V.; Armes, S. P.; Duccini, Y. *Langmuir* **2004**, *20*, 8992.

(26) De Paz-Banez, M. V.; Robinson, K. L.; Bütün, V.; Armes, S. P. *Polymer* **2001**, *42*, 29.

Table 1. Miniemulsion Polymerizations of Styrene Using the St-poly(DEA)-*b*-poly(Q₉₅DMA) Diblock Macromonomer, the St-poly(DEA)-*b*-poly(Q₂₀DMA) Diblock Macromonomer, and the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) Diblock Copolymer as Polymeric Stabilizers

expt	stabilizer	wt % of polymeric stabilizer relative to the mass of styrene	solution pH during polym.	polym. time (h)	fractional conversion	particle diameter DLS (nm)	N_p^b L_{latex}^{-1}	particle diameter TEM (nm)	
						D_z		D_n	D_z
1	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	1	9	7	0.57	415 + coagulum	3.03×10^{15}	290 + coagulum	405 + coagulum
2	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	2	9	4	0.95	280	1.8×10^{16}	205	415
3	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	4	9	3	1	230	3.26×10^{16}	160	590
4	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	4	2	4	biphasic solution + coagulum				
5	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	6	9	2	0.95	200	4.96×10^{16}	90	175
6	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	8	9	2	0.99	180	6.74×10^{16}	80	260
7	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	10	9	1.5	1	170	8.80×10^{16}	80	160
8	St-poly(DEA)- <i>b</i> -poly(Q ₂₀ DMA)	1	9	8	0.58	700 + coagulum	1.04×10^{15}		
9	St-poly(DEA)- <i>b</i> -poly(Q ₂₀ DMA)	2	9	7	0.55	460 + coagulum	1.19×10^{15}		
10	St-poly(DEA)- <i>b</i> -poly(Q ₂₀ DMA)	4	9	6	0.65	250	2.27×10^{16}		
11	St-poly(DEA)- <i>b</i> -poly(Q ₂₀ DMA)	8	9	6	0.79	280	1.60×10^{16}		
12	St-poly(DEA)- <i>b</i> -poly(Q ₂₀ DMA)	10	9	4	0.95	250	2.25×10^{16}		
13	Bz-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	1	9	8	0.70	365	5.5×10^{15}	250	375
14	Bz-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	2	9	8	0.85	350	7.0×10^{15}	220	360
15	Bz-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	4	9	5	0.97	280	1.16×10^{16}	170	660

^a Experimental conditions: $T = 70^\circ\text{C}$, 20 wt % solids content; $[\text{AIBN}] = 8.6 \times 10^{-3} \text{ mol } L_{\text{latex}}^{-1}$; $[n\text{-hexadecane}] = 1.14 \times 10^{-1} \text{ mol } L_{\text{latex}}^{-1}$; $[\text{NaHCO}_3] = 7.0 \times 10^{-3} \text{ mol } L_{\text{latex}}^{-1}$. ^b The number of latex particle per liter (N_p) is calculated from the diameter measured by DLS.

Subsequently, freshly distilled DEA (20.1 mL, 18.5 g, 100 mmol, target DP = 50) was added dropwise to the reaction flask, and polymerization commenced via the in situ generated potassium 4-vinylbenzyl alcoholate initiator. After 20 min (the conversion of the DEA monomer was complete), freshly distilled DMA (16.9 mL, 15.7 g, 100 mmol, target DP = 50) was added dropwise to the living PDEA solution at 50°C . After 2 h to reach complete conversion, the second-stage polymerization was terminated with methanol. The crude diblock macromonomer was purified by passing the reaction mixture through a silica column, and THF was removed under vacuum. The resulting solid was washed three times with *n*-heptane to remove traces of unreacted 4-vinylbenzyl alcohol initiator and also any PDEA homopolymer contamination (less than 10 wt %). Finally, the purified diblock macromonomer was dried in a vacuum oven overnight at room temperature. The overall yield of isolated, purified diblock macromonomer was 25.7 g (75%). THF GPC analysis gave an M_n of $14\,800 \text{ g mol}^{-1}$ and an M_w/M_n of 1.25 and ^1H NMR analysis indicated that the block composition was 51 mol % DMA. This diblock macromonomer was given the acronym St-poly(DEA)-*b*-poly(DMA).

The analogous nonreactive potassium benzyl alcoholate-initiated Bz-poly(DEA)-*b*-poly(DMA) diblock copolymer was synthesized as described previously.²⁶ THF GPC analysis indicated an M_n of $13\,660 \text{ g mol}^{-1}$, and an M_w/M_n of 1.36. The DMA content calculated from ^1H NMR analysis was 51 mol %.

Selective Quaternization of the Diblock Macromonomer. The DMA residues of the St-poly(DEA)-*b*-poly(DMA) macromonomer were selectively quaternized with methyl iodide using a methyl iodide/DMA molar ratio of 1.00 in a 4:1 THF/water mixture at 20°C for 20 h. The degree of quaternization of the DMA residues of the macromonomer was estimated to be 95% [appearance of the nine trimethylammonium protons at 3.2 ppm, with a weak signal still visible at 2.2 ppm due to the six 2-(dimethylamino) protons of the unquaternized DMA residues] as judged by ^1H NMR spectroscopy (d_4 -methanol). This diblock macromonomer was named St-poly(DEA)-*b*-poly(Q₉₅DMA).

Essentially the same protocol was used to obtain a lower degree of quaternization of the DMA residues. In this case, a methyl iodide/DMA molar ratio of 0.20 was employed and the derivatization was performed in THF for 20 h at 20°C . Thus, the St-poly(DEA)-*b*-poly(DMA) macromonomer (10.7 g) was dissolved in 150 mL of THF, and 0.88 g (0.0062 mol) of methyl iodide

dissolved in 5 mL of THF was added to this macromonomer solution. Inspecting the ^1H NMR spectrum (d_4 -methanol) of the quaternized diblock macromonomer indicated a mean degree of quaternization of approximately 20% for the DMA block of the diblock macromonomer, which was named St-poly(DEA)-*b*-poly(Q₂₀DMA).

Batch Miniemulsion Polymerizations of Styrene. A typical recipe for the miniemulsion of styrene using the AIBN initiator is as follows. First, a mixture of styrene (30.0 g, 0.29 mol), AIBN (0.216 g, 1.3 mmol), and *n*-hexadecane (1.5 g, 7 mmol) was poured into an aqueous solution containing the amphiphilic cationic diblock copolymer St-poly(DEA)-*b*-poly(Q₉₅DMA) (1.2 g , $7.5 \times 10^{-5} \text{ mol}$), NaHCO_3 (0.09 g, 1.07 mmol), and water (120 g). The unstable 20 wt % styrene emulsion that was formed was gently stirred for 15 min, and a stable miniemulsion was then obtained by ultrasonication (Branson 450 Sonifier, power 7 for 10 min, performed in an ice bath to avoid premature initiation). Afterward, the stable miniemulsion was subjected to nitrogen bubbling for 20 min and was poured into a 0.25 L thermostated glass reactor, preheated at 70°C . The beginning of the polymerization was arbitrarily taken to be when the temperature of the reaction mixture reached 70°C . Polymerizations were allowed to proceed for 3 h at 70°C using a stirring rate of 300 rpm under a nitrogen atmosphere. Samples were taken at regular time intervals to follow the monomer conversion by gravimetry and to analyze the average particle diameter by dynamic light scattering (DLS). Table 1 summarizes the data obtained from these miniemulsion polymerizations.

Latex Characterization. The monomer conversion was determined by gravimetry. The average particle diameter was measured by dynamic light scattering (DLS; Malvern Zetasizer 4 instrument equipped with a 5 mW He-Ne laser operating at 633 nm) at 25°C and a fixed angle of 90° and also by transmission electron microscopy (TEM, JEOL JEM 100 cx II CHR, 500 particles were counted per sample). The number concentration of latex particles N_p per liter of the suspension (particle + water) was calculated according to eq 1²⁹

$$N_p = \frac{6\tau_p}{d_p \pi D_p^3} (L_{\text{latex}}^{-1}) \quad (1)$$

where D_p is the average particle diameter in cm, d_p is the

polystyrene density ($d_p = 1.05 \text{ g cm}^{-3}$)³⁰ and τ_p is the latex concentration ($\text{g L}_{\text{latex}}^{-1}$).

Prior to the zeta potential measurements, the FTIR and XPS analyses, all latexes were centrifuged (Beckman MC J2 instrument, 20 000 rpm) and the supernatant was removed and replaced by distilled water (at pH 5 for FTIR). This centrifugation-dispersion cycle was repeated 10 times. The latex was dispersed again in water for zeta potential measurements and dried as a powder for the FTIR and XPS analyses. The re-dispersion of the centrifuged latex was easy and the average diameter measured by DLS was close to the initial one.

Aqueous Electrophoresis Measurements. Aqueous electrophoresis data were obtained using a Malvern Instruments Zetasizer Nano series instrument. The zeta potential, ζ , was calculated from the electrophoretic mobility (u) using the Smoluchowsky relationship, $\zeta = \eta u / \epsilon f(\kappa a)$, where it is assumed that $\kappa a \gg 1$ (where η is the solution viscosity, ϵ is the dielectric constant of the medium, and κ and a are the Debye–Hückel parameter and the particle radius, respectively, $f(\kappa a)$ is the Henry's function, and its value is 1.5 (Smoluchowski approximation) when the electrophoretic determinations of zeta potential are made in aqueous media and moderate electrolyte concentration). The solution pH was adjusted as required by the addition of either NaOH or HCl using a MPT-2 multi-purpose auto-titrator. All measurements were carried out at 20 °C on dilute aqueous solutions (0.2 g L^{-1}) of the latex particles.

Fourier Transform Infrared Spectroscopy (FTIR). FTIR spectra were recorded from KBr pellets at room temperature using a Nicolet Avatar FTIR spectrometer.

XPS Analyses. XP spectra were recorded using a Thermo VG Scientific ESCALAB 250 system fitted with a micro-focused, monochromatic Al K α X-ray source (1486.6 eV) and a magnetic lens which increases the electron acceptance angle and hence the sensitivity. An X-ray beam of $650 \mu\text{m}$ size was used at a power of $10 \text{ mA} \times 15 \text{ kV}$. The spectra were acquired in the constant analyzer energy mode, using pass energies of 150 and 40 eV for the survey and the narrow regions, respectively. The Advantage software, version 1.85, was used for digital acquisition and data processing. Spectral calibration was determined by setting the aliphatic C–C/C–H C1s peak at 285 eV.

Results and Discussion

The oxyanionic polymerizations were carried out successfully at 50 °C: high monomer conversions, low polydispersities, and reasonably good control over the target molar masses were obtained under the stated conditions. The Armes research group had previously reported the synthesis of both polyDMA macromonomers¹⁹ and poly(DMA)-*b*-poly(DEA) diblock copolymers²⁶ via oxyanionic polymerization. However, as far as we are aware, this is the first report of the synthesis of well-defined diblock macromonomers using oxyanionic polymerization. Similarly, Armes et al. had reported the selective quaternization of DMA residues in poly(DMA)-*b*-poly(DEA) diblock copolymers using methyl iodide,^{31,32} but this post-polymerization derivatization had not been reported for diblock macromonomers.

All of the miniemulsion polymerizations presented in this paper were initiated using a hydrophobic initiator (AIBN) to enhance the droplet nucleation. A set of miniemulsion polymerizations of styrene was first performed using the 95% quaternized St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer as a reactive polymeric stabilizer. The amount of this cationic diblock macromonomer stabilizer ranged from 1 to 10 wt % with

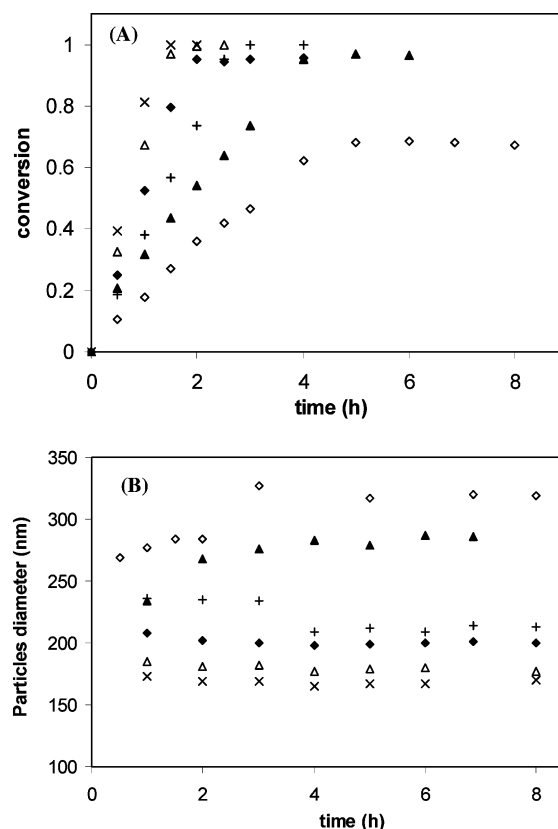


Figure 1. Miniemulsion polymerizations of styrene initiated by AIBN at 70 °C using various amounts of the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (wt % vs St), conversion versus time plots (A) and particle diameter from DLS versus time plots (B). See Table 1 for the experimental conditions (×) 10 wt %, expt 7; (Δ) 8 wt %, expt 6; (◆) 6 wt %, expt 5; (+) 4 wt %, expt 3; (▲) 2 wt %, expt 2; (◇) 1 wt %, expt 1.

respect to styrene. As expected, the final average particle diameter decreased and polymerization rate increased with increasing stabilizer concentration (Figure 1). When the stabilizer concentration ranged between 4 and 10 wt %, the average particle diameter remained constant along the polymerization. Nevertheless, for the lowest stabilizer concentrations (1–2 wt % with respect to styrene), the increase in particle diameter with conversion was probably due to particle coalescence (Figure 1B). The discrepancy between the *z*-average particle diameter measured by DLS and the number-average diameter calculated from TEM could be assigned first to the hydrophilic shell expanded in water for DLS and second to the relatively high polydispersity of the latexes particle size distribution (see Table 1 and Figure 2). Indeed, the small population of larger particles (see Figure 2) accounts for most of the light scattering due to the strong a^6 dependence of the scattering light intensity on the particle radius a . In a review article, Asua³ summarized several quantitative relationships for the dependence of the number of particles N_p on the surfactant concentration. Depending on the experimental conditions, N_p was proportional to [surfactant] $^\alpha$ with the α exponent ranging from 0.25 to 1.4.³ When using the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer as stabilizer, the α exponent was equal to unity for the intensity-average particle diameters determined by DLS (see Figure 3). However, no linear relationship was observed for the $\log(N_p)$ versus $\log([\text{copolymer}])$ plot when N_p was calculated using the number-average diameters calculated from TEM (Figure 3). Thus, some caution should be used when attempting to interpret these data.

(29) Gilbert, R. G. *Emulsion Polymerization. A mechanistic approach*; Academic Press: New York, 1995.

(30) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley and Sons: New York, 1989.

(31) Bütün, V.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2001**, *34*, 1148.

(32) Vamvakaki, M.; Unali, G. F.; Bütün, V.; Boucher, S.; Robinson, K. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2001**, *34*, 6839.

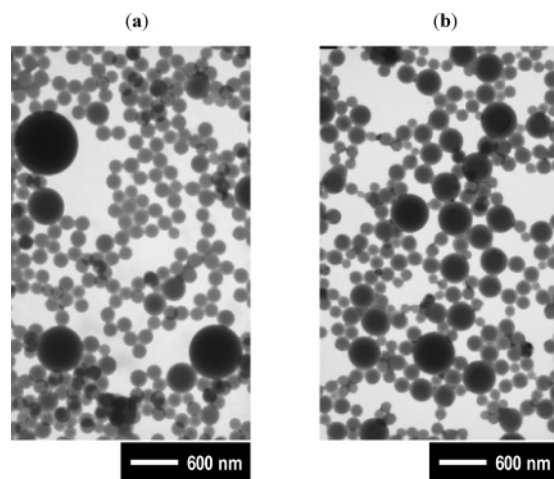


Figure 2. TEM images of latexes stabilized by 2 wt % of the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (a, expt 2, Table 1) and of the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (b, expt 14, Table 1).

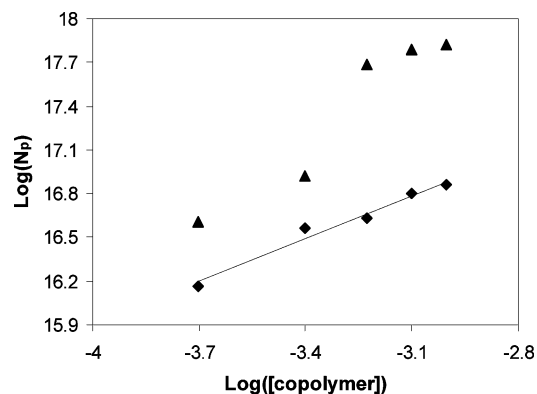


Figure 3. Miniemulsion polymerization of styrene initiated by AIBN at 70 °C. Final number of particles as a function of the St-poly(DEA)-*b*-poly(Q₉₅DMA) copolymer concentration from number-average diameter measured by TEM (▲), and from intensity-average diameter measured by DLS (◆).

In principle, the amphiphilic copolymer surfactant, which copolymerizes *in situ* with styrene, might be located either at the surface or buried inside the latex particles. However, consideration of the surface thermodynamics suggests that the cationic surfmer should be located primarily at the latex surface, and this is consistent with the positive zeta potentials observed below pH 7 (Figure 4). The benzyl-terminated (and supposedly nonreactive) diblock copolymer also gave strongly positive zeta potentials, which suggests that this stabilizer is also present on the outside of the latex particles. The zeta potentials measured at low pH were lower for the latexes stabilized by the diblock macromonomers than for the one stabilized by the diblock copolymer. The theoretical average numbers of cationic charges per particle (N_{cp}), calculated from the experimental number of particles (N_p) were gathered in Table 2 for the three latexes used for the zeta potential analyses. Actually, the calculation of the total number of cationic charges per particle cannot explain the results observed by aqueous electrophoresis measurements. Indeed, N_{cp} decreased in the following order: $N_{cp}(\text{Bz-poly}(\text{DEA})\text{-}b\text{-poly}(\text{Q}_{95}\text{DMA})) \approx N_{cp}(\text{St-poly}(\text{DEA})\text{-}b\text{-poly}(\text{Q}_{20}\text{DMA})) > N_{cp}(\text{St-poly}(\text{DEA})\text{-}b\text{-poly}(\text{Q}_{95}\text{DMA}))$ and zeta potential values decreased in a different order: $\zeta(\text{Bz-poly}(\text{DEA})\text{-}b\text{-poly}(\text{Q}_{95}\text{DMA})) > \zeta(\text{St-poly}(\text{DEA})\text{-}b\text{-poly}(\text{Q}_{20}\text{DMA})) \approx \zeta(\text{St-poly}(\text{DEA})\text{-}b\text{-poly}(\text{Q}_{95}\text{DMA}))$. Although the high polydispersity of the latex induces heterogeneity in

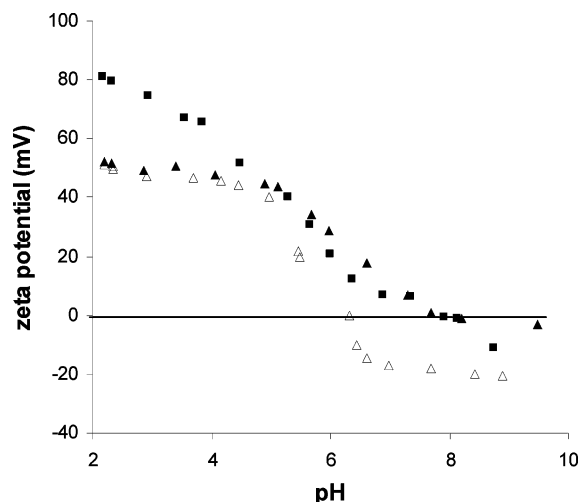


Figure 4. Zeta potential vs pH curves for a polystyrene latex synthesized by miniemulsion polymerization using (▲) 4 wt % of the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (expt 7, Table 1), (△) 4 wt % of the St-poly(DEA)-*b*-poly(Q₂₀DMA) diblock macromonomer (expt 10, Table 1), (■) 4 wt % of the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (expt 15, Table 1).

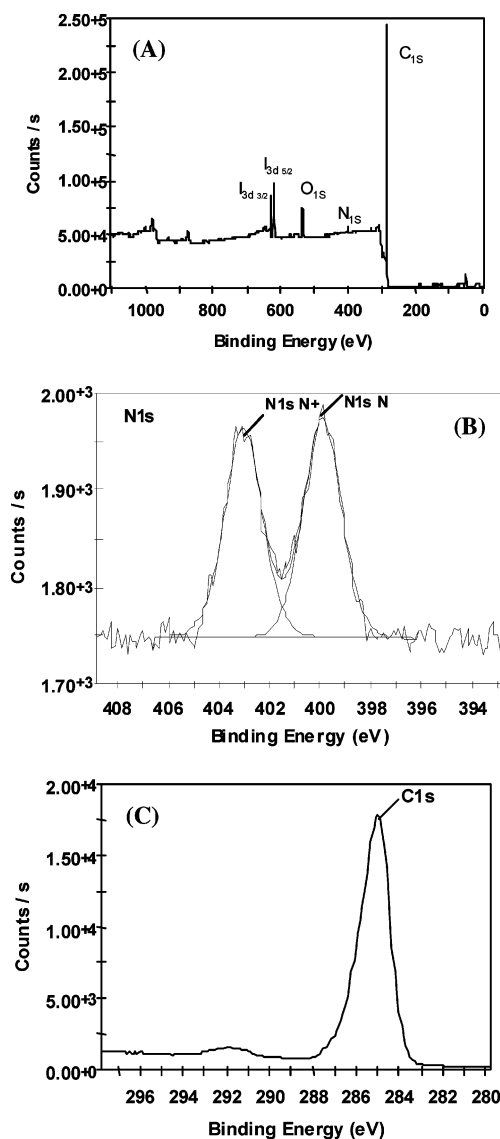
the number of chain per particle and may influence the measured ensemble average zeta potential, it is likely that the copolymerization reaction might induce a stronger burial of the DEA block. Consequently, the protonation of the less accessible DEA block would be more difficult, leading to a lower amount of positive charges at low pH for the latexes stabilized by the reactive copolymer. The diblock macromonomer at a lower degree of quaternization produced latex particles that had a lower isoelectric point (around pH 6.25 rather than pH 7.95; see Figure 4); presumably these differences are due to the lower cationic charge density on this stabilizer. The low anionic zeta potentials observed in alkaline media for all three latexes suggests the adsorption of hydroxide ions on the latex surface, which eventually overrides the cationic charge density on the stabilizer chains.

The polystyrene latexes were also analyzed by X-ray photoelectron spectroscopy (XPS), which is an established spectroscopic technique for assessing the surface compositions of colloidal particles. Four elements were detected at the latex surface, namely oxygen (O_{1s}, 532.9 eV), carbon (C_{1s}, 285 eV), nitrogen (N_{1s}, 399.9 eV), and iodine (I_{3d5/2}, 618.9 eV; Figure 5A). The relative atomic compositions estimated from the XPS peaks were 95.4% C, 2.5% O, 1.4% N, and 0.7% I (for the latex corresponding to entry 7 in Table 1) and the theoretical overall composition calculated from the molar concentration of the reagents (styrene and macromonomer) is 98.25% C, 1.0% O, 0.5% N, and 0.25% I. The higher experimental values of nitrogen, oxygen, and iodine atoms compared with the theoretical ones is in favor of a higher stabilizer concentration at the surface of the particle than in the bulk (the typical XPS analysis depth is approximately 2–5 nm). The nitrogen core-line spectrum (Figure 5B) revealed two components at 399.9 and 403 eV that are characteristic of neutral amine (N⁰) and cationic amine (N⁺) functions, respectively. The relative nitrogen and iodine compositions estimated from the XPS (0.71% N_{1s} (N⁰), 0.68% N_{1s} (N⁺), 0.70% (I_{3d})) were consistent with the expected equimolar composition of the quaternized DMA residues and the neutral DEA residues of the 95% quaternized diblock macromonomer. The C_{1s} region exhibited a main peak at 285 eV and a shake-up satellite centered at 291.5 eV, which is due to the aromatic groups on the styrene residues

Table 2. Colloidal Characteristics of the Latexes Used for Zeta Potential (4 wt % of the Stabilizer Relative to the Mass of Styrene)

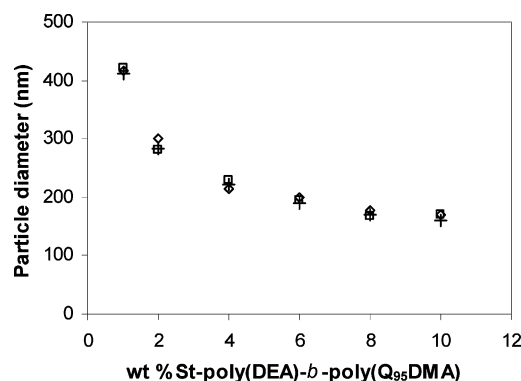
expt from Table 1	stabilizer	[stabilizer] mol/L	N_p/L_{latex}	theoretical $N_{s/p}^a$	theoretical $N_{c/p}$ (at low pH) ^b
15	Bz-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	4.1×10^{-4}	1.6×10^{16}	1.5×10^4	1.2×10^6
3	St-poly(DEA)- <i>b</i> -poly(Q ₉₅ DMA)	3.7×10^{-4}	3.3×10^{16}	6.9×10^3	5.9×10^5
10	St-poly(DEA)- <i>b</i> -poly(Q ₂₀ DMA)	4.8×10^{-4}	2.3×10^{16}	1.3×10^4	1.1×10^6

^a $N_{s/p}$ = number of copolymer chain per particle = $([\text{stabilizer}] \times 6.02 \times 10^{23})/N_p$. ^b $N_{c/p}$ = number of cationic charges per particle at low pH = $N_{s/p} \times \text{DP}$ with DP the degree of polymerization of the copolymer (at low pH, all the monomer units are positively charged).

**Figure 5.** XPS survey (A), nitrogen core-line (B) and high-resolution C1s region (C) spectra of the polystyrene latex particles stabilized by the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (expt 7, Table 1).

(Figure 5C). In conclusion, both XPS analyses and zeta potential measurements confirmed the presence of the cationic stabilizer at the surface of the polystyrene latex particles.

The polystyrene latexes prepared using the cationic St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer were stored at either pH 9 or pH 2 for six months at ambient temperature in order to assess possible aging effects. Regardless of the solution pH of the aged latex, the average particle diameter remained the same before and after aging over the stabilizer concentration range examined (from 1 to 10 wt %, Figure 6). Due to the broad particle size distribution of the latexes (see Figure 2), any pH-

**Figure 6.** Aging of latexes stabilized by the St-poly(DEA)-*b*-poly(Q₉₅DMA) reactive diblock copolymer (experiments 1–3 and 5–7 in Table 1). Effect of time and pH on the latex stability: (◇) pH 9, freshly prepared latex; (□) after six months storage at pH 9 (+) after six months storage at pH 2. The latex diameters were measured by DLS.

induced thickness variation of the poly(DEA) corona was not measurable. The excellent latex stability observed at low pH is consistent with strong anchoring of the cationic diblock macromonomer on the particle surface. Indeed, it has been shown previously that the cationic diblock copolymer becomes completely hydrophilic at pH 2 and loses its surface activity.³² On the other hand, poor colloidal stability was observed when the miniemulsion polymerization of styrene was carried out at pH 2 because the highly hydrophilic diblock copolymer was unable to stabilize the initial sonicated emulsion (Table 1, entry 4).

It has been shown by Vamvakaki and co-workers³² that lightly quaternized poly(DMA)-*b*-poly(DEA) diblock copolymers exhibit significantly lower surface tensions (37–38 mN m⁻¹) than highly (selectively) quaternized poly(DMA)-*b*-poly(DEA) diblock copolymers (56–58 mN m⁻¹) for 0.5% w/v aqueous solutions of the diblock copolymer at 20 °C. Consequently, the 20% quaternized St-poly(DEA)-*b*-poly(Q₂₀DMA) diblock macromonomer was tested as a reactive stabilizer for the miniemulsion polymerization of styrene. However, complete conversion was not attained after 8 h even when employing up to 8 wt % of the St-poly(DEA)-*b*-poly(Q₂₀DMA) diblock macromonomer (Figure 7). This slower polymerization rate was consistent with the higher final latex particle diameters observed when using the partially quaternized macromonomer (Table 1, expts 1–7 and 8–12). In summary, the lightly quaternized St-poly(DEA)-*b*-poly(Q₂₀DMA) diblock macromonomer exhibited significantly poorer stabilization performance than the fully quaternized diblock macromonomer for the miniemulsion polymerization of styrene. It appears that the adsorption behavior of these cationic diblock copolymers at the styrene–water interface cannot be directly related to their surface activities measured at the air–water interface. It seems likely that the copolymer containing less cationic charges might be more buried inside the particles.

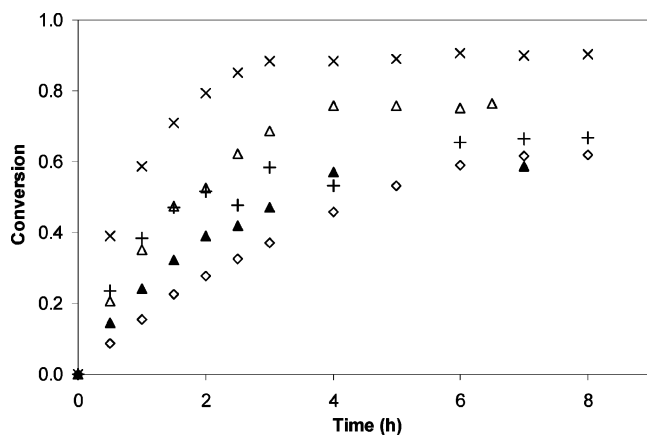


Figure 7. Miniemulsion polymerizations of styrene initiated by AIBN at 70 °C using the St-poly(DEA)-*b*-poly(Q₂₀DMA) copolymer, time-conversion plots: (x) 10 wt %, expt 12; (Δ) 8 wt %, expt 11; (+) 4 wt %, expt 10; (▲) 2 wt %, expt 9; (◇) 1 wt %, expt 8. See Table 1 for the experimental conditions.

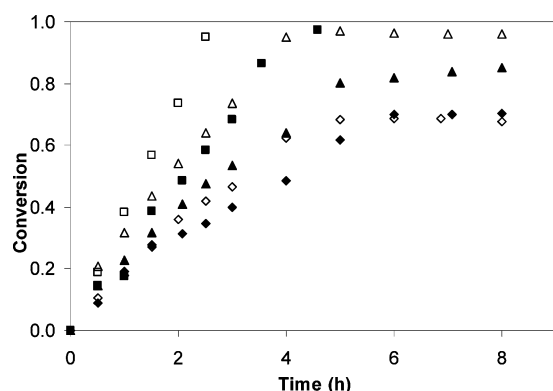


Figure 8. Conversion-time plots for the miniemulsion polymerization of styrene at 70 °C. Comparison between the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (filled symbols) and the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (open symbols) for varying amounts of stabilizer (wt. %/styrene). See Table 1 for experimental conditions. (◆) 1 wt % (expt 13); (▲) 2 wt % (expt 14); (■) 4 wt % (expt 15) (◇) 1 wt % (expt 1), (Δ) 2 wt % (expt 2), (□) 4 wt % (expt 3).

The preceding discussion and experimental data support the hypothesis that the two cationic diblock macromonomers are mainly located at the surface of the particle and are strongly anchored, as expected. However, there was no direct evidence of a covalent link between the copolymer and the particle. Thus, the results of the experiments carried out with the analogous Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer, containing a benzyl group rather than a copolymerizable styrenic group, will be compared to the ones presented in the first part of this paper. For the same degree of quaternization (95%), the kinetic plots exhibited a slightly faster polymerization when using the amphiphilic diblock macromonomer (Figure 8), but the latex particle diameters were in the same range (Table 1, expt 1–7 and 13–15). The final latex prepared using the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) remained stable after two months aging at low pH, despite copolymer desorption being expected due to the hydrophilic nature of the protonated DEA block. One possible explanation is that the DEA block could be buried inside the latex particle. The latexes prepared using 4 wt % of either the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer or the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer were purified by several centrifugation cycles keeping the overall pH below 5. The recovered latex particles were dried and analyzed by infrared spectroscopy. As shown in Figure 9,

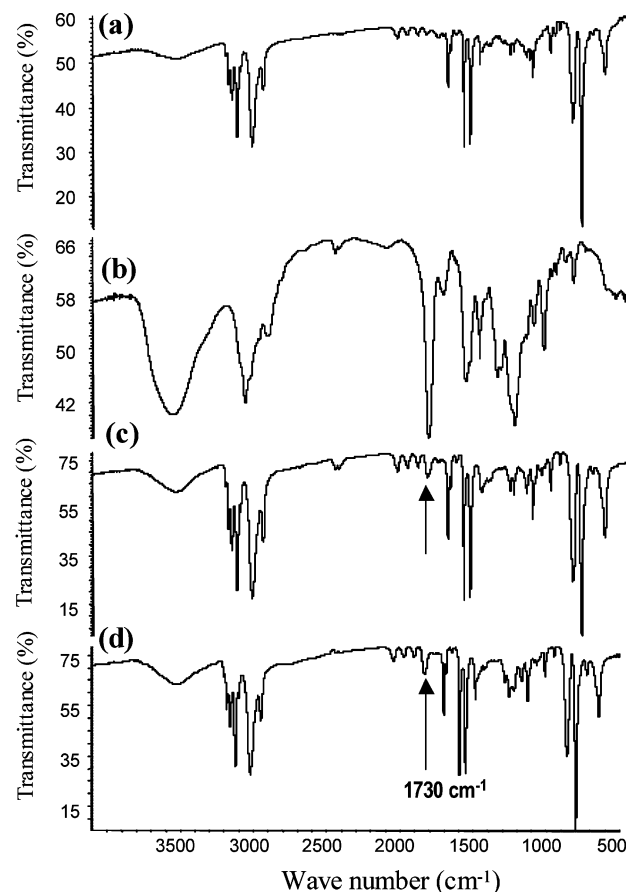


Figure 9. Infrared spectra of (a) polystyrene (b) St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (c) latex from expt 6 (Table 1) cleaned by 10 ultracentrifugation cycles at pH 5 (d) latex from expt 15 (Table 1) cleaned by 10 ultracentrifugation cycles at pH 5.

the characteristic carbonyl band of the copolymer at 1730 cm⁻¹ was observed in both cases. Obviously, the cationic copolymers are strongly anchored to the PS latex particles but it is difficult to distinguish between physical adsorption and chemical grafting. A final experiment consisted in purifying the latexes by numerous centrifugation cycles in the presence of a cationic surfactant [cetyltrimethylammonium chloride (CTACl)] to induce desorption of the polymeric stabilizer. After centrifugation of the latex with CTACl, the intensity of the 1730 cm⁻¹ band decreased by around 30% for the latex prepared with the St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (Figure 10A) and around 55% for the latex prepared with the Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (Figure 10B). This provides some evidence for stronger anchorage of the diblock macromonomer at the latex surface.

In view of the above observations, it seems likely that some degree of stabilizer grafting occurs under the free radical conditions employed in our miniemulsion polymerization syntheses, regardless of whether these chains contain polymerizable styrene end-groups. If one considers the possibility of chemical grafting of the stabilizer via transfer to polymer, the literature value for the chain transfer constant C_{tr} to triethylamine (a reasonable model compound for the DEA-based block of the stabilizer) during styrene polymerization at 60 °C suggests a relatively low extent of transfer of around 0.3 mol %.^{33,34} Thus, on average only 1 DEA unit in every 300 DEA units is likely to be involved in transfer to polymer. Nevertheless, given that the mean degree of polymerization of the DEA block

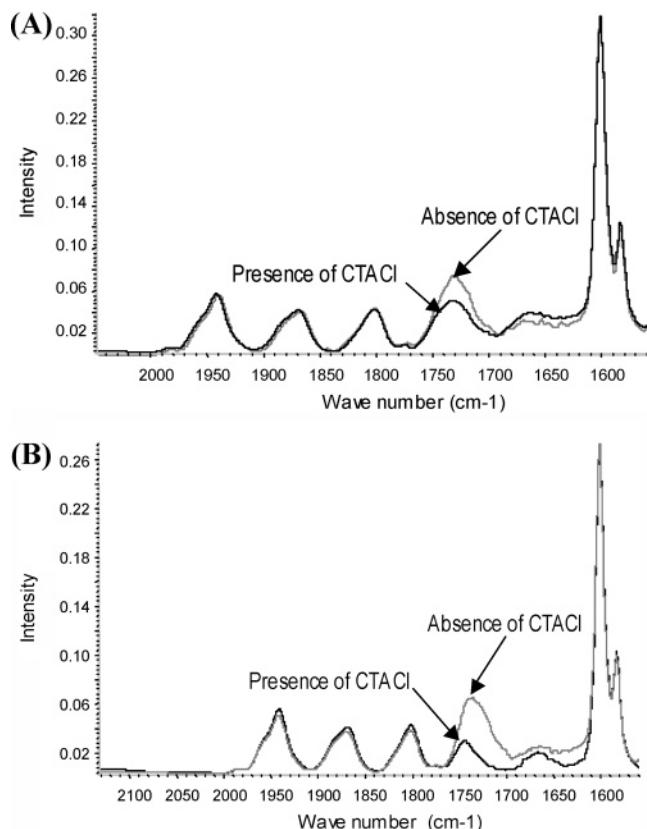


Figure 10. Comparison of the IR spectra for the latex purified by five centrifugation cycles either in the absence (grey line) or in the presence (black line) of cetyltrimethylammonium chloride. (A) 4 wt % of St-poly(DEA)-*b*-poly(Q₉₅DMA) diblock macromonomer (expt 3, Table 1) (B) 4 wt % of Bz-poly(DEA)-*b*-poly(Q₉₅DMA) diblock copolymer (expt 15, Table 1).

is approximately 33, this means that approximately 10% of the diblock copolymer chains become chemically grafted to the latex particles due to this side reaction. The benzyl ether group present in both the copolymer and the macromonomer could be an additional transfer site; hence, 2% of the macromolecular surfactant could be chemically grafted through this reaction.^{33,34} FTIR spectroscopy studies indicate a greater extent of desorption of the benzyl-terminated diblock copolymer from the latex particles compared to the diblock macromonomer.

(33) (a) Brandup, J.; Immergut, E. H. *Polymer Handbook*, 3rd ed.; John Wiley and Sons: New York, 1989. (b) Fontanille, M.; Gnanou, Y. *Chimie et Physico-chimie des Polymères*; Ed Dunod, 2002.

(34) For styrene polymerization carried out at 60 °C, the chain transfer constant to triethylamine or to benzyl ether molecules were respectively $C_{tr} = 7 \times 10^{-4}$ and $C_{tr} = 6.2 \times 10^{-3}$ (see refs 33 listed above). According to the equation $X = 1 - (1 - X_m)^{C_{tr}}$, the conversion (X) of the "triethylamine transfer agent" (tertiary amine functions) is only 0.3% for 98% monomer conversion (X_m) (one has to remind that each copolymer chain contains approximately 30 units). The conversion (X) of the "benzyl ether transfer agent" (chain end of the surfactant) is 2% for 98% monomer conversion (X_m).

Hence, the experimental data are consistent with both cationic stabilizers being covalently grafted via either transfer to polymer (diblock copolymer) or copolymerization (diblock macromonomer), in addition to some degree of physical adsorption via the hydrophobic DEA-based block.

Conclusions

A new styrene-functionalized diblock macromonomer based on poly(2-(dimethylamino)ethyl methacrylate) (PDMA) and poly(2-(diethylamino)ethyl methacrylate) (PDEA) has been synthesized via oxyanionic polymerization. The DMA residues can be selectively quaternized using methyl iodide, which provides a permanent cationic polyelectrolyte block. The PDEA block is known to be hydrophobic above pH 7 and hence the amphiphilic diblock macromonomer has been used successfully as a reactive stabilizer in the miniemulsion polymerization of styrene. A 95% quaternized diblock macromonomer exhibited better stabilization performance than the corresponding 20% quaternized diblock macromonomer. The recovered colloidal particles were stable over a wide pH range; the absence of any flocculation at low pH, where the protonated PDEA block is water-soluble, highlighted the strong adsorption of the macromonomer chains to the surface of the latex particles. XPS analyses confirmed that the highly quaternized diblock macromonomer was located at the latex particle surface. Perhaps surprisingly, the analogous benzyl-terminated cationic diblock copolymer also proved to be an effective stabilizer for the miniemulsion polymerization of styrene, despite having no polymerizable terminal styrene group. The latex particles stabilized by this latter cationic diblock copolymer exhibited unexpectedly good long-term stability at low pH, which probably indicates that some degree of chemical grafting also occurs with this stabilizer. In one pot synthesis, stable cationic functional latex containing tertiary amine groups at the surface is recovered, which offers future functionalization possibilities.

Acknowledgment. The CNRS and the UPMC are acknowledged for financial support. EPSRC is thanked for postdoctoral support for Y.T.L. (Platform Grant GR/S25845/01). We thank Arkema for funding a PhD for J.N. The authors gratefully acknowledge Dr. M. M. Chehimi from the University Paris 7, ITODYS laboratory for the XPS analyses.

Supporting Information Available: H NMR spectra of the two diblock copolymer precursors and the corresponding quaternized diblock macromonomers and the diblock copolymer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

LA050495B