

Environmentally Responsive Amphiphilic Cationic Block Copolymers Synthesized by 2,2,6,6-Tetramethylpiperidinyloxy Mediated Living Free-Radical Polymerization

Kuo-Chung Cheng,¹ Chen-How Lin,¹ Yuan-Hung Hsu,¹ Tsu-Hwang Chuang,¹ Wenjeng Guo,¹ Wen-Yen Chiu²

¹Department of Chemical Engineering and Biotechnology, National Taipei University of Technology, Taipei 106, Taiwan

²Department of Chemical Engineering, National Taiwan University, Taipei 106, Taiwan

Correspondence to: K.-C. Cheng (E-mail: gordon@ntut.edu.tw)

ABSTRACT: Polychloromethylstyrene (PCMS)-*block*-polystyrene (PS) copolymers were prepared by controlled free-radical polymerization in the presence of 2,2,6,6-tetramethylpiperidinoxy and 2,2'-azobisisobutyronitrile (AIBN) initiator. The PCMS-*b*-PS copolymers had narrow molecular weight distributions, and the block lengths were controlled by the reaction time and the molar ratios of chloromethylstyrene/AIBN and styrene/PCMS macroinitiator. The block copolymers were further quaternized with triethylamine. The amphiphilic cationic block copolymers formed colloidal particles; the effects of the pH value, salt concentration, and solvent polarity on the particle size were investigated with a dynamic light scattering analyzer. The average colloid size increased with increasing pH value and salt concentration. This implied that the colloid formed a protonated hydrophilic shell and hydrophobic styrene core in water. Furthermore, with the addition of tetrahydrofuran to the aqueous solution, the styrene segments in the core could be inverted to the outside of the colloid. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Many researchers have synthesized and characterized various amphiphilic block copolymers because these polymers can form micelles or colloids with unique morphologies that can be changed by temperature, ionic strength, and solvent polarity.^{1–3} Some of the amphiphilic copolymers have been reported to undergo reversible micellization behavior.^{4–7} For example, the diblock copolymer of poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly(methacrylic acid), which was synthesized with group transfer polymerization, exhibited temperature- and pH-responsive reversible aggregation.^{8,9} Therefore, many amphiphilic block and graft polymers are used as emulsifiers or stabilizers, and some of these polymers can be extended to biomedical applications.^{10–16}

In recent years, many researchers have developed well-defined block copolymers by stable free-radical polymerization (SFRP),^{17–21} which could replace the traditional living ionic and group transfer polymerization methods.^{22,23} In the case of nitroxide-mediated SFRP, the radicals formed during the initial step and the living polymer radicals can be capped with stable nitroxyl radicals, such as 2,2,6,6-tetramethylpiperidinoxy

(TEMPO), to form dormant chains. This procedure would retard termination by radical coupling. Because the dormant chains are thermally labile, they can be extended by further reactions with monomers. The SFRP method reveals the controlled character of living polymerization; there is rapidly growing interest in this technique for the preparation of polymers with narrow polydispersities and block copolymers.^{24–27}

A series of acidic and zwitterionic water-soluble diblock copolymers was synthesized directly with TEMPO-capped poly(sodium 4-styrenesulfonate) and a well-defined macroinitiator and extended with various styrenic monomers.²⁸ Polychloromethylstyrene (PCMS)-*block*-polystyrene (PS) copolymers were synthesized by TEMPO-mediated living free-radical polymerizations, where the PCMS macroinitiators provided good control of the polymerization, and the polymerization rate was fast in the presence of 2,2'-azobisisobutyronitrile (AIBN) initiator. Benzoic anhydride was added to accelerate the polymerization, but it broadened the molecular weight distribution. The PCMS-*b*-PS copolymers were further quaternized with tertiary amines, and the micellization of the amphiphilic block copolymers was investigated.^{29,30}

Table I. Growth of the Molecular Weights of the PCMS Polymers for Various Molar Ratios of TEMPO/AIBN

Sample	Time (h)	M_n	M_w	PDI	Conversion (%)
[TEMPO]/[AIBN] = 1.2 (mol/mol)					
A1	1	17,300	23,300	1.4	11
A2	1.5	27,100	38,700	1.4	26
A3	2	31,600	46,100	1.5	34
A4	2.5	35,000	51,200	1.5	41
A5	3	36,000	54,600	1.5	44
[TEMPO]/[AIBN] = 1.5 (mol/mol)					
B1	1.5	21,700	28,300	1.3	20
B2	2	32,400	43,600	1.3	30
B3	2.5	36,800	50,800	1.4	38
B4	3	37,700	53,700	1.4	39
B5	3.5	39,400	55,600	1.4	40
[TEMPO]/[AIBN] = 2 (mol/mol)					
C1	2	12,300	17,400	1.4	11
C2	2.5	20,500	28,500	1.4	22
C3	3	22,400	31,500	1.4	24
C4	3.5	23,100	33,400	1.4	27
C5	4	25,500	35,700	1.4	30
C6	4.5	27,100	36,500	1.4	31

M_w , weight-average molecular weight. [CMS] = 7.43 mol/L, [AIBN] = 0.015 mol/L, [CMS]/[AIBN] = 495.

To our knowledge, the effects of the ionic strength and solvent polarity on the morphology of the amphiphilic block copolymers formed by quaternized PCMS-*b*-PS copolymers have not been discussed. In this study, PCMS macroinitiators were synthesized by SFRP in the presence of TEMPO and AIBN initiator; then, the TEMPO-capped PCMS macroinitiators were extended by polymerization with styrene monomers to produce PCMS-*b*-PS block copolymers. Block copolymers with different lengths of PS segments were further modified with triethylamine. The amphiphilic block copolymers formed colloids; the dependence of the particle size on the pH value, salt concentration, and solvent polarity was investigated with a dynamic light scattering (DLS) analyzer.

EXPERIMENTAL

Synthesis of the PCMS Macroinitiators

Chloromethylstyrene (CMS) monomers (meta/para = 60 : 40, Acros, New Jersey, USA), TEMPO (Acros), and AIBN (Showa, Tokyo, Japan) were mixed at room temperature; then, polymerization was carried out under a nitrogen purge at 125°C. Samples were collected at intervals, dissolved in tetrahydrofuran (THF), precipitated in methanol, filtered, washed with methanol, and dried in a vacuum oven at 50°C. The CMS monomers were purified by vacuum distillation before polymerization, and the other materials were used without further purification.

Synthesis of the PCMS-*block*-PS Copolymers

The TEMPO-capped PCMS macroinitiators (prepared previously) were added to styrene monomers and heated to 125°C for further polymerization. The products were purified (as done previously) for further characterization.

Quaternization of the PCMS-*b*-PS Block Copolymers

The PCMS-*b*-PS block copolymers were quaternized by triethylamine in THF (Tedia, Charlotte, NC, USA) for 24 h at 50°C.

Characterizations of the Block Copolymers

The polymer molecular weights were determined with a gel permeation chromatograph coupled with two columns (Waters 510 high-performance liquid chromatography pump/410 RI Waters 103, PLgel mixed-C and PLgel 100 Å, Milford MA, USA). THF was the carrier solvent. The columns were calibrated with PS standards. ¹H-NMR spectra were obtained on a Bruker AVA300 spectrometer (Billerica, MA, USA) in CDCl₃. Fourier transform infrared (FTIR) spectra were recorded on a PerkinElmer 2000 spectrometer (Waltham, MA, USA). Thermogravimetric analysis (TGA) was performed on a TA-951 analyzer (Castle, DE, USA) under a nitrogen purge at a heating rate of 10°C/min. The diameters of the colloid particles formed by the amphiphilic block copolymers in various solutions were measured with a DLS analyzer (Brookhaven Zeta Plus, wavelength = 658 nm, 90°, Holtsville, NY, USA).

RESULTS AND DISCUSSION

Molecular Weights of the PCMS Macroinitiators and PCMS-*b*-PS Copolymers

Table I shows the changes in the average molecular weight and polydispersity index (PDI) of the PCMS as determined by gel permeation chromatography during the TEMPO-mediated free-radical polymerization. With a TEMPO/AIBN molar ratio of 1.2, the number-average molecular weight (M_n) of PCMS reached 36,000 with a PDI of 1.5 after polymerization for 3 h, whereas at a TEMPO/AIBN molar ratio of 2, M_n was only

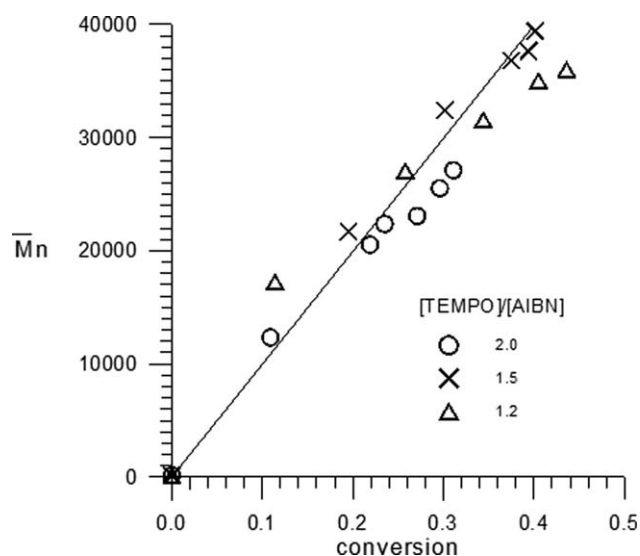


Figure 1. M_n of PCMS versus the conversion for various TEMPO/AIBN molar ratios.

27,100 with a PDI of 1.4 after 4.5 h. Increasing the TEMPO concentration increased the rate of capping in the living chains to form dormant chains and, therefore, decreased the rate of chain propagation. The increase in the polymer size with monomer conversion was almost linear (Figure 1), and the PDI of the polymers was approximately 1.4; this revealed the controlled character of the living polymerization. However, we believe that the benzylic site in the CMS monomer was prone to undergoing transfer reactions, and the side reactions increased the PDI for PCMS in comparison with PS via the TEMPO-mediated SFRP.^{30–33}

The effect of the CMS/AIBN molar ratio on the growth of the polymer size is shown in Tables I and II. The increase in M_n of PCMS with the conversion of monomer is plotted in Figure 2. The molecular weight increased rapidly for PCMS synthesized at the higher ratio of monomer to initiator than at the lower ratio. For example, M_n was 27,100 at 26% conversion when the

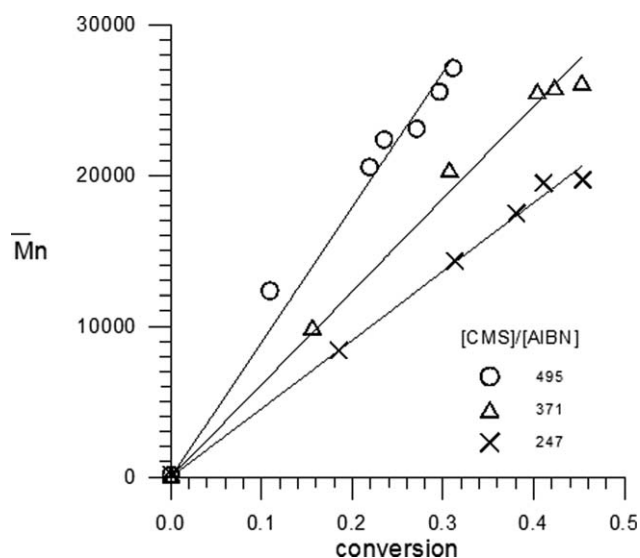


Figure 2. M_n of PCMS versus the conversion for various CMS monomer/AIBN molar ratios.

initial ratio of CMS to AIBN was 495, whereas M_n was only 14,300 at 31% conversion when $[CMS]/[AIBN] = 247$. According to the previous results, we could synthesize PCMS with a desired molecular size by controlling either the conversion or the $[CMS]/[AIBN]$ ratio.

The PCMS synthesized via the TEMPO-mediated living free-radical polymerization was believed to be a TEMPO-capped macroinitiator that could be further extended by the addition of styrene monomers. Table III shows the increase in the molecular weight of the PCMS-*b*-PS copolymers that were obtained with different sizes of macroinitiators and various ratios of styrene to PCMS. The increase in M_n of the copolymers with the conversion of styrene monomers was almost linear, as shown in Figure 3, and the PDI value of the PCMS-*b*-PS block copolymers was approximately 1.6–1.7. The increase in the molecular weight of the copolymers depended on the initial ratio of styrene to PCMS. Therefore, the block chain length of the styrene segment

Table II. Growth of the Molecular Weights of the PCMS Polymers for Various Molar Ratios of CMS/AIBN

Sample	Time (h)	M_n	M_w	PDI	Conversion (%)
$[CMS]/[AIBN] = 371$ (mol/mol)					
D1	2.5	10,000	14,700	1.3	16
D2	3	20,400	28,200	1.3	31
D3	3.5	25,600	36,000	1.4	40
D4	4	25,900	38,700	1.4	42
D5	4.5	26,200	41,200	1.4	45
$[CMS]/[AIBN] = 247$ (mol/mol)					
E1	3	8,400	12,400	1.4	19
E2	3.5	14,300	21,200	1.4	31
E3	4	17,500	25,700	1.4	38
E4	4.5	19,500	28,200	1.5	41
E5	5	19,700	29,800	1.5	45

M_w , weight-average molecular weight. CMS = 7.43M, $[TEMPO]/[AIBN] = 2$.

Table III. Growth of the Molecular Weights of the PCMS-*b*-PS Copolymers

Sample	Time (h)	M_n	M_w	PDI	Conversion of styrene monomers (%)
[St]/[PCMS] = 20 (mol/mol)					
PCMS(6500)	0	6,500	9,800	1.4	0
F1	1	11,100	17,600	1.6	9
F2	2	20,700	33,300	1.6	24
F3	3	26,200	43,200	1.7	33
[St]/[PCMS] = 30 (mol/mol)					
PCMS(6500)	0	6,500	9,800	1.4	0
G1	1	21,600	37,200	1.6	16
G2	2	30,600	48,600	1.6	33
G3	3	37,100	56,500	1.6	45
[St]/[PCMS] = 20 (mol/mol)					
PCMS(9300)	0	9,300	14,400	1.4	0
H1	1	15,100	25,800	1.7	8
H2	2	26,200	44,800	1.7	22
H3	3	34,600	59,900	1.7	43
[St]/[PCMS] = 30 (mol/mol)					
PCMS(9300)	0	9,300	14,400	1.4	0
I1	1	25,200	40,200	1.7	11
I2	2	36,300	62,500	1.7	24
I3	3	43,500	75,200	1.7	45

M_w , weight-average molecular weight; St, styrene.

in the PCMS-*b*-PS copolymer depended on either the reaction time or the molar ratio of styrene to PCMS.

Characterizations of the Quaternized PCMS-*b*-PS Copolymer

It has been reported that CMS is one of the most important functional monomers because the nucleophilic substitutions on

benzylic chlorine are indeed feasible.^{30,34} Therefore, the PCMS-*b*-PS block copolymer prepared via TEMPO-mediated living free-radical polymerization is a good candidate for a versatile route toward the synthesis of polymeric surfactants. In this

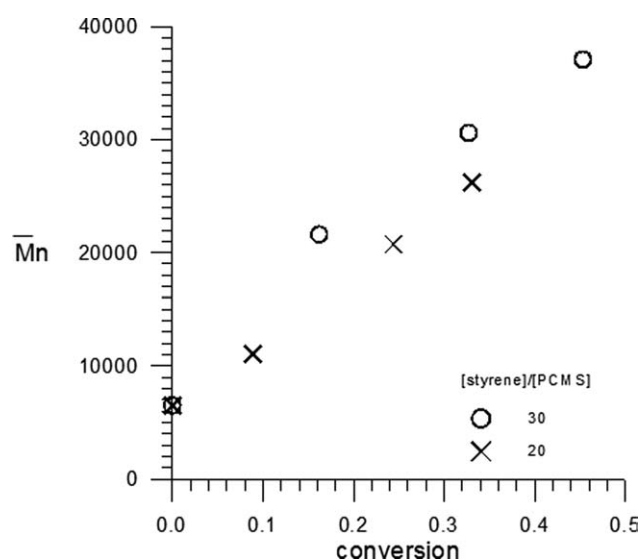


Figure 3. M_n of PCMS versus the conversion for various styrene/PCMS molar ratios.

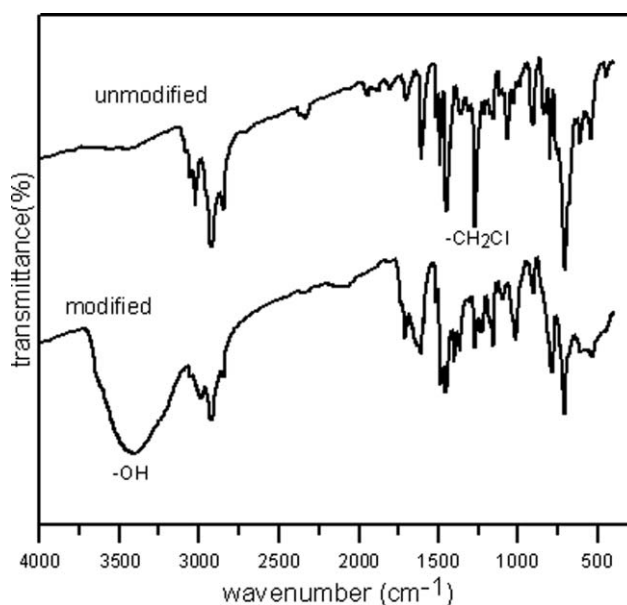


Figure 4. FTIR spectra of the unmodified and modified PCMS-*b*-PS copolymers (CMS/styrene unit ratio = 43/44).

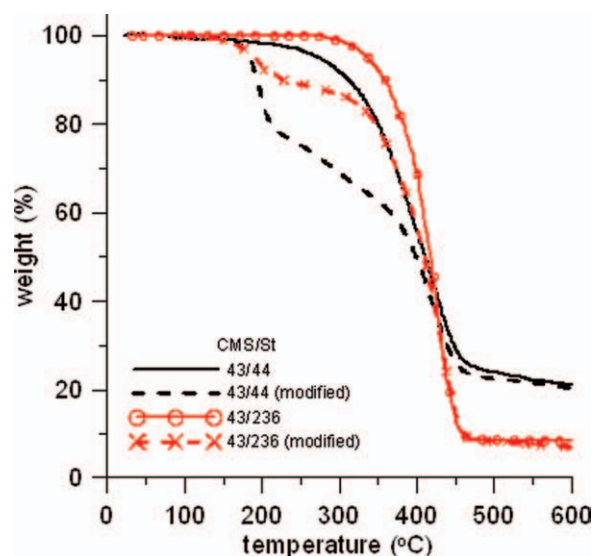


Figure 5. TGA thermograms of the unmodified and modified PCMS-*b*-PS copolymers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

study, block copolymers of PCMS-*b*-PS block with various lengths of PS chains were further modified with triethylamine in THF. Then, amphiphilic block copolymers with cationic segments, vinylbenzyltriethylammonium chloride, were expected to be formed.

The $\delta = 3.0\text{--}3.7$ ppm peak on the $^1\text{H-NMR}$ spectrum confirmed the $-\text{N}-(\text{C}_2\text{H}_5)_3$ structure after modification. The chemical structures of the synthesized block copolymers copolymers and the quaternized copolymer were further characterized by FTIR spectroscopy, and the spectra are shown in Figure 4. The band at about 1266 cm^{-1} was caused by C-H bending vibrations in $-\text{CH}_2\text{Cl}$, in which the IR absorption decreased after quaternization. In the meantime, the absorption peak around 3400 cm^{-1} in the IR spectra of the modified copolymer was due to the intensity of the O-H bond; we believe this resulted from the water absorbed by the quaternary ammonium group.^{35,36}

The results of TGA of the PCMS-*b*-PS are shown in Figure 5 and Table IV. The temperatures at a weight loss of 5% were from 273 to 337°C; this temperature increased with decreasing ratio of CMS units in the copolymers. We believe that dehydro-

chlorination caused the weight loss at the lower temperature. Meanwhile, the dehydrochlorination could have also resulted in crosslinking under further heating; thus, a higher residue was observed for the copolymers with a higher ratio of CMS units.³⁷ There were two steps of degradation found in the TGA curves of the modified copolymers. The first transition region, lower than about 220°C, might have been caused by the removal of modified groups. Therefore, the quaternization ratio of the block copolymer could be estimated by the weight loss in the first degradation stage, and the results are listed in Table IV.

Effect of pH on the Particle Size of the Amphiphilic Block Copolymers

It is well known that the morphology of block copolymer aggregates is not only dependent on the polymer chemical structures but also on the solution conditions.³⁸ In this study, the size of the colloids formed by the amphiphilic block copolymers in various solvents was further determined with the DLS analyzer. As shown in Figure 6, a bimodal distribution of the colloid size was observed in aqueous solution. At pH 2, the average diameter of the majority of the colloidal particles was approximately 94 nm, and the larger colloids were approximately 169 nm. At low pH, colloids with a protonated vinylbenzyltriethylammonium chloride coronal shell and hydrophobic styrene core were formed. As the pH increased, the cationic segments were progressively neutralized, and the colloid particles aggregated to form larger particles. The average diameter of colloids increased with the pH, as shown in Figure 7. Copolymers with longer styrene segments formed larger colloids than copolymers with shorter styrene segments at the same pH; this implied that longer hydrophobic chains in the block copolymers may have formed larger cores in the colloid particles.

Effect of the Salt Concentration on the Particle Size of the Amphiphilic Block Copolymers

The effects of the concentration of salt (NaCl) on the size of the colloids formed by the modified PCMS-*b*-PS block copolymers in water are plotted in Figures 8 and 9. The multiple distribution of the colloid size was observed by DLS. At low salt concentrations, such as 0.025 mol/L, the diameter of the majority of the colloid particles was approximately 122 nm, and the diameter was approximately 220 nm for the minority of the particles. The addition of salts to the solution resulted in the shielding of charges along the protonated vinylbenzyltriethylammonium chloride chains. One consequence of the salts was the reduction

Table IV. Thermal Stabilities of the Block Copolymers and Quaternization Ratios Estimated by the TGA Curves

	CMS/styrene	Temperature at 5% weight loss (°C)	T_{max} (°C)	Residue at 550°C (%)	Quaternization (%)
Unmodified	43/44	273.0	424.0	22.2	—
	43/139	316.1	427.0	16.1	—
	43/236	337.0	425.9	8.4	—
Modified	43/44	184.0	197.4, ^a 420.6	21.6	65
	43/139	188.6	200.5, ^a 414.3	14.0	77
	43/236	191.0	200.7, ^a 431.1	7.7	69

T_{max} , temperature at the maximum decomposition rate.

^aDenotes the first stage.

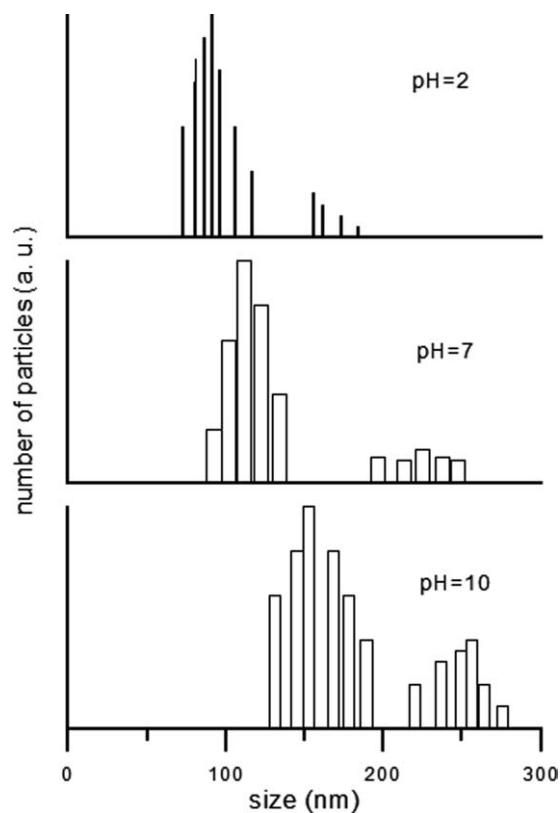


Figure 6. Colloid size distribution of the modified PCMS-*b*-PS at various pH values (CMS/styrene unit ratio = 43/44).

of electrostatic repulsions and the aggregation of the smaller colloids to form a larger particle. Therefore, the average diameter and the number ratio of larger colloids increased with the salt concentration. At $[\text{NaCl}] = 0.1 \text{ mol/L}$, large colloids with diameters of up to 420 nm appeared, as shown in Figure 8. The solution became turbid, and precipitation occurred. The average size

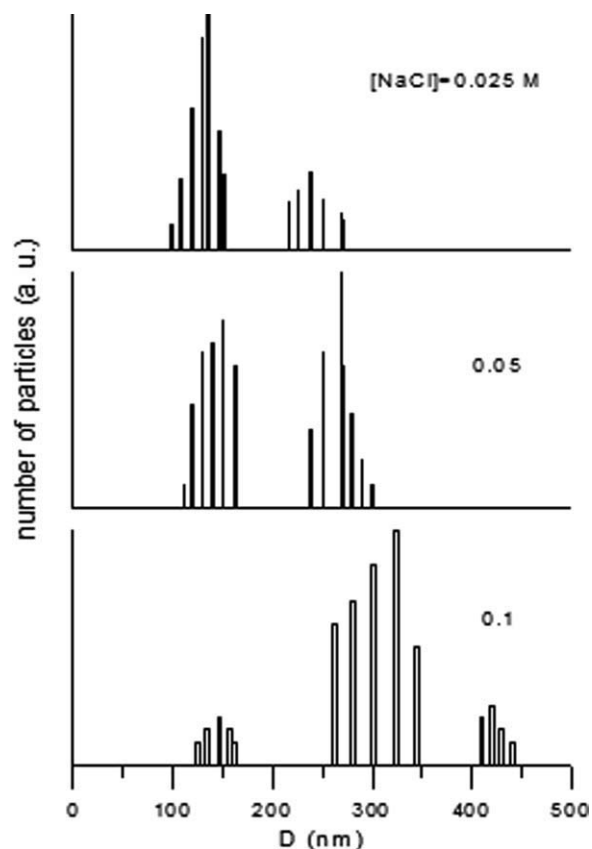


Figure 8. Colloid size distribution of the modified PCMS-*b*-PS at various concentrations of NaCl (CMS/styrene unit ratio = 43 : 44).

of the colloids formed by the block copolymers with different lengths of styrene segments increased with the concentration of NaCl, as shown in Figure 9. At the same salt concentration, the size of the colloid formed by the block copolymers with longer styrene segments was larger than the particles formed from copolymers with shorter segments.

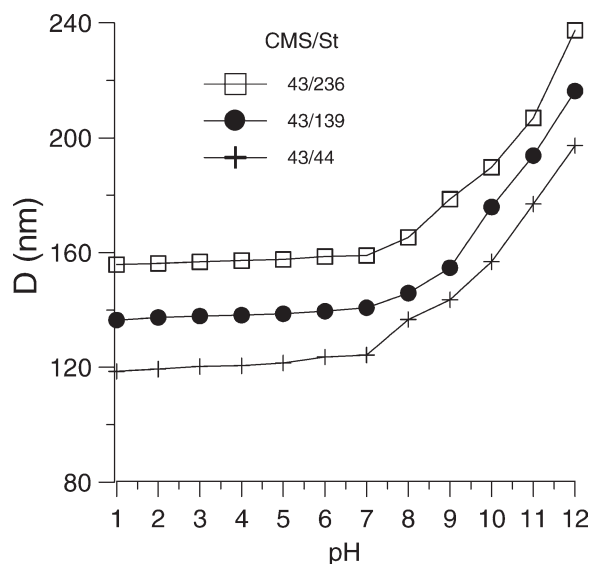


Figure 7. Average diameter (D) of the colloid of the modified PCMS-*b*-PS at various pH values.

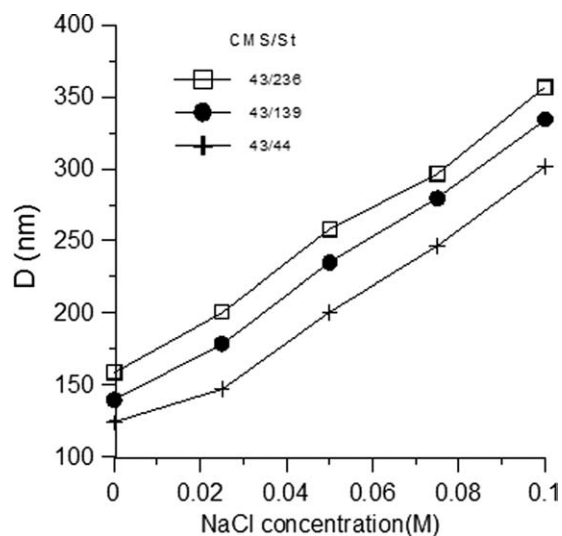


Figure 9. Average diameter of the colloid particles of the modified PCMS-*b*-PS at various NaCl concentrations.

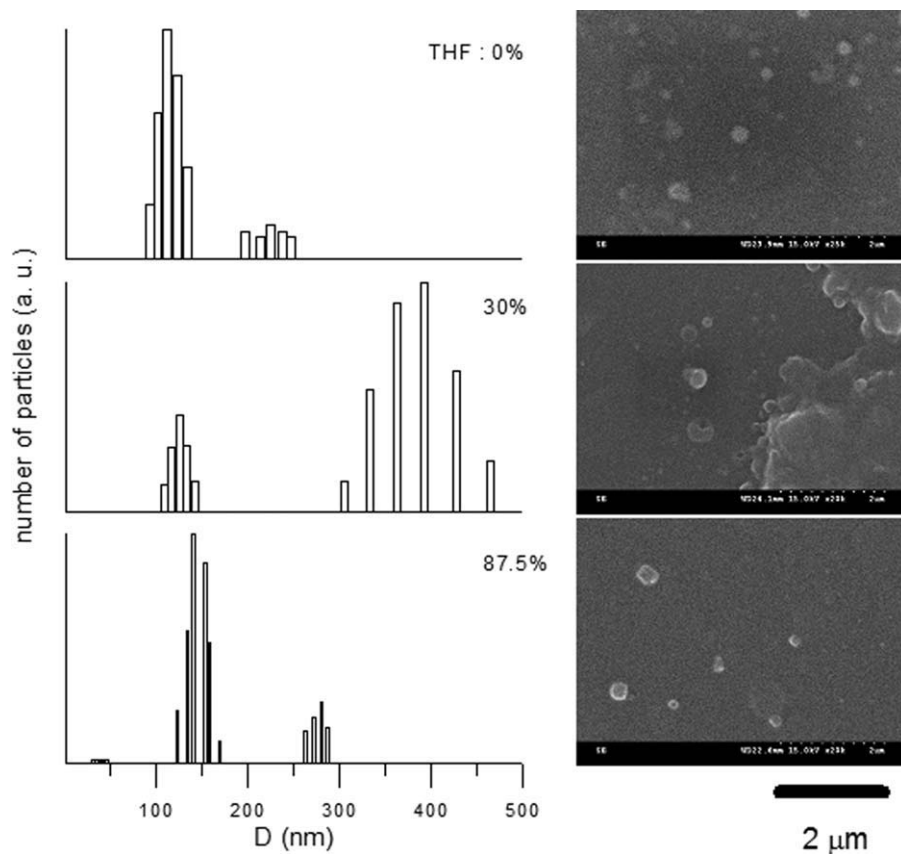


Figure 10. Colloid size distributions and SEM photographs of the modified PCMS-*b*-PS when various levels of THF were added to aqueous solutions (CMS/styrene unit ratio = 43 : 44).

Effect of the Solvent Polarity on the Particle Size of the Amphiphilic Block Copolymers

The effects of the solvent polarity on the colloid size are plotted in Figures 10 and 11. First, the colloid particles formed by the amphiphilic block copolymers were dispersed in water; the ma-

jority of the hydrophilic chains would be on the outside of the colloids. Bimodal distributions were observed, where the majority of colloids were approximately 122 nm, and the minority of the particles were approximately 215 nm. After THF was added to the aqueous solution, the colloidal particles grew with the

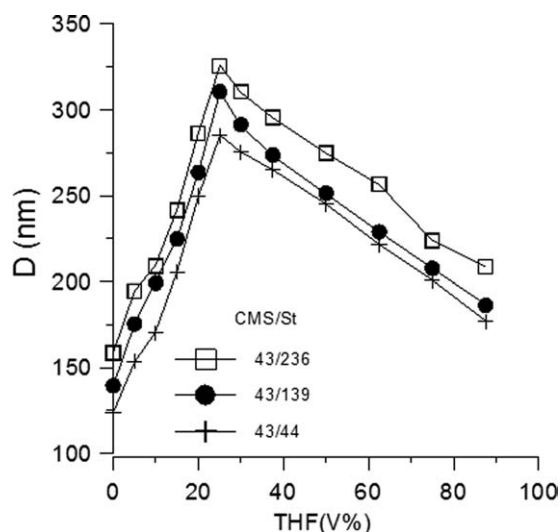


Figure 11. Average diameter of the colloid of the modified PCMS-*b*-PS versus the concentration of THF in aqueous solutions.

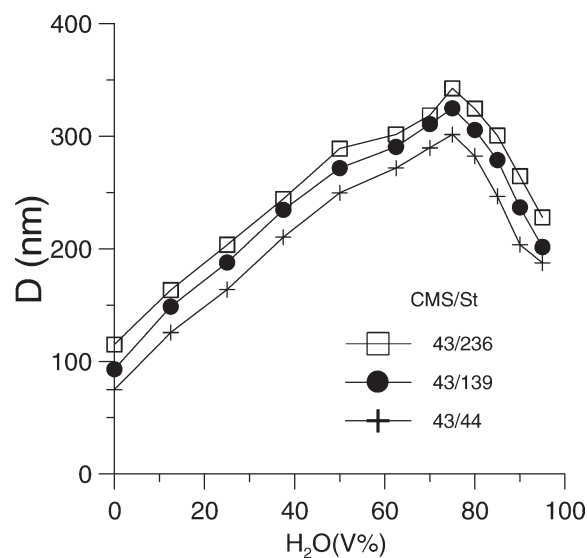


Figure 12. Average diameter of the colloid of the modified PCMS-*b*-PS versus the concentration of water added to THF solutions.

amount of THF. These results imply that the aggregation occurred when the outside hydrophilic segments were not well-dissolved in the water/THF mixture, and the hydrophobic PS core of the colloid was swollen by THF. The colloid size reached its maximum at approximately 25 vol % THF. At 30% THF, the colloid diameters were as large as 300–500 nm, and the solution became cloudy, as shown in Figure 10. Next, the average particle size decreased gradually with the addition of THF, and the solution turned clear again. This implied that the styrene segments may have been inverted to the outside of the colloid at higher concentrations of THF.

To further investigate the phenomena observed by DLS, drops of the various solutions (discussed previously) were placed on glass slides and evaporated quickly in a vacuum freeze drier. Although the morphologies of the dried samples differed from those of the colloids in solution, aggregation appeared to occur at approximately 30% THF (SEM photos, Figure 10). This was consistent with the results obtained by DLS.

Similar phenomena were also observed by the contrasting process of adding water to THF solutions (Figure 12). In the THF solvent, inverse micelles may have formed, where the hydrophobic chains of the block copolymers were on the outside of the colloids and the hydrophilic segments of the copolymers were in the cores. When the hydrophobic segments were not well-dissolved in the THF/water mixture, the small colloids aggregated to form larger ones. The average colloid diameter reached a maximum in a solution with approximately 75% water and decreased with further addition of water. This implied that the hydrophilic modified PCMS chains on the block copolymers might have been inverted to the outside of the colloid (Figures 11 and 12).

CONCLUSIONS

PCMS-*b*-PS block copolymers with narrow molecular weight distribution indices were synthesized via TEMPO-mediated living free-radical polymerization. The block lengths of the CMS and styrene segments in the PCMS-*b*-PS copolymer could be controlled by the conversion of the monomers and the molar ratios of CMS to AIBN and styrene to PCMS macroinitiator. The PCMS-*b*-PS block copolymers could be further modified with triethylamine to form amphiphilic cationic block copolymers.

The response of the amphiphilic block copolymers to the pH, ionic strength, and solvent polarity were observed. The diameters of the majority of the colloids formed by the amphiphilic block copolymers in the water were approximately 122 nm. Because the outside hydrophilic segments could not be well-dissolved in water with the addition of THF, aggregation occurred, and the solution became cloudy. However, at higher concentrations of THF, the colloid size decreased again, and the solution became clear; this implied that the styrene segments could be inverted to the outside of the colloid at higher ratios of THF. Similar phenomena were also observed in the contrasting process where water was added to THF. Therefore, the amphiphilic block copolymers prepared in this study could be useful for smart materials.

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