Poly(solketal methacrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(allyl methacrylate): Synthesis and Micelle Formation

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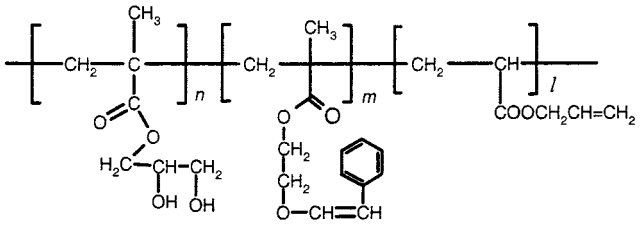
Received September 19, 2000; Revised Manuscript Received December 6, 2000

ABSTRACT: A triblock copolymer, poly(solketal methacrylate)-*block*-poly(2-trimethylsiloxylethyl methacrylate)-*block*-poly(allyl methacrylate) or PSMA-*b*-P(HEMA-TMS)-*b*-PAMA, was synthesized by anionic polymerization. The TMS groups were removed from the P(HEMA-TMS) block by hydrolysis in methanol to yield poly(2-hydroxylethyl methacrylate) or PHEMA. Reacting PSMA-*b*-PHEMA-*b*-PAMA with cinnamoyl chloride yielded PSMA-*b*-PCEMA-*b*-PAMA, where PCEMA denotes poly(2-cinnamoyloxyethyl methacrylate). The PSMA-*b*-PCEMA-*b*-PAMA triblock was characterized by gel permeation chromatography, NMR, and light scattering and possessed the weight-average repeat units of 300 for SMA, 190 for CEMA, and 180 for AMA. The triblock was further derivatized by hydrolyzing the acetonide groups of the PSMA block to yield PGMA-*b*-PCEMA-*b*-PAMA, where PGMA denotes poly(glyceryl methacrylate). PGMA-*b*-PCEMA-*b*-PAMA formed spherical micelles in methanol with 5%, by volume, of THF and branched cylindrical micelles in pure methanol. The micelles formed had the soluble PGMA block as the coronas and the insoluble PCEMA and PAMA blocks as the shells and cores, respectively. In toluene containing 2% methanol, only the PGMA block was insoluble. PGMA-*b*-PCEMA-*b*-PAMA formed spherical micelles, consisting of PAMA coronas, PCEMA shells, and PGMA cores. Electron microscopy and NMR studies were performed to elucidate the structure of the micelles.

I. Introduction

Diblock copolymers with cross-linkable and/or degradable blocks have been used in the preparation of stable functional polymer nanostructures of various shapes. These include nanofibers,[1,2] nanotubes,[3] thin films with nanochannels,[4,5] cross-linked polymer brushes (monolayers),[6] star polymers,[7] nanospheres,[8−11] hollow nanospheres,[12,13] nanospheres with cross-linked shells,[14−16] and shaved nanospheres.[17] More sophisticated nanostructures can be obtained from ABC triblock copolymers, where A, B, and C denote different monomers. This is partially due to the many more morphologies a triblock may have than a diblock in solution or in bulk.[18] Then, further functionality can be introduced to the nanostructures via the additional third block. In this paper, we report the synthesis of a triblock copolymer, poly(solketal methacrylate)-*block*-poly(2-trimethylsiloxylethyl methacrylate)-*block*-poly(allyl methacrylate) or PS-*b*-P(HEMA-TMS)-*b*-PAMA by anionic polymerization and the derivatization of it to poly(glyceryl methacrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(allyl methacrylate) or PGMA-*b*-PCEMA-*b*-PAMA.



PGMA-*b*-PCEMA-*b*-PAMA

The latter triblock was targeted, because of its functionalities. The PCEMA block could, for example, be cross-linked photochemically, the water-soluble PGMA block could be cross-linked chemically by species such as glutaraldehyde,[19] and the allyl groups could be removed by hydrolysis,[20] partially degraded by ozonolysis,[3,17] or made water-soluble by adding hydroxyl groups across the double bonds.[21] Also reported in this paper is the formation of three types of micelles from the triblock PGMA-*b*-PCEMA-*b*-PAMA with $n = 300$, $m = 190$, and $l = 180$.

Although there have been relatively many studies of ABC triblock copolymer morphologies in the solid state,[18] the study of their morphologies in block-selective solvents has been rare.[22−24] There have been even fewer reports on the preparation of triblocks with easily cross-linkable and degradable blocks. Prior to this, we reported the preparation of PI-*b*-PCEMA-*b*-P*t*BA and their use in the preparation of nanotubes,[3] hollow nanospheres,[12c] and thin films with nanochannels.[4d] Hollow nanospheres derived from the triblock were also used as templates for magnetic[25] or metal[26] nanoparticle synthesis. Bütün et al.[15b] reported the preparation of nanospheres from cross-linking a triblock containing a 2-dimethylaminoethyl methacrylate block.

II. Experimental Section

Materials and Reagents. Tetrahydrofuran (THF) was dried from refluxing with potassium and benzophenone under an argon atmosphere. Allyl methacrylate (AMA, Aldrich) and 2-(trimethylsiloxyl)ethyl methacrylate (HEMA-TMS, Aldrich) were each stirred with CaH_2 for 40 h before their distillation under vacuum. They were distilled again in the presence of triethylaluminum (TEA) immediately before polymerization. Monomer solketal methacrylate (SMA) was prepared from isopropylidene glycerol (also named solketal) and methacryloyl chloride following a literature method.[27] The product was purified by distillation under reduced pressure and its structure was confirmed by ^{1}H NMR analysis in $CDCl_3$: δ 6.10 (s,

10.1021/ma0016230 CCC: $20.00
Published on Web 01/23/2001

1H, HC═C, trans), 5.59 (s, 1H, HC═C, cis), 3.7−4.5 (m, 5H, CH_2CHCH_2), 1.94 (s, 3H, $═CCH_3$), 1.43, 1.38 (two s, 6H, $C(CH_3)_2$). Immediately before polymerization, SMA was redistilled in the presence of triethylaluminum. All other regents were used as received from Aldrich.

Polymer Synthesis. PSMA-*b*-P(HEMA-TMS)-*b*-PAMA was prepared by sequential living anionic polymerization in THF at −78 °C using the standard vacuum line technique. 1,1-Diphenyl-3-methylpentyllithium was used as the initiator and lithium chloride was used to decrease the polydispersity of the resultant polymers.[28] SMA, HEMA-TMS, and AMA were each polymerized for 3 h. The polymerization was terminated by the addition of several drops of methanol. Stirring the triblock in THF/methanol (v/v = 75/25) overnight hydrolyzed the TMS groups to yield PS-*b*-PHEMA-*b*-PAMA. The polymer solution was then concentrated under reduced pressure and the copolymer was precipitated in hexane.

The PHEMA block of the copolymer was converted to PCEMA by reacting with 1.5 molar equivalences of cinnamoyl chloride in dry pyridine at room temperature overnight. The polymer solution was filtered to remove pyridinium salt and added to excess methanol/ice mixture to precipitate out PSMA-*b*-PCEMA-*b*-PAMA. The polymer powder was dried at room temperature under vacuum.

PGMA-*b*-PCEMA-*b*-PAMA was produced after hydrolyzing PSMA-*b*-PCEMA-*b*-PAMA in THF containing 6 M aqueous HCl solution. A detail procedure is as follows. PSMA-*b*-PCEMA-*b*-PAMA, 3 g, was dissolved in 20 mL of THF. After 5 mL of methanol was added to the above stirring mixture, 3 mL of 6 M HCl was added dropwise. As hydrolysis proceeded, more methanol, 15 mL, was added gradually so that a micelle solution was maintained throughout the process. After 3 h, the mixture was concentrated under reduced pressure to 10 mL and then added to ethyl ether to precipitate out PGMA-*b*-PCEMA-*b*-PAMA. The polymer powder was dried at room temperature under vacuum.

Polymer Characterization. GPC analysis of PSMA-*b*-PCEMA-*b*-PAMA was done with THF as the eluant. The Waters HT-4 column used was calibrated using poly(methyl methacrylate) standards. The SMA to CEMA and to AMA ratios in PSMA-*b*-PCEMA-*b*-PAMA, *n*/*m*/*l*, were determined using ^{1}H NMR. The difference, Δn_r, between the refractive index of a polymer solution and that of chloroform, the solvent, was determined uisng a differential refractometer (Precision Instruments Co.). The absolute weight-average molar masses were measured in chloroform using a light scattering instrument (Brookhaven model 9025) equipped with a 632-nm He−Ne laser.

Micelle Preparation. To prepare cylindrical micelles with PGMA coronas, PCEMA middle layers, and PAMA cores, the triblock, 0.10 g, was stirred with 100 mL of methanol for 3 days for triblock dispersion. To prepare spherical micelles in methanol/THF, the triblock, 0.10 g, was dissolved in a 10-mL mixture of THF/methanol (1/1). Methanol, 90 mL, was then added under stirring to the above mixture. To prepare spherical micelles in toluene/methanol, 0.10 g of the triblock was dispersed in 10 mL of toluene/methanol containing 20% methanol. To the dispersion was then added 90 mL of toluene.

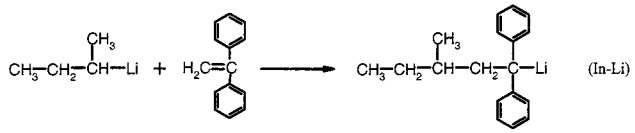
Micelle Cross-linking. The triblock micellar solutions were irradiated at 22 °C under vigorous stirring with UV light passed through a 260-nm cutoff filter from a 500-W mercury lamp. Samples (1.00 mL each) were taken at different irradiation times. Of the 2.00 mL, 0.2 mL was diluted with methanol and used for absorbance analysis at 274 nm to determine the conversion of the aliphatic double bonds of CEMA. Cross-linked micellar samples with either PGMA or PAMA coronas were purified by precipitation in diethyl ether.

Transmission Electron Microscopy. TEM images were obtained using a Hitachi H-7000 instrument operated at 75 kV. TEM samples were obtained by aspirating a fine mist of a dilute solution (∼0.1 mg/mL) of the polymer nanospheres onto a carbon-coated copper grid using a home-built device.[29] The samples were then placed in a vial containing osmium tetraoxide (Aldrich) vapor for 4 h to stain the double bonds.

Dynamic Light Scattering (DLS) Measurements. Dynamic light scattering (DLS) measurements were performed with a Brookhaven model 9025 instrument equipped with a 15-mW He−Ne laser at the scattering angle of 90°. The micellar solutions, at ≈1 mg/mL, were clarified by passing them through 0.45-μm filters before light scattering measurements. The filters retained cross-linked micelles easily. For this, light scattering was performed without filtering the samples. The samples were, however, filtered before they were cross-linked by photolysis. DLS data were analyzed following the method of cumulants.[30] The polydispersity in the diffusion coefficient distribution of the micelles was obtained from K_2/K_1^2, where K_1 and K_2 were the first and second moments of the correlation curve. The viscosity and refractive index of toluene were used to approximate those of toluene containing 2% methanol. Those of methanol were used to approximate those of methanol containing 5% THF.

III. Results and Discussion

PSMA-*b*-PCEMA-*b*-PAMA Synthesis and Characterization. The initiator 1,1-diphenyl-3-methylpentyllithium was prepared, in situ, by reacting equal molar equivalences of *sec*-butyllithium and 1,1-diphenyl ethylene in THF at −78 °C. Formation of the initiator was demonstrated by the quick appearance of red color in the solution. 1,1-Diphenyl-3-methylpentyllithium rather than *sec*-butyllithium was used as the initiator to minimize the attack of the ester groups of SMA.



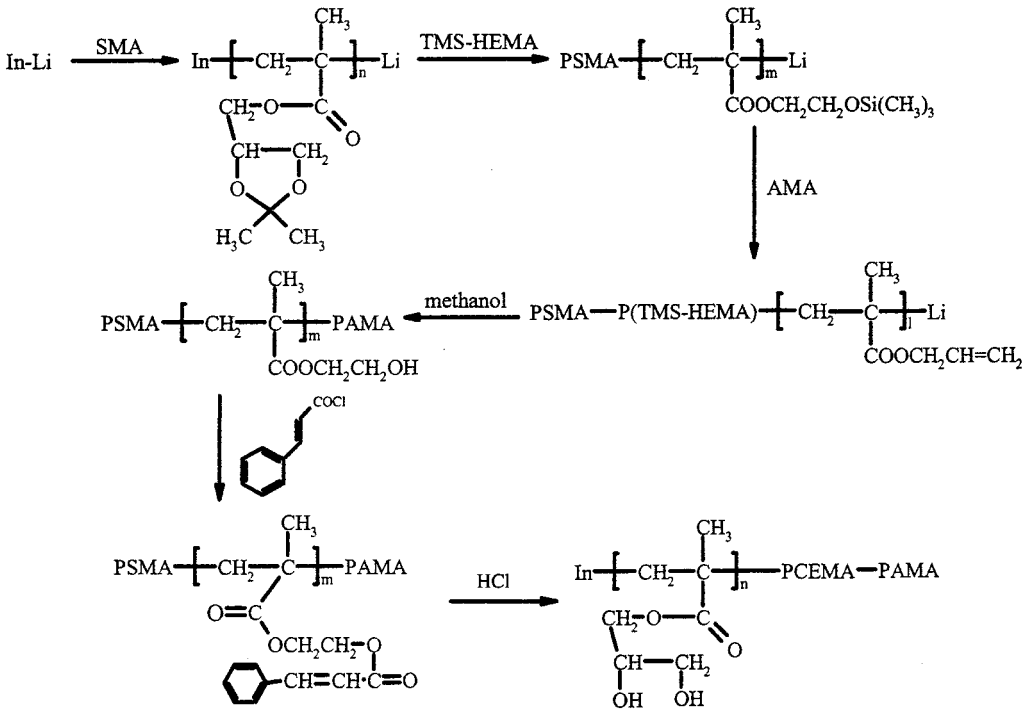
The triblock used in this study was synthesized following Scheme 1.

Although the specific triblock copolymer PSMA-*b*-P(HEMA-TMS)-*b*-PAMA had not been prepared previously, anionic living polymerization of the individual blocks had been demonstrated by Mori et al.[27] for SMA, by Hirao et al.[31] for HEMA-TMS, and by Zhang and Ruckenstein[32] for AMA. According to the results of the previous studies, the polymerization time of 3 h for each block was sufficient for quantitative conversion of the monomers. For this, we did not perform any further kinetic studies of the polymerization.

Our success in preparing PSMA-*b*-PCEMA-*b*-PAMA was best demonstrated by the ^{1}H NMR spectrum of Figure 1. Also illustrated in Figure 1 are the peak assignments. The peak positions and relative areas are in agreement with the proposed structure. From analyzing the relative intensities of peaks of the three different blocks, we obtained the *n*/*m*/*l* values of 100/64/60, which compare well with the feed ratios of 3/2/2.

The variation in refractive index differences, Δn_r, of PSMA-*b*-PCEMA-*b*-PAMA solutions and chloroform were plotted in the form of $\Delta n_r/c$ vs c.[33] Extrapolating the $\Delta n_r/c$ data to zero concentration yielded a refractive index increment dn_r/dc of 0.115 mL/g for the sample. Figure 2 gives a set of light scattering data of the sample shown in the Zimm plot form, where K contains system optical constants such as dn_r/dc and laser beam wavelength λ and so forth and ΔR_θ is the excess Rayleigh ratio. Extrapolation of the data to zero scattering angle

Scheme 1. Triblock Synthesis



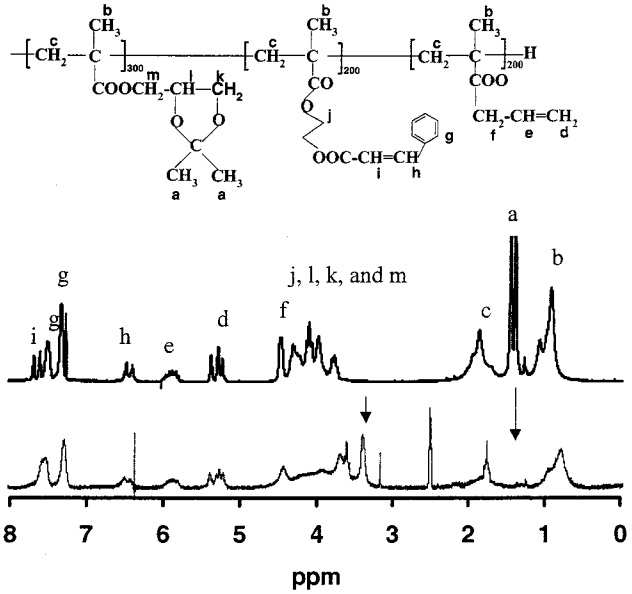


Figure 1. ^{1}H NMR spectra of PSMA-*b*-PCEMA-*b*-PAMA (top) and PGMA-*b*-PCEMA-*b*-PAMA (bottom). The former sample was run in $CDCl_3$ and the latter was run in DMSO-d_6.

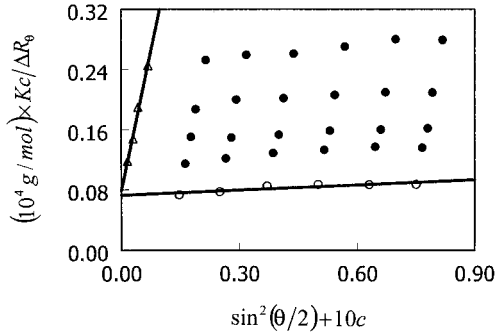


Figure 2. Zimm plot analysis of light scattering data of PSMA-*b*-PCEMA-*b*-PAMA in chloroform. Data (●) were obtained at six angles (45°, 60°, 75°, 90°, 105°, and 120°) and four concentrations (1.59×10^{-3}, 2.99×10^{-3}, 4.22×10^{-3}, and 6.82×10^{-3} g/mL). Symbols ○ represent $Kc/\Delta R_\theta$ data extrapolated to zero angle at different concentrations. Symbols △ represent $Kc/\Delta R_\theta$ data extrapolated to zero concentration at different scattering angles.

or $\theta \rightarrow 0$ and zero concentration or $c \rightarrow 0$ using

$$\frac{Kc}{\Delta R_\theta} = \frac{1}{\bar{M}_w}\left(1 + \frac{16\pi^2 n_0^2 R_G^2}{3\lambda^2}\sin^2(\theta/2)\right) + 2A_2c \quad (1)$$

yielded an apparent molar mass of 1.32×10^5 g/mol for the sample. The molar mass was apparent because the dn_r/dc values for the three blocks were different and no attempt was made to correct this. We, however, expected this correction to be minor, as the three blocks were all methacrylates and their dn_r/dc values should be close. Combining the light scattering and NMR results, we obtained the weight-average *n*, *m*, and *l* values of 300, 190, and 180, which compared well with the targeted values of 300, 200, and 200.

GPC analysis gave $\bar{M}_w/\bar{M}_n = 1.18$, suggesting a narrow molar mass distribution for the triblock. The GPC molar masses were not correct due to the use of poly(methyl methacrylate) homopolymers as the standards. The weight-average GPC molar mass shown in Table 1 was nevertheless reasonably close to the light scattering value.

PGMA-*b*-PCEMA-*b*-PAMA Characteristics. Hydrolysis of PSMA-*b*-PCEMA-*b*-PAMA in THF containing aqueous HCl yielded PGMA-*b*-PCEMA-*b*-PAMA. The hydrolysis conditions used were mild and should not result in the cleavage of any −C−C− bonds. The *n*, *m*, and *l* numbers should thus remain unchanged. Our success in hydrolyzing the acetonide groups of PSMA is evident from comparing the NMR spectra of PSMA-*b*-PCEMA-*b*-PAMA and PGMA-*b*-PCEMA-*b*-PAMA in Figure 1. After hydrolysis, the acetonide group peak at 1.40 ppm disappeared. The comparison also indicates the intactness of the vinyl groups of PCEMA and PAMA after acetonide group removal.

Table 1. Characteristics of PSMA-*b*-PCEMA-*b*-P*t*BA.

dn_r/dc (mL/g)	LS $\bar{M}_w$ (g/mol)	GPC $\bar{M}_w$ (g/mol)	GPC $\bar{M}_w/\bar{M}_n$	feed *n*/*m*/*l*	NMR *n*/*m*/*l*	*n*	*m*	*l*
0.115	$(13.2 \pm 0.06) \times 10^4$	8.1×10^4	1.18	3/2/2	100/64/60	300	190	180

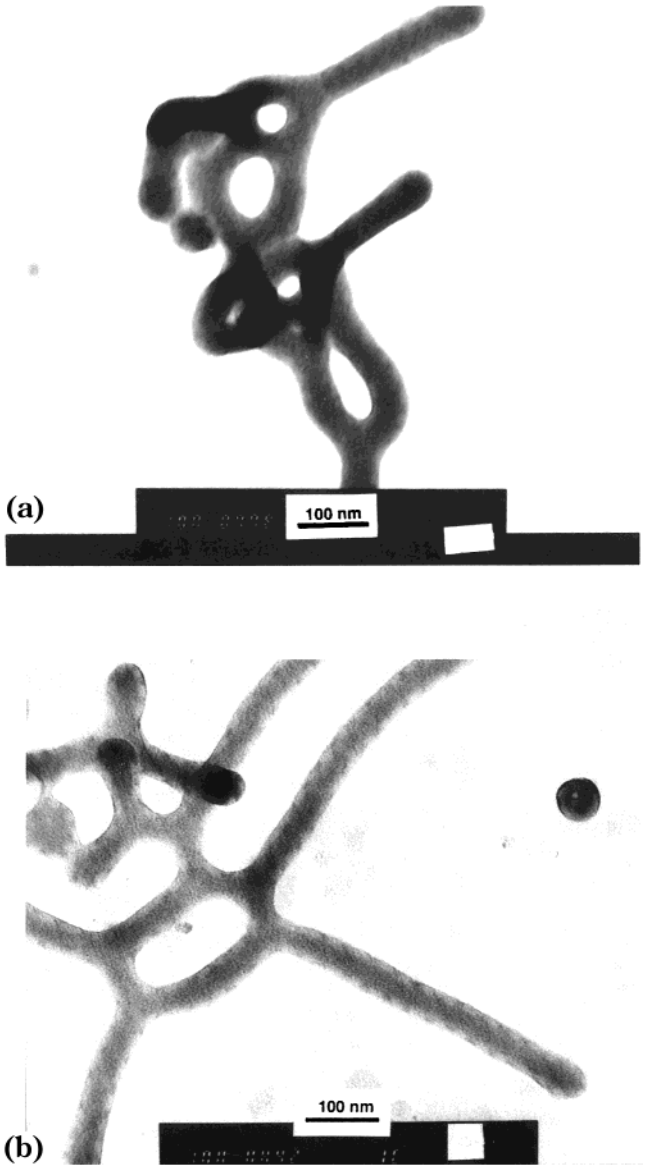


Figure 3. TEM images of branched cylindrical micelles of PGMA-*b*-PCEMA-*b*-PAMA before (a) and after (b) PCEMA cross-linking. The CEMA double-bond conversion in the latter sample was 35%.

Branched Cylindrical Micelles of PGMA-*b*-PCEMA-*b*-PAMA. Stirring PGMA-*b*-PCEMA-*b*-PAMA with methanol for several days yielded a whitish dispersion. Such a dispersion was stable for days if unperturbed. Illustrated in Figure 3a is a TEM image of the solid content of such a dispersion after it was sprayed onto a carbon-coated copper grid and then stained with OsO_4. Shown for comparison in Figure 3b is a TEM image of such a sample after 35% of the PCEMA double bonds had been consumed by photolysis due to double-bond dimerization.[34,35] The TEM images clearly indicate that the solid content in the dispersion is made of branched and looped cylinders. Because PGMA cannot be stained with OsO_4 and there are no white domains inside the cylinders, the PGMA block must have formed the invisible coronas in agreement with the fact that only the PGMA block was soluble in methanol. The diameter of the visible or the dark portion of the cylinders is ≈48 nm and this value was not changed by sample photolysis. Photolysis, however, increased the contrast between the central and outer regions of the visible portion of the cylinders. The fact that the outer region turned lighter after photolysis suggests that PCEMA and PAMA must have formed the middle layers and cores of the cylindrical micelles, respectively. The PCEMA layer became lighter relative to the core because some PCEMA bonds had been consumed and thus fewer were left for staining.

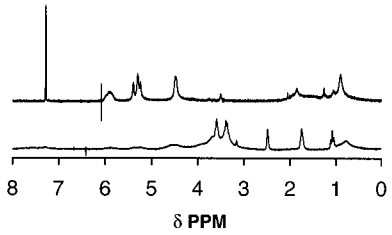


Figure 4. Comparison of ^{1}H NMR spectra of cross-linked PGMA-*b*-PCEMA-*b*-PAMA micelles. The micelles were prepared in methanol (bottom) and toluene/methanol with 2% methanol (top). The samples were run in DMSO-d_6 and $CDCl_3$, respectively.

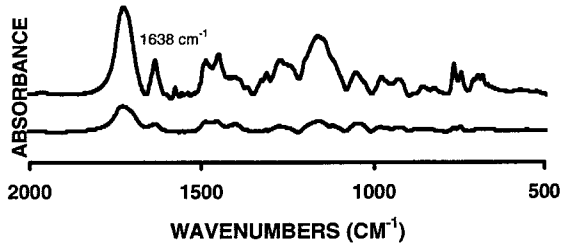


Figure 5. Comparison of FTIR spectra of branched PGMA-*b*-PCEMA-*b*-PAMA cylindrical micelles before (top) and after CEMA photolysis (bottom). The CEMA double-bond conversion in the latter sample was 35%.

An NMR study provided further support for corona formation from PGMA. The fact that all the PGMA ^{1}H peaks appeared in the bottom spectrum of Figure 4 suggests the high mobility of this block and thus its occurrence in the coronas. The absence of many of the PCEMA and PAMA peaks coincides with the TEM observation that PCEMA formed the middle layers and PAMA formed the cores.

Illustrated in Figure 5 is a comparison between the FTIR spectra of such cylindrical micelles before and after UV cross-linking. The conversion of some PCEMA double bonds is manifested by a decrease in the relative intensity of the 1638-cm^{-1} peak. After photolyzing the cylindrical micelles, the PCEMA shell became cross-linked. This made the micelles stable in solvents such as dimethylforamide in which the un-cross-linked micelles disintegrated.

Spherical Micelles of PGMA-*b*-PCEMA-*b*-PAMA in Methanol/THF. In methanol with 5% THF, the triblock formed spherical micelles. Illustrated in Figure 6a,b are the TEM images of the spherical micelles stained with OsO_4 before and after 32% of the CEMA double bonds were consumed due to photolysis. Pho-

Table 2. Characteristics of PSMA-*b*-PCEMA-*b*-P*t*BA Spherical Micelles.

	before crosslinking		after cross-linking			TEM
solvent	diameter (nm)	K_2/K_1^2	PCEMA conversion	diameter (nm)	K_2/K_1^2	diameter (nm)
methanol/THF (98/2)	68	<0.01	35%	71	<0.01	≈40
toluene/ methanol (95/5)	102	0.03	28%	98	0.07	≈53

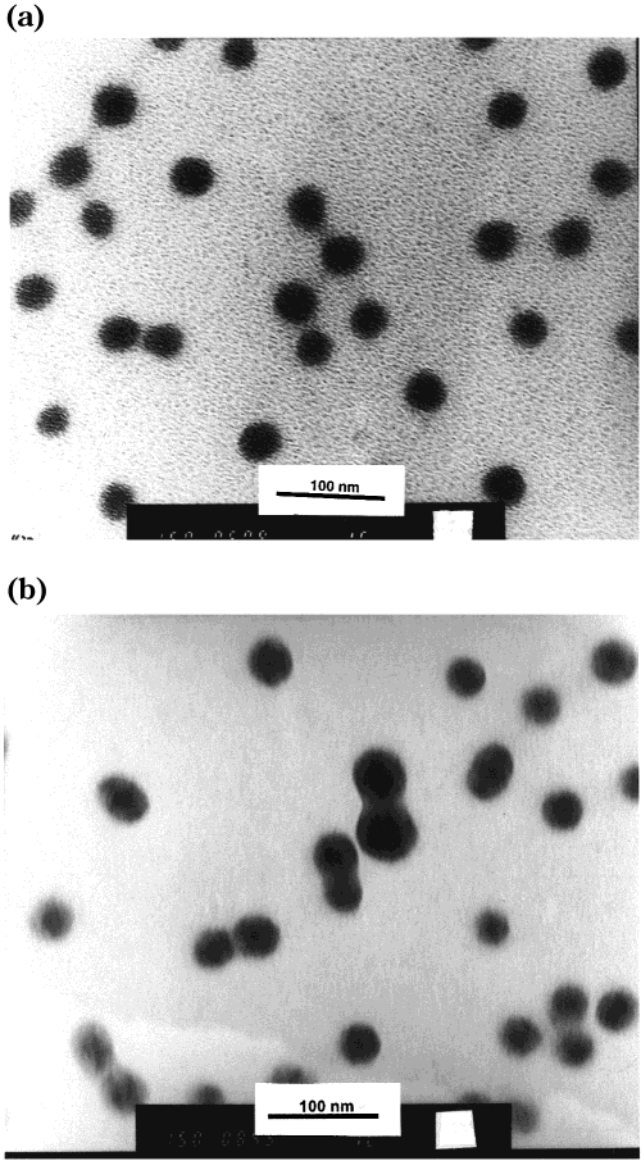


Figure 6. TEM images of spherical micelles of PGMA-*b*-PCEMA-*b*-PAMA before (a) and after (b) PCEMA cross-linking in methanol containing 5% THF. The CEMA double-bond conversion in the latter sample was 32%.

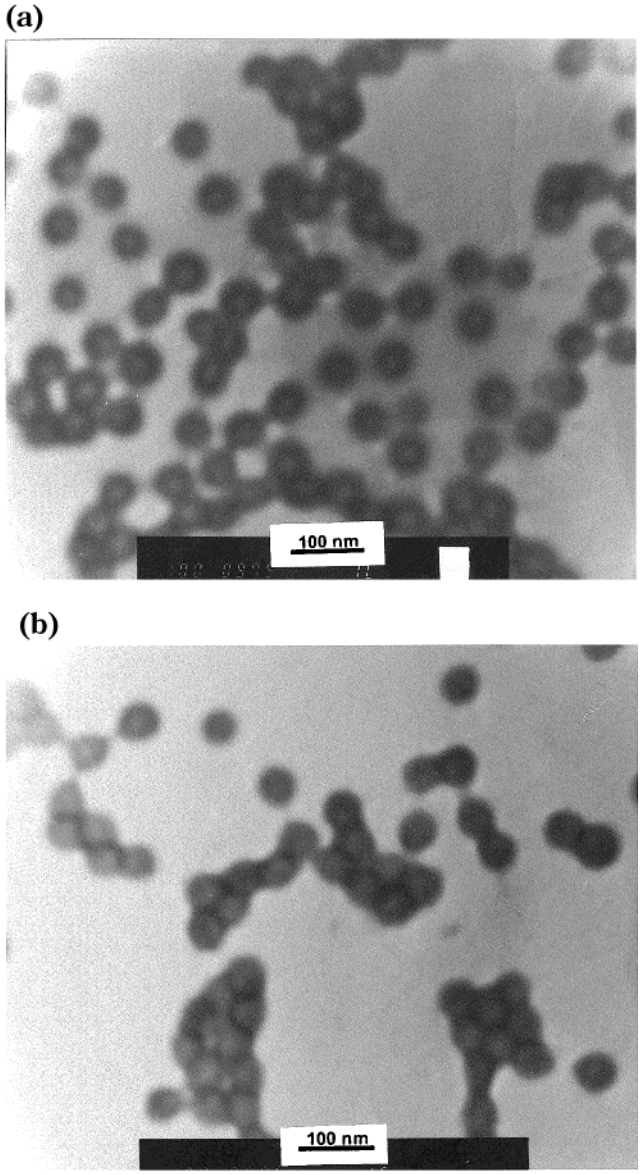


Figure 7. TEM images of spherical micelles of PGMA-*b*-PCEMA-*b*-PAMA before (a) and after (b) PCEMA cross-linking in toluene containing 2% methanol. The CEMA double-bond conversion in the latter sample was 20%.

tolysis did not change the diameter of ≈40 nm for the spheres but improved the contrast between the middle layer and core. This improved contrast can again be justified with a drop in double-bond concentration due to PCEMA cross-linking. Thus, the spherical micelles also have PCEMA middle layers and PAMA cores. We also performed NMR analysis of the cross-linked micelles and the result showed that PGMA formed the corona in this case as well.

Our dynamic light scattering study indicated that both the micelles and cross-linked micelles had low polydispersity (Table 2). The hydrodynamic diameters for the micelles and cross-linked micelles were 68 and 71 nm, respectively. These were the same, within experimental error, and suggested the insignificant perturbation of the structure of the micelles by cross-linking. The hydrodynamic diameter was larger than the TEM diameter of ≈40 nm because DLS gave the size of the solvent-swollen micelles and TEM the size of dry particles. Furthermore, TEM gave the size of the PCEMA and PAMA portion only and DLS measured the size of the whole sphere. Assuming spherical shape, no swelling and a density of 1.0 g/mL for the PCEMA and PAMA portion of the micelles, we estimated the molar mass of 3.4×10^7 g/mol for the micellar particles or an aggregation number of 280.

While branched or looped cylinders were formed in pure methanol, the presence of 5% THF changed the

morphology of the micelles to spheres. Such morphological transitions due to changes in the solvation medium have been well documented for AB diblock copolymers.[36,37] A similar argument[36b] can be used to justify the trend observed for the triblock copolymer.

Spherical Micelles of PGMA-*b*-PCEMA-*b*-PAMA in Toluene/Methanol. Shown in Figure 7a is a TEM image of the spherical micelles formed in toluene with 2% methanol. The center of such micelles is distinctly light. This suggests that PGMA made up the cores. Illustrated also in Figure 5 is an NMR spectrum of such micelles at a CEMA conversion of 20%. The disappearance of the PCEMA and PGMA peaks and the retention of those of PAMA suggest that PAMA formed the coronas in this case. Thus, PCEMA must have formed the intermediate layer. That PCEMA did not form the coronas can also be judged from the observation that the micelles remained dispersed at CEMA double conversions as high as 49%, in contrast to the precipitation of corona-cross-linked diblock micelles at high CEMA conversions.[16] Further proof to the middle layer assignment of PCEMA can arguably be obtained from comparing Figures 7a and 7b. After 20% of the CEMA double bonds have been consumed from photolysis, the light domains of the micelles appear larger.

A DLS study yielded the hydrodynamic diameters of 102 and 98 nm for the micelles and cross-linked micelles, which are again much larger than the TEM diameter of ≈53 nm. The agreement between the hydrodynamic diameters before and after photolysis and the low polydispersity, K_2/K_1^2, indicated insignificant intermicellar cross-linking. Assuming spherical shape and a density of 1.0 g/mL, we estimated from the TEM radius a molar mass of 4.7×10^7 g/mol for the micelles, which corresponds to an aggregation number of ≈360.

IV. Conclusion

We have demonstrated the successful synthesis of PGMA-*b*-PCEMA-*b*-PAMA with 300 GMA, 190 CEMA, and 180 AMA units. PGMA-*b*-PCEMA-*b*-PAMA formed spherical micelles with an aggregation number of ≈280 in methanol with 5%, by volume, of THF. It formed branched or looped cylindrical micelles in pure methanol. The micelles formed had the soluble PGMA block as the coronas and the insoluble PCEMA and PAMA blocks as the intermediate layers and cores, respectively. In toluene containing 2% methanol, only the PGMA block was insoluble. PGMA-*b*-PCEMA-*b*-PAMA formed spherical micelles, consisting of PAMA coronas, PCEMA middle layers, and PGMA cores. The aggregation number of the micelles was ≈360.

Acknowledgment. The Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged for sponsoring this research.

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MA0016230