Triblock Nanospheres with Amphiphilic Coronal Chains

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Received September 30, 2002; Revised Manuscript Received December 4, 2002

ABSTRACT: A poly(butyl methacrylate)-*block*-poly(2-cinnamoyloxyethyl methacrylate)-*block*-poly(*tert*-butyl acrylate) or PBMA-*b*-PCEMA-*b*-P*t*BA triblock copolymer was synthesized and characterized. The triblock formed spherical aggregates with PBMA and P*t*BA coronas and PCEMA cores in 2-propanol containing 1 vol % THF. Triblock nanospheres were obtained after photo-cross-linking the PCEMA cores. Nanospheres with amphiphilic coronal chains were obtained after hydrolyzing the *tert*-butyl groups selectively.

Introduction

In this paper we report on the preparation and characterization of polymer nanospheres containing poly(acrylic acid), PAA, and poly(butyl methacrylate), PBMA, chains in their coronas. Like emulsion particles formed from dispersion polymerization using "ambidextrous" di- or triblock copolymers as stabilizers,[1,2] such nanospheres are dispersible in organic solvents due to steric stabilization provided by the PBMA chains and dispersible in aqueous media by the electrostatic and probably also steric stabilization provided by the deprotonated PAA chains.

The nanospheres were prepared from a triblock copolymer, PBMA-*b*-PCEMA-*b*-P*t*BA, where PCEMA and P*t*BA denote poly(2-cinnamoyloxyethyl methacrylate) and poly(*tert*-butyl acrylate), respectively (see Chart 1). Spherical aggregates were prepared by dissolving the triblock in THF/2-propanol and adding then 2-propanol to the volume fraction of 99%. Nanospheres with PBMA and PtBA coronas were obtained after PCEMA photo-cross-linking. PAA coronal chains were produced after selective hydrolysis of the *tert*-butyl groups.

Chemical processing of segregated diblocks has been practiced extensively in the past to yield stable functional polymer nanostructures of various geometry and shape[3] including nanofibers,[4−6] thin films containing nanochannels,[7,8] cross-linked polymer brushes,[9] star polymers,[10] nanospheres,[11−14] hollow nanospheres,[15,16] nanospheres with cross-linked shells,[17−19] and shaved nanospheres.[20] Block-segregated diblocks have been used also as hosts for inorganic nanoparticles[21−26] and as masks in nanolithography.[27] Reports on the use of segregated triblocks as precursors for nanostructures are only emerging.[28−32]

Experimental Section

Polymer Synthesis. There has been no report of PBMA-*b*-P(HEMA-TMS)-*b*-P*t*BA preparation by anionic polymerization, where HEMA-TMS denotes 2-trimethylsiloxyethyl methacrylate. Anionic polymerization has, however, been used to prepare P(HEMA-TMS)-*b*-P*t*BA by us[11] and random copolymers of BMA and methyl methacrylate by Haddleton et al.[33] Thus, the preparation and purification procedures for the monomers will not be repeated here. PBMA-*b*-P(HEMA-TMS)-*b*-P*t*BA was prepared from sequential living anionic polymerization in THF at −78 °C using the vacuum line technique.[34] The initiator used was 1,1-diphenyl-3-methylpentyllithium produced from reacting equal moles of *sec*-butyllithium and 1,1-diphenylethylene. Lithium chloride was used to decrease the polydispersity of the resultant polymer.[35] BMA, HEMA-TMS, and *t*BA were each polymerized for 3 h. The polymerization was terminated by methanol. Stirring the triblock in THF/methanol (v/v = 75/25) overnight hydrolyzed the TMS groups to yield PBMA-*b*-PHEMA-*b*-P*t*BA, where PHEMA denotes poly(2-hydroxyethyl methacrylate). The polymer solution was then concentrated under reduced pressure, and the copolymer was precipitated on ice. The PHEMA block of the copolymer was converted to PCEMA from reacting with cinnamoyl chloride following procedures used previously.[10]

Polymer Characterization. Gel permeation chromatography (GPC) analysis of PBMA-*b*-PCEMA-*b*-P*t*BA was performed using THF as the eluant. The Waters HT-4 column used was calibrated using poly(methyl methacrylate) standards. The BMA to CEMA and to *t*BA ratios, $n/m/l$, were determined using ^{1}H NMR spectroscopy. The difference, Δn_r, between the refractive index of a polymer solution and that of chloroform, the solvent, was determined using a differential refractometer (Precision Instruments Co.) with light that had passed a band-pass filter centered at 633 nm. The weight-average molar mass was measured in chloroform using a light scattering instrument (Brookhaven model 9025) equipped with a 632 nm He−Ne laser.

Aggregate Preparation and Derivatization. Aggregates in 2-propanol containing 1% THF were prepared by dissolving 100 mg of PBMA-*b*-PCEMA-*b*-P*t*BA in 5.0 mL of THF/2-propanol with 20% THF first. More 2-propanol, 95 mL, was then added slowly to induce aggregate formation. The aggregates were equilibrated for at least 24 h before any physical analyses were performed. Cylindrical aggregates were obtained after dispersing the triblock in cyclohexane, cyclopentane, or 2-propanol directly. Procedures to cross-link the PCEMA block[10] and hydrolyze the *tert*-butyl groups[11] have been described previously. The amphiphilic nanospheres prepared were dispersible readily in THF. To prepare an aqueous dispersion, a 0.01 M Na_2HPO_4 buffer at pH = 9 was added gradually into a nanosphere dispersion in THF until the water content reached 90%. The mixture was then dialyzed against distilled water to remove THF and Na_2HPO_4.

Dynamic Light Scattering Studies. Dynamic light scattering (DLS) measurements were performed with a Brookhaven model 9025 instrument equipped with a 15 mW He−Ne laser at a scattering angle of 90°. Solutions of triblock aggregates, at ~0.1 mg/mL, were filtered through 0.45 μm filters before light scattering measurements. DLS data were analyzed following the method of cumulants.[36] The polydispersity of the micelles or nanospheres 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 refractive index and viscosity of 2-propanol at 22

10.1021/ma021535a CCC: $25.00

Chart 1

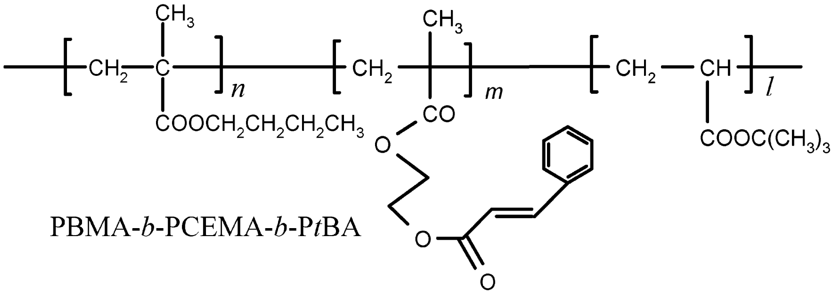


Table 1. Characteristics of PBMA-*b*-PCEMA-*b*-P*t*BA

dn_r/dc (mL/g)	LS $\bar{M}_w$ (g/mol)	GPC $\bar{M}_w/\bar{M}_n$	feed $n/m/l$	NMR $n/m/l$	n	m	l
0.069	(16.9 ± 0.06) × 10^4	1.19	2/1/1	100/46/52	510	240	270

°C were used to approximate those of 2-propanol containing 1% THF.

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 aggregates or nanospheres onto a carbon-coated copper grid using a home-built device.[37] The samples were then placed in a vial containing osmium tetraoxide (Aldrich) for 4 h to stain the PCEMA double bonds. To stain the PAA chains after nanosphere spraying, a drop of a 0.05 M uranium acetate solution in water containing 10 wt % ethanol was dispensed on the carbon-coated copper grid. After 15 min, the excess staining liquid was sucked away with a filter paper placed on the bottom side of the copper grid. The grid was then rinsed with water droplets thrice.

NMR Study. The NMR spectra shown in Figure 1 were acquired at 309 K on a Bruker DRX 500 instrument equipped with a CRP TXI probe. The spectra were recorded with a 45° pulse, an acquisition time of 2.73 s, a 4.00 s delay between scans, and 128 scans.

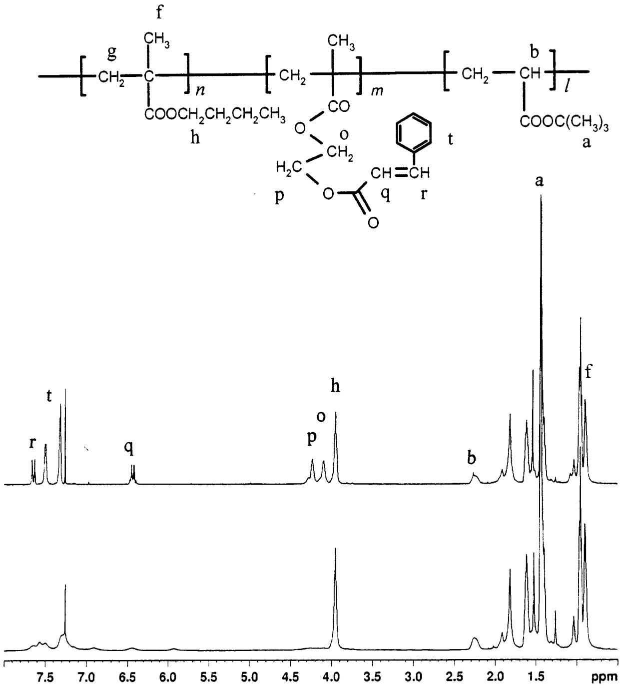


Figure 1. ^{1}H NMR spectrum of the triblock sample (top). Also shown for comparison is the spectrum of the cross-linked triblock nanospheres (bottom).

Results and Discussion

Triblock Characterization. The successful synthesis of the triblock was confirmed from end-product analysis by ^{1}H NMR spectroscopy. Figure 1 shows a NMR spectrum of the triblock together with assignments of the key proton peaks. From the relative intensities of the peaks of the different blocks we obtained $n/m/l$ = 1.00/0.46/0.52, which agree reasonably well with the targeted ratios of 1.00/0.50/0.50.

The differences between the refractive indices, Δn_r, of PSMA-*b*-PCEMA-*b*-PAMA solutions and chloroform were measured and $\Delta n_r/c$ were plotted as a function of polymer concentration c.[38] Extrapolating the $\Delta n_r/c$ data to zero concentration yielded the refractive index increment dn_r/dc of 0.069 mL/g for the triblock (Table 1) in chloroform. Chloroform was chosen as the solvent for the light scattering study to ensure positive {dn_r}/{dc} values for all of the blocks. Specifically, the refractive index, n_r, of $CHCl_3$ at 20 °C is 1.446, which is smaller than 1.483 for PBMA and 1.466 for poly(butyl acrylate), which is structurally close to P*t*BA.[39] In toluene with a refractive index of 1.4961, we reported a dn_r/dc value of 0.0935 mL/g for PCEMA.[40] Thus, the dn_r/dc value of PCEMA in chloroform should be positive as well. Its weight-average molar mass was determined by light scattering using the Zimm method to be (16.9 ± 0.6) × 10^4 g/mol. The molar mass was apparent, because we could not correct for sample composition fluctuation from chain to chain and for the difference in the dn_r/dc values of the blocks.[38] By combining the light scattering and NMR results, we obtained the weight-average n, m, and l values of 510, 240, and 270, respectively, for the triblock. These values agree well with the targeted values of 400, 200, and 200, considering that the light scattering molar mass was apparent, and the n, m, and l values determined were weight-average and the targeted ones were number-average. GPC analysis, without correcting for the limited number of theoretical plates of the column, gave a polydispersity index of 1.19 for the sample.

Aggregate Formation. Micelles or aggregates form in solvents that solubilize only one or two blocks of a triblock copolymer. To identify block selective solvents, we employed PBMA, PCEMA, and P*t*BA homopolymers for solubility tests. The PMMA-equivalent GPC molar masses and polydispersity for the three homopolymers used are shown in Table 2. Also shown are the solubility test results. Since only PCEMA was insoluble in cyclohexane, cyclopentane, or 2-propanol, the triblock should form micelles or aggregates with P*t*BA and PBMA coronas and PCEMA cores in any of the three solvents.

Figure 2a shows a TEM image of aggregates formed from the triblock sprayed from cyclopentane onto a

Table 2. GPC Characteristics of the Homopolymers and Their Solubility in Different Solvents

sample	GPC $\bar{M}_n$/(g/mol)	GPC $\bar{M}_w/\bar{M}_n$	cyclohexane	2-propanol	cyclopentane	chloroform	THF
P*t*BA	1.25×10^4	1.29	+[a]	+	+	+	+
PBMA	4.6×10^4	1.12	+	+	+	+	+
PCEMA	12.8×10^4	1.20	-	-	-	+	+

[a] + and − are used to indicate solubility and insolubility, respectively.

Table 3. Molecular Properties of the Nanospheres at Different Stages

reaction stage	LS $\bar{M}_w$/(g/mol)	LS R_G/nm solvent	LS R_h/nm, solvent	DLS polydispersity	TEM *R*/nm, spraying solvent
spherical aggregates			23, 2-propanol with 1% THF	0.03	8, 2-propanol with 1% THF
cross-linked aggregates	8.9×10^6	33, chloroform	31, toluene	0.08	10, THF
			31, THF	0.08	
cross-linked and cleaved aggregates			30, THF	0.18	8, THF
			30, toluene	0.41	8, water
			29, water	0.20	

carbon-coated copper grid. The triblock evidently formed mostly cylindrical aggregates in this case. Since OsO_4 was used to stain the sample, the visible part of the cylinders with a diameter of ~14 nm must consist of PCEMA. Mostly cylindrical aggregates were formed also in neat 2-propanol or cyclohexane.

Figure 2b presents a TEM image of a sample sprayed from 2-propanol containing 1% THF. Spherical aggregates were formed in this case. The aggregates have a uniform core radius of ~8 nm. Similar images were obtained at a THF volume fraction of 5%. We were also able to obtain spherical aggregates in THF/cyclohexane and THF/cyclopentane mixtures.

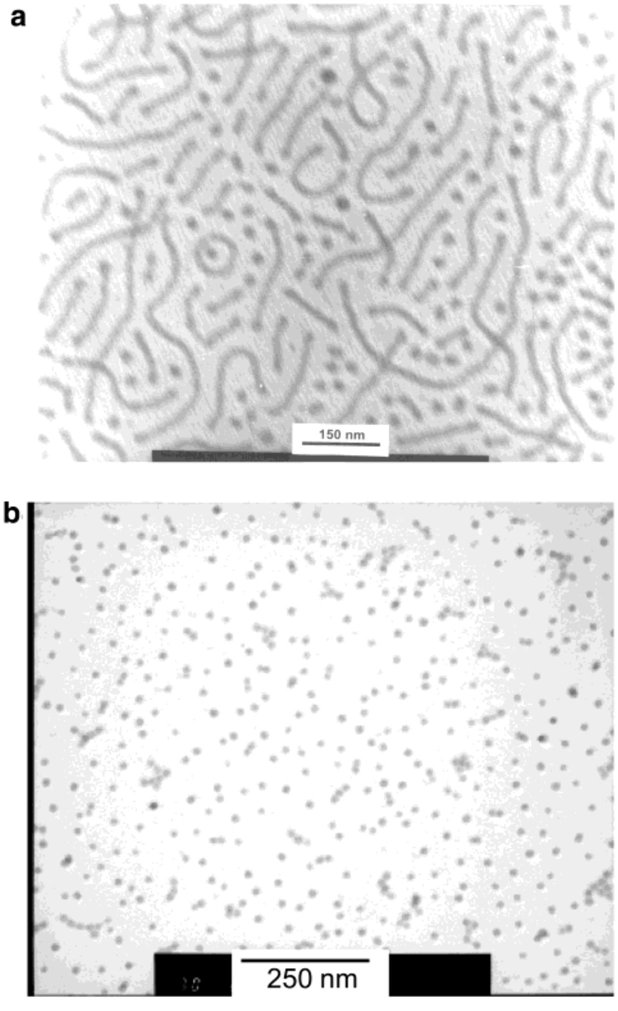


Figure 2. TEM images of triblock aggregates sprayed from cyclopentane (a) and 2-propanol containing 1% THF (b).

Micelles are the equilibrium products, and micelles of the same shape and size should form under a given set of conditions independent of their preparation methods.[41] To check whether the spherical aggregates in 2-propanol containing 1% THF were micelles, we attempted their preparation from three different approaches. The first approach involved dissolving the triblock in THF/2-propanol containing 20% THF and adding then slowly 2-propanol to a volume fraction of 99%. In the second approach, we prepared the aggregates by dispersing the triblock in 2-propanol containing 1% THF directly. In the third approach, the triblock was dispersed in neat 2-propanol. THF was then added. In all approaches, the final mixture was stirred for at least 24 h before the morphology was examined by TEM. While exclusively spherical aggregates were obtained from approach 1, a mixture of mostly spheres and cylinders was produced from approach 2, and mostly cylinders and spheres were produced from approach 3. The pathway dependence of product formation makes the equilibrium morphology of the triblock micelles uncertain, and we have thus referred to the particles prepared from approach 1 as "spherical aggregates" rather than micelles.

A dynamic light scattering study yielded a hydrodynamic radius, R_h, of 23 nm and a polydispersity index of 0.03 for the spherical aggregates (Table 3). The R_h value is larger than the TEM radius, as R_h gives a measure of the overall size of the aggregates including the coronal chains and only the PCEMA cores were seen by TEM.

Nanospheres with P*t*BA and PBMA Coronal Chains. Nanospheres were prepared from photo-cross-linking spherical aggregates formed in 2-propanol containing 1% THF. This chemistry has been used extensively by our group to prepare various stable nano structures, and UV absorbance analysis was used to follow the cross-linking reaction.[10] A typical CEMA double-bond conversion of ~40% was used in this study. Figure 3a shows a TEM image of the cross-linked aggregates sprayed from THF. The average radius is ~10 nm, which is larger than ~8 nm found for the cores of the aggregates sprayed from 2-propanol containing 1% THF. The size difference could reflect different degrees of swelling in the spraying solvents and the partial or full retention of the swollen state of the nanosphere cores in THF due to fast solvent evaporation. The different degrees of swelling were confirmed

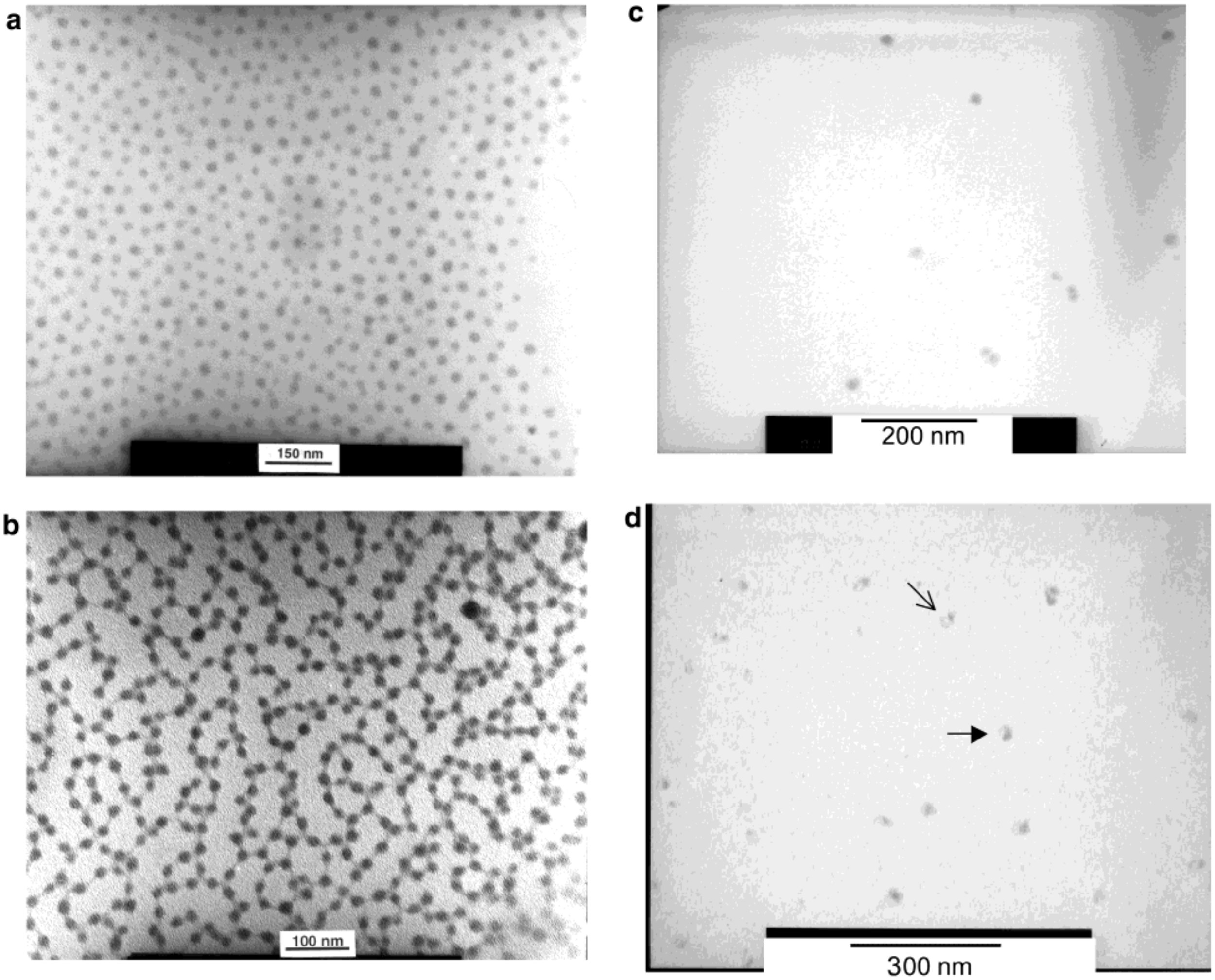


Figure 3. TEM image of the cross-linked spherical aggregates (a) sprayed from THF. Also shown are the TEM images of the aggregates after PCEMA cross-linking and *tert*-butyl group cleavage sprayed from THF (b), water (c), and 2-propanol (d). The last sample was stained with uranium acetate.

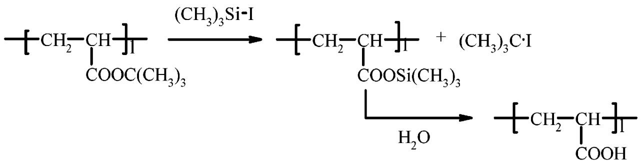
by a R_h value increase from 23 nm for the aggregates in THF/2-propanol (Table 3) to 31 nm for the nanospheres in either THF or toluene. This size increase was also accompanied by a more surprising DLS polydispersity index increase from 0.03 to 0.08, despite the fact that our TEM results of Figure 3a suggested no significant fusion of nanospheres.

Assuming an insignificant change in the dn_r/dc value of the triblock after PCEMA cross-linking, a static light scattering study yielded a weight-average molar mass of 8.9×10^6 g/mol for the cross-linked aggregates. From the ratio of molar masses of the nanospheres to the triblock we obtained an aggregation number of ~53 for the nanospheres. Using the molar mass M_W of 8.9×10^6 g for the nanospheres, a weight fraction w_{CEMA} of 0.36, and a density ρ_{CEMA} of 1.25 g/cm^3 for PCEMA,[7c] we calculated from

$$M_W w_{CEMA} = (4/3) N_A \pi R_C^{\,3} \qquad (1)$$

an average radius R_C of 10 nm for the PCEMA cores, which is close to ~8 nm obtained from TEM observations from Figure 2b. In eq 1, N_A is the Avogardro number. The static light scattering study also yielded a radius of gyration R_G value of 33 nm for the nanospheres in chloroform, which is close to the R_h values determined in THF or toluene.

Scheme 1



The core–shell structure of the nanospheres was confirmed by the ^{1}H NMR spectrum of the nanospheres of Figure 1. The nanospheres have broad and weak PCEMA peaks, in agreement with the fact that the PCEMA cores were cross-linked and the segmental motions were slow there. On the other hand, the relative intensities of the P*t*BA and PBMA peaks were not affected because they were in the more mobile coronas.

Ambidextrous Spheres. Treating the nanospheres with $(CH_3)_3SiI$ in dry dichloromethane for 1 h followed by wet methanol addition led to the selective cleavage of the *tert*-butyl groups from P*t*BA. The reactions involved are shown in Scheme 1. The selectivity of the above reaction toward *tert*-butyl over *n*-butyl groups has been demonstrated for small-molecule systems before;[42] i.e., *n*-butyl groups were cleaved at moderate rate only at 50 °C, and *tert*-butyl groups were cleaved quantitatively within 1 h at 25 °C. This selectivity in our system has been confirmed by a NMR experiment. It involved adding $(CH_3)_3SiI$ into a cross-linked nanosphere solution

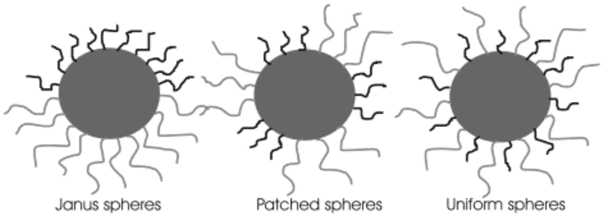


Figure 4. Possible PBMA and P*t*BA chain distribution patterns.

in $CDCl_3$. Within 1 h, the ^1H peak of the *tert*-butyl ester groups of P*t*BA at 1.43 ppm disappeared completely. At the same time, no change occurred to the peak at 3.95 ppm for the "h" protons of PBMA (Figure 1). The most visual evidence for the selective hydrolysis of *tert*-butyl groups is that the resultant nanospheres were dispersible in both water and toluene. After *tert*-butyl group removal, the nanospheres became ambidextrous, showing dispersibility in aqueous solutions and organic solvents.

Figure 3b shows a TEM image of the nanospheres sprayed from THF after *tert*-butyl group removal and staining with OsO_4. The integrity of the spheres at this stage is evident. Table 3 shows the hydrodynamic radii of the amphiphilic nanospheres dispersed in different solvents. They are all ~30 nm, close to the values obtained for the nanospheres before *tert*-butyl group removal. This was somewhat unexpected, as the PAA block would collapse in toluene or THF and the PBMA block would collapse in water. The collapsing of half of the coronal chains should lead to a decrease in the coronal layer thickness. Furthermore, the PCEMA core would be negligibly swollen in water and would also cause a decrease in R_h. This invariance in R_h with *tert*-butyl group removal was then accompanied by a drastic increase in the DLS polydispersity indices. Such increases were possible only if there had been nanosphere aggregation, which would be favored if PAA and PBMA chains were laterally segregated.

Coronal Chain Distribution. P*t*BA and PBMA block-segregated in the solid state.[43] The distribution of the P*t*BA and PBMA chains on the nanosphere core surfaces in this case deserves a detailed study by techniques such as nuclear Overhauser enhancement spectroscopy (NOESY). The chains, due to their incompatibility, may be packed in a two-faced fashion to yield Janus spheres as those from solid-state synthesis reported by Saito et al.[31] and Erhardt et al.[32] In these cases, the middle block, which was much shorter than terminal blocks, formed spherical domains decorating the interface between lamellae formed by the terminal blocks in bulk. The spherical domains were then cross-linked. After dispersion in solvents that solubilized the terminal blocks, Janus or two-faced nanospheres were obtained. Janus spheres have asymmetric coronal layer thickness as depicted in Figure 4 and have been shown by Erhardt et al.[32] to aggregate even in solvents good for both types of coronal chains. Our spheres do not seem to aggregate as manifested by the low DLS polydispersity indices observed for the spherical aggregates before and after PCEMA core cross-linking. This is understandably so, because our spheres were derived from spherical aggregates formed in block-selective solvent. Before core cross-linking or even before triblock aggregation, the corona PBMA and P*t*BA chains could have adjusted their packing to minimize coronal thickness asymmetry.

The coronal chains can then be packed either uniformly or in a patched fashion as shown in Figure 4. TEM evidence seems to suggest that the chains, at least after *tert*-butyl group removal, are patched on the core surfaces. This is best appreciated from comparing parts a and b of Figure 3. Before *tert*-butyl removal, the aspirated spheres appear mostly separated from one another as expected for spheres with repulsive coronal layers. The nanospheres appeared sticky in Figure 3b. Our experiment with a PAA homopolymer revealed that THF did not dissolve but swelled PAA. If the original P*t*BA and PBMA chains were distributed uniformly in the coronas, the PAA chains formed after *tert*-butyl group removal would collapse under the PBMA chains in THF. The PBMA chains, which are substantially longer than the PAA chains, would prevent the aggregation of the nanospheres. The fact that they got sticky and each sphere was stuck to more than one neighbors suggested the presence of probably several PAA patches on each core surface.

Figure 3c shows a TEM image of the amphiphilic spheres sprayed from water at a very low concentration, e.g., <0.01 mg/mL. Even at such a dilution, some doublets were seen. When sprayed from a more concentrated solution, e.g., at 0.1 mg/mL, mostly doublets, triplets, quadruplets, etc., were seen. The aggregation of the nanospheres in water again suggests the lateral segregation of PBMA and PAA chains.

Figure 3d illustrates a TEM image of the amphiphilic spheres sprayed from 2-propanol and then stained with uranium acetate, which binds to PAA only. For the particle marked with a hollow arrow, the PAA chains are concentrated at the top right corner on the core surface. The PAA chains are localized on the right side (the imagined left part not seen) for the particle marked with a solid arrow. If the PAA chains are distributed uniformly on the PCEMA surfaces, we should see rings with approximately uniform darkness around the light PCEMA circles, as has been seen for PAA-*b*-PHEMA fluorescent nanospheres with cross-linked PHEMA core and PAA corona.[44]

Conclusion

We have prepared a PBMA-*b*-PCEMA-*b*-P*t*BA sample with 510 BMA, 240 CEMA, and 270 *t*BA units. The triblock formed spherical aggregates in 2-propanol with 1% THF. Nanospheres with PCEMA cores and P*t*BA and PBMA coronas were obtained after photo-cross-linking the PCEMA block. Amphiphilic nanospheres were obtained after cleaving the *tert*-butyl groups selectively from the P*t*BA block. Such nanospheres dispersed both in water and in organic solvents and seemed to have patched PAA and PBMA chain distribution on the PCEMA core surface.

Acknowledgment. The authors thank NSERC of Canada for financial support. Drs. Futian Liu and Xiaohu Yan are gratefully acknowledged for preparing and characterizing the triblock copolymer. Drs. R. Cook and H. Vogel are thanked for obtaining the NMR spectra shown in Figure 1 and attempting the P*t*BA and PBMA chain distribution study by NOESY.

References and Notes

(1) Yates, M. Z.; Li, G. J.; Shim, J. J.; Maniar, S.; Johnston, K. P.; Lim, K. T.; Webber, S. E. *Macromolecules* **1999**, *32*, 1018.

(2) Li, G.; Yates, M. Z.; Johnston, K. P.; Lim, K. T.; Webber, S. E. *Macromolecules* **2000**, *23*, 1606.

(3) Liu, G. J. *Curr. Opin. Colloid Interface Sci.* **1998**, *3*, 200.

(4) Liu, G. J.; Qiao, L. J.; Guo, A. *Macromolecules* **1996**, *29*, 5508. (b) Liu, G. J. *Adv. Mater.* **1997**, *9*, 437. (c) Liu, G. J.; Ding, J. F.; Qiao, L. J.; Guo, A.; Gleeson, J. T.; Dymov, B.; Hashimoto, T.; Saijo, K. *Chem. Eur. J.* **1999**, *5*, 2740. (d) Tao, J.; Stewart, S.; Liu, G. J.; Yang, M. L. *Macromolecules* **1997**, *30*, 2738.

(5) Massey, J.; Power, K. N.; Manners, I.; Winnik, M. A. *J. Am. Chem. Soc.* **1998**, *120*, 9533. (b) Raez, J.; Barjovanu, R.; Masseay J. A.; Winnik, M. A.; Manners, I. *Angew. Chem., Int. Ed.* **2000**, *39*, 3862.

(6) Won, Y.-Y.; Davis, H. T.; Bates, F. S. *Science* **1999**, *283*, 960.

(7) Liu, G. J.; Ding, J. F.; Guo, A.; Herfort, M.; Bazett-Jones, D. *Macromolecules* **1997**, *30*, 1851. (b) Liu, G. J.; Ding, J. F. *Adv. Mater.* **1998**, *10*, 69. (c) Liu, G. J.; Ding, J. F.; Hashimoto, T.; Saijo, K.; Winnik, F. M.; Nigam, S. *Chem. Mater.* **1999**, *11*, 2233. (d) Liu, G.; Ding, J.; Stewart, S. *Angew. Chem.* **1999**, *38*, 835.

(8) Lee, J.-S.; Hirao, A.; Nakahama, S. *Macromolecules* **1989**, *22*, 2602.

(9) Liu, G.; J. Hu, N. X.; Xu, X. Q.; Yao, H. *Macromolecules* **1994**, *27*, 3892−3895. (b) Ding, J. F.; Birss, V. I.; Liu, G. J. *Macromolecules* **1997**, *30*, 1442. (c) Ding, J. F.; Liu, G. J. *Langmuir* **1999**, *15*, 1738. (d) Tao, J.; Guo, A.; Liu, G. J. *Macromolecules* **1996**, *29*, 1618. (e) Ding, J. F.; Tao, J.; Guo, A.; Stewart, S.; Hu, N. X.; Birss, V. I.; Liu, G. J. *Macromolecules* **1996**, *29*, 5398.

(10) Guo, A.; Tao, J.; Liu, G. J. *Macromolecules* **1996**, *29*, 2487.

(11) Wang, G. C.; Henselwood, F.; Liu, G. J. *Langmuir* **1998**, *14*, 1554. (b) Henselwood, F.; Liu, G. J. *Macromolecules* **1997**, *30*, 488.

(12) Ishizu, K.; Onen, A. *J. Polym. Sci., Polym. Chem.* **1989**, *27*, 3721. (b) Ishizu, K.; Kuwahara, K. *J. Polym. Sci., Polym. Chem.* **1993**, *31*, 661.

(13) Prochazka, K.; Baloch, M. K.; Tuzar, Z. *Makromol. Chem.* **1979**, *180*, 2521.

(14) Wilson, D. J.; Riess, G. *Eur. Polym. J.* **1988**, *24*, 617.

(15) Ding, J. F.; Liu, G. J. *Chem. Mater.* **1998**, *10*, 537. (b) Ding, J. F.; Liu, G. J. *J. Phys. Chem. B* **1998**, *102*, 6107. (c) Stewart, S.; Liu, G. J. *Chem. Mater.* **1999**, *11*, 1048. (d) Ding, J. F.; Liu, G. J. *Macromolecules* **1997**, *30*, 655.

(16) Huang, H.; Remsen, E. E.; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1999**, *121*, 3805.

(17) Thurmond, K. B., II; Kowalewski, T.; Wooley, K. L. *J. Am. Chem. Soc.* **1996**, *118*, 7239.

(18) Butun, V.; Lowe, A. B.; Billingham, N. C.; Armes, S. P. *J. Am. Chem. Soc.* **1999**, *121*, 4288. (b) Butun, V.; Wang, X.-S.; de Paz Banez, M. V.; Robinson, K. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2000**, *33*, 1.

(19) Ding, J. F.; Liu, G. J. *Macromolecules* **1998**, *31*, 6554.

(20) Tao, J.; Liu, G. J.; Ding, J. F.; Yang, M. L. *Macromolecules* **1997**, *30*, 4084.

(21) Boontongkong, Y.; Cohen, R. E.; Rubner, M. F. *Chem. Mater.* **2000**, *12*, 1628.

(22) Fink, Y.; Urbas, A. M.; Bawendi, G. G.; Joannopoulos, J. D.; Thomas, E. L. *Lightwave Technol.* **1999**, *17*, 1963.

(23) Hashimoto, T.; Tsutsumi, K.; Funaki, Y. *Langmuir* **1997**, *13*, 6869.

(24) Templin, M.; Franck, A.; DuChesne, A.; Leist, H.; Zhang, Y. M.; Ulrich, R.; Schadler, V.; Wiesner, U. *Science* **1997**, *278*, 5344.

(25) Spatz, J. P.; Roescher, A.; Sheiko, S.; Krausch, G.; Möller, M. *Adv. Mater.* **1995**, *7*, 1000.

(26) Antonietti, M.; Wenz, M.; Bronstein, L.; Seregina, M. V. *Adv. Mater. 7*, **1995**, 1000. (b) Förster, S.; Antonietti, M. *Adv. Mater.* **1998**, *10*, 195.

(27) Park, M.; Harrison, C.; Chaikin, P. M.; Register, R. A.; Adamson, D. H. *Science* **1997**, *276*, 1401.

(28) Stewart, S.; Liu, G. J. *Angew. Chem., Int. Ed.* **2000**, *39*, 340. (b) Yan, X. H.; Liu, G. J.; Liu, F. T.; Tang B. Z.; Peng, H.; Pakhomov, A. B.; Wong, C. Y. *Angew. Chem., Int. Ed.*, in press.

(29) Underhill, R. S.; Liu, G. J. *Chem. Mater.* **2000**, *12*, 3633. (b) Underhill, R. S.; Liu, G. J. *Chem. Mater.* **2000**, *12*, 2082.

(30) Butun, V.; Wang, X.-S.; de Paz Banez, M. V.; Robinson, K. L.; Billingham, N. C.; Armes, S. P. *Macromolecules* **2000**, *33*, 1.

(31) Saito, R.; Fujita, A.; Ichimuru, A.; Ishizu, K. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2091.

(32) Erhardt, R.; Boker, A.; Zettl, H.; Kaya, H.; Pyckhout-Hintzen, W.; Krausch, G.; Abetz, V.; Muller, A. H. E. *Macromolecules* **2001**, *34*, 1069.

(33) Haddleton, D. M.; Crossman, M. C.; Hunt, K. H.; Topping, C.; Waterson, C.; Suddaby, K. G. *Macromolecules* **1997**, *30*, 3992.

(34) Morton, M. *Anionic Polymerization: Principles and Practice*; Academic Press: New York, 1983.

(35) Creutz, S.; Teyssié, Jérôme, R. *Macromolecules* **1997**, *30*, 6.

(36) Koppel, D. E. *J. Chem. Phys.* **1972**, *57*, 4814.

(37) Ding, J. F.; Liu, G. J. *Macromolecules* **1999**, *32*, 8413.

(38) Huglin, M. B. *Light Scattering from Polymer Solutions*; Academic Press: London, 1972.

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

(40) Tao, J.; Guo, A.; Liu, G. J. *Macromolecules* **1997**, *30*, 2738.

(41) Zhang, L. F.; Eisenberg, A. *Science* **1995**, *268*, 1728. (b) Cameron, N. S.; Corbierre, M. K.; Eisenberg, A. *Can. J. Chem.* **1999**, *77*, 1311.

(42) Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* **1976**, *99*, 968.

(43) Yan, X. H.; Liu, F. T.; Li, Z.; Liu, G. J. *Macromolecules* **2001**, *34*, 9112.

(44) Li, Z.; Liu, G. J.; Law, S. J.; Sells, T. *Biomacromolecules* **2002**, *3*, 984.

MA021535A