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Block Copolymer Microspheres Containing Intricate Nanometer-Sized Segregation Patterns

Zhihua Lu, Guojun Liu,* and Futian Liu

Department of Chemistry, University of Calgary,
2500 University Dr., NW,
Calgary, Alberta, Canada T2N 1N4

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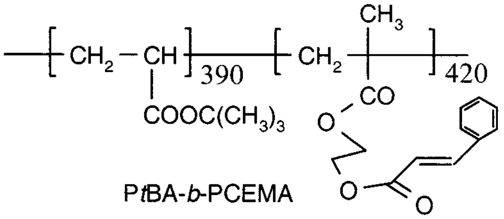
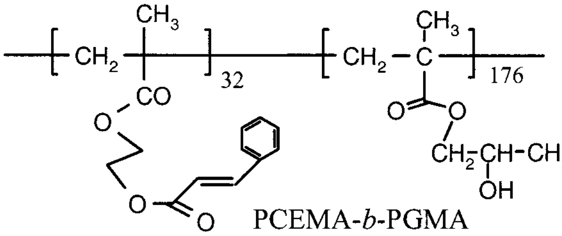
Introduction

Block copolymers self-assemble, forming a number of intricate block segregation patterns.[1] Such assembled structures can serve as precursors to nano- or microstructures with numerous potential applications. For many applications such as catalysis, a high surface area-to-volume ratio is desirable, which requires "breaking up" block copolymer solid into dispersed particles. One approach involves cross-linking spherical or cylindrical domains formed by one block of a diblock copolymer and then separating the cross-linked domains via solvating chains of the other block, which forms the matrix of a block-segregated solid, to yield nanospheres[2] or nanofibers.[3,4] The cross-linked cores of the nanofibers or nanospheres thus prepared are, however, not easily derivatized for synthesizing polymer/inorganic hybrid materials. Here we report on the novel preparation of water-dispersible microspheres containing block-segregated P*t*BA-*b*-PCEMA using an emulsion method,[5,6] utilizing PCEMA-*b*-PGMA as the surfactant:



P*t*BA-*b*-PCEMA



PCEMA-*b*-PGMA

We also show that *tert*-butyl groups can be removed from the segregated P*t*BA domains to yield internal hydrophilic poly(acrylic acid) or PAA channels or layers.

Experimental Section

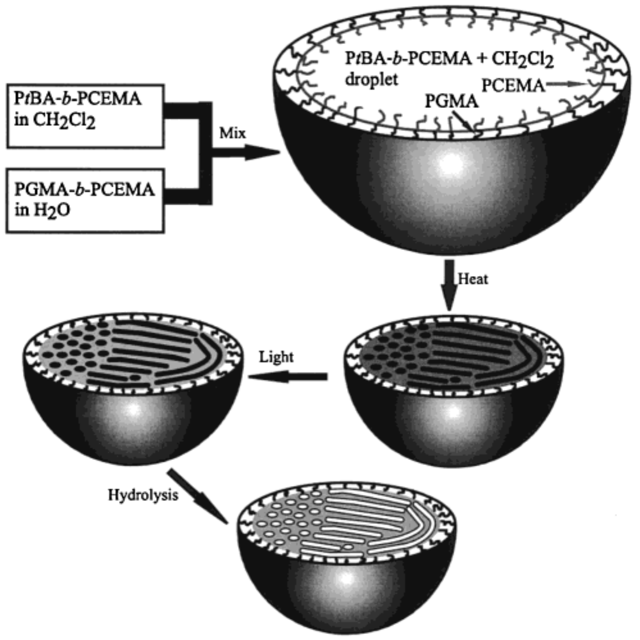
Polymer Synthesis and Characterization. The precursors to P*t*BA-*b*-PCEMA and PCEMA-*b*-PGMA were prepared by anionic polymerization. The synthesis of P*t*BA-*b*-PCEMA has been reported previously.[7] The synthesis of PCEMA-*b*-PGMA has not been reported but is similar to that of PGMA-*b*-PCEMA-*b*-PAMA,[8] where PAMA denotes poly(allyl methacrylate). For these, the detailed procedures for monomer and polymer purification and polymerization will not be repeated here. The diblock, P*t*BA-*b*-PCEMA, and the surfactant, PCEMA-*b*-PGMA, were characterized by light scattering, nuclear magnetic resonance spectroscopy, and gel permeation chromatography (GPC) using procedures described previously.[5] The characterization results for the polymers are given in Table 1.

Table 1. Characteristics of the Diblock and Surfactant

sample	dn_r/dc (mL/g)	LS $\bar{M}_w$ (g/mol)	GPC $\bar{M}_w/\bar{M}_n$	NMR n/m	n	m
P*t*BA-*b*-PCEMA	0.095 (in CHCl$_3$)	1.59× 10^5	1.18	0.93	390	420
PCEMA-*b*-PGMA	0.100 (in DMF)	0.36× 10^5	1.15^a	0.18	32	176

[a] Measured in THF in the PCEMA-*b*-PSMA form, where PSMA denotes poly(solketal methacrylate).

Scheme 1. Preparation and Processing of P*t*BA-*b*-PCEMA Microspheres Containing Nanometer-Sized Cylindrical Domains



Microsphere Preparation and Derivatization. Two variations of the oil-in-water method were used to prepare the microspheres. Since PCEMA-*b*-PGMA was not directly dispersible in water, the surfactant, 250 mg, was dissolved in 2 mL of methanol, and then the solution was diluted with water to 100 mL. In variation 1, 250 mg of the diblock was dissolved in 10 mL of CH$_2$Cl$_2$ and then mixed with the surfactant solution under magnetic stirring to yield a cloudy mixture. The mixture was further sonicated (Branson 1200) for 5 min to yield an emulsion. The emulsion was added over 45 min into 100 mL of water stirred at 500 rpm at 45 °C in a three-neck round-bottomed Pyrex flask. Evaporating CH$_2$Cl$_2$ at 50 °C under stirring for 1 h yielded CH$_2$Cl$_2$-free diblock spheres (Scheme 1). The microspheres were cross-linked using UV light from a 500 W mercury lamp. PCEMA double-bond conversion obtained from CEMA absorbance decrease at 274 nm was 29%. The microspheres were separated from the supernatant by centrifugation and rinsed with distilled water. This

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procedure was repeated four times to remove excess surfactant. After vacuum-drying at 60 °C for 6 h and then at room temperature for 48 h, 241 mg of microspheres was obtained at a yield of 96% with respect to P*t*BA-*b*-PCEMA, suggesting a low degree of surfactant incorporation. This low degree of surfactant incorporation has been also confirmed by the lack of PGMA peaks from the ^{13}C solid-state NMR spectrum of the microspheres.

In variation 2, 10 mL of toluene rather than dichloromethane was used to disperse the diblock. The emulsion was prepared by mixing the oil phase with 100 mL of methanol/water (2/98) containing the surfactant under mechanical stirring at 1400 rpm at 80 °C in a three-neck round-bottomed flask. After 10 min, the temperature was raised to 90 °C to distill ~85% of the toluene. The spheres were then irradiated to obtain a PCEMA double-bond conversion of 26%.

The *tert*-butyl groups of P*t*BA were removed at room temperature by stirring 50 mg of the microspheres with 4 mL of trifluoroacetic acid (CF_3COOH) in 20 mL of dichloromethane for 1 h. The quantitative removal of the *tert*-butyl groups was confirmed from the disappearance of the *tert*-butyl rocking peak at 846 cm^{-1}.

SEM and TEM Studies. To obtain scanning electron microscopic (SEM) images of the microspheres, the powder was spread on a conductive carbon adhesive tape. The spheres were then sputter-coated with a ~6 nm Au−Pt layer and scanned using a SEI XL30 ESEM instrument operated at 20 kV. To obtain the internal structures of the microspheres using transmission electron microscopy (TEM), the microspheres, 5 mg, were mixed with 0.05 mL of a 20 wt % polystyrene (Aldrich, $\bar{M}_w = 20\,000$ g/mol, $\bar{M}_w/\bar{M}_n = 5$) solution in THF. The mixture was spread on a glass plate and dried in air overnight to obtain a film that was ~300 μm thick. After drying at 70 °C for 48 h, the film was sandwiched between two polystyrene plates heated at 110 °C, ~3 mm thick, and then microtomed (Ultracut-E, Reichert-Jung) to obtain 50 nm slices. The slices were picked up with Formvar-coated copper grids and stained with OsO_4 vapor for 12 h before viewing under a Hitachi-700 electron microscope operated at 75 kV. No staining was used for thin sections containing *tert*-butyl-removed microspheres.

Cu^{2+} Sequestering. For kinetic studies, 10.0 mg of microspheres was stirred with 10.0 mL of a 250 ppm Cu^{2+} or 628 ppm $CuSO_4$ solution in water. At different times, the microspheres were separated from the supernatant by centrifugation followed by filtration through 0.45 μm filters. The resultant solution was then analyzed for Cu^{2+} concentration by spectrophotometric analysis at 800 nm. The final and initial Cu^{2+} concentrations were compared to calculate the amount of Cu^{2+} uptaken by the microspheres. For isothermal studies, 2.0 mg of Cu^{2+} and 10.0 mg of microspheres were equilibrated in a predesignated amount of water for at least 24 h. The supernatant, depending on Cu^{2+} concentration, was then concentrated or used directly for Cu^{2+} concentration measurement.

Results and Discussion

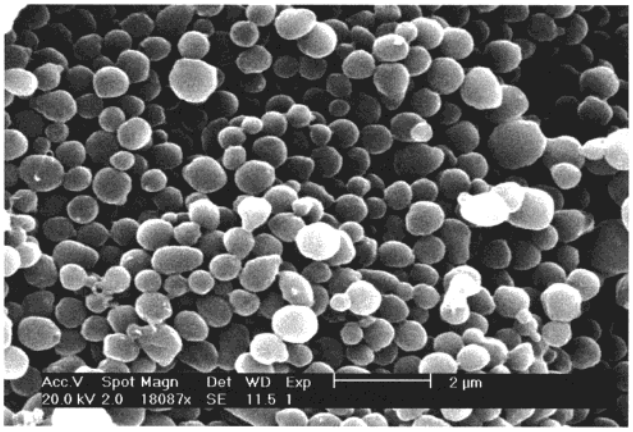

Figure 1. SEM image of variation 1 microspheres.

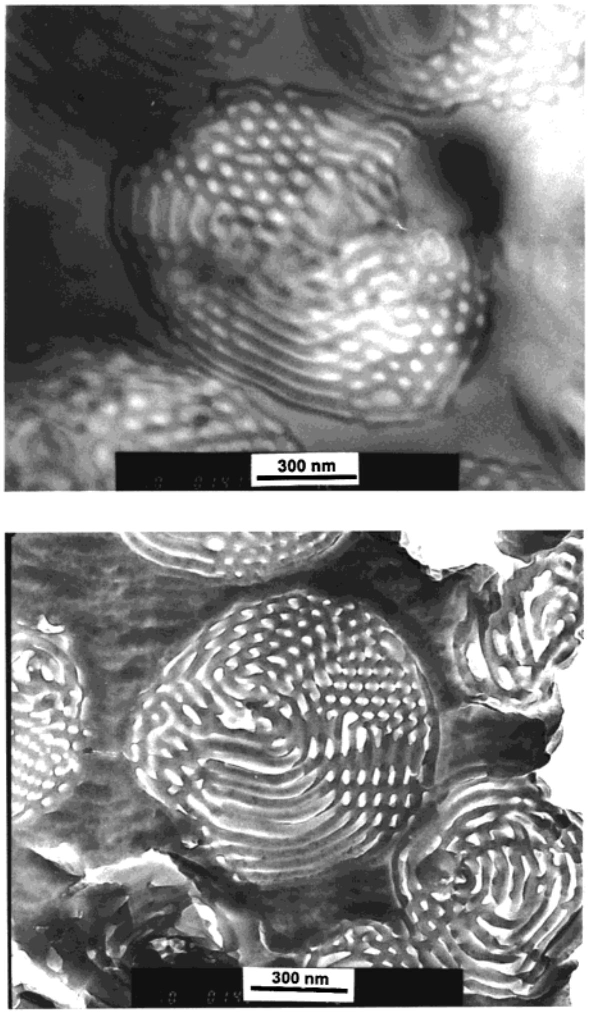

Figure 2. TEM images of thin setions of variation 1 microspheres before (a, top) and after (b, bottom) *tert*-butyl removal.

Figure 1 shows a SEM image of microspheres obtained from variation 1 of the emulsion method. Most of the variation 1 particles are spherical and seem to have a narrow size distribution. Figure 2a presents a TEM image of a slice of such microspheres. The hexagonally packed light circles or ellipses at the upper left corner of the center sphere represent P*t*BA cylindrical domains cut approximately perpendicular to the cylinder axis. The average diameter of the light ellipses measured along the short axes is ~36 nm. This is the cylinder diameter, because an elliptic projection arises from a cylinder pointing slightly off the normal direction of an image with the length of the long axis offering a measure for the degree of cylinder slanting. When the cylinders lie in the image plane, the cylinders appear as light stripes as seen in the central bottom part of the central sphere of Figure 2a. The light stripes bend following the surface curvature.

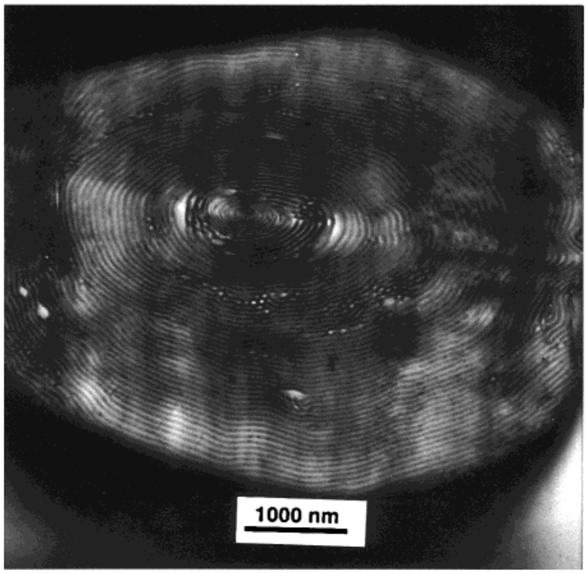

Figure 3. TEM image of a thin section of a variation 2 microsphere.

Elliptic or circular defects much larger in size than P*t*BA domains are sometimes found inside the microspheres. An example of such a defect is seen in the sphere at the top right of Figure 2a. Because of its dark shade, the defect cannot be a void or a domain consisting of a segregated P*t*BA homopolymer. It can plausibly consist of a segregated PCEMA homopolymer, *h*PCEMA. While some *h*PCEMA may be present in PCEMA-*b*-PGMA due to the deactivation of some chains upon the addition of the second monomer during polymer synthesis, such *h*PCEMA should mix well with the PCEMA block of P*t*BA-*b*-PCEMA. On the basis of these considerations, we are presently not sure of the cause and composition of these defects.

We also examined the morphology of the diblock in bulk following methods described previously.[7] P*t*BA formed cylindrical domains with a diameter of ~36 nm in bulk as well. This is reasonable for this diblock with a P*t*BA volume fraction of 36%.[7] Thus, neither copolymer confinement in the restricted volume of a microsphere nor the microsphere preparation process affected block segregation pattern in this case. The major difference between the morphologies of the diblock in a microsphere and in bulk lies in the degree of ordering. In a microsphere, the cylinders are packed with a shorter-range order, because cylinder orientation varies from region to region in a sphere of the size of ~2 μm. Also, the cylinders bend more. In bulk, the cylinders are mostly straight, and their orientations are the same inside grains of micrometers to tens of micrometers.[7]

A SEM study revealed that the variation 2 spheres were larger and had a wider size distribution. More interesting is, however, the change in the internal structure of the spheres as shown in Figure 3. PCEMA and P*t*BA now form alternating concentric layers with a periodicity of ~53 nm. While a change in casting solvent and annealing temperature was known to affect the morphology of block copolymers,[1] we are not sure of the exact cause for the shift to lamellar morphology in this case.

Figure 2b shows a TEM image of a thin section of variation 1 microspheres after treatment with CF_3COOH. The sample was not stained with OsO_4, and the contrast between the light and dark domains is, however, improved relative to that in Figure 2a. These suggest that the light domains are now void or much less dense in polymer than the dark domains. The diameter of the light ellipses along the short axis is ~30 nm, which is smaller than 36 nm observed for the original P*t*BA domains. This smaller diameter is justified by the fact that only 45 wt % of the P*t*BA domains was removed by hydrolysis. We also made several attempts to obtain TEM images of hydrolyzed variation 2 spheres but found only void-ridden thin PS slices presumably because microspheres with layers of void space inside could not survive the microtoming step.

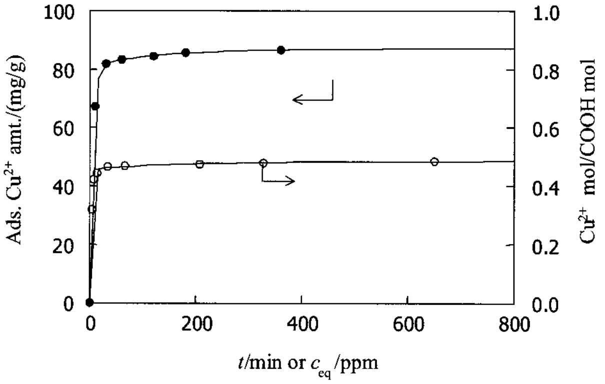

Figure 4. Kinetic (●) and isothermal (○) curves of Cu^{2+} adsorption by variation 2 microspheres in water.

We also performed SEM examination of the microspheres after *tert*-butyl removal. The variation 1 spheres had no shape change after treatment with CF_3COOH. Many of the variation 2 spheres disintegrated after *tert*-butyl hydrolysis, as witnessed by the presence of plate-like pieces in the SEM images. Only a fraction, ~30%, of the spheres survived the treatment. Regardless of their shapes, the hydrolyzed variation 2 particles dispersed well in water.

Figure 4 shows a set of kinetic data of Cu^{2+} uptake by variation 2 spheres after *tert*-butyl removal. It took ~30 min to reach the saturation uptake of ~80 mg of Cu^{2+} for each gram of microspheres. Assuming that most of the unbound surfactant was removed during the microsphere rinsing step after their preparation and the weight fraction of surfactant in the spheres was low, the isothermal data could also be presented in terms of moles of Cu^{2+} uptaken by each mole of carboxyl groups. The binding of ~0.50 Cu^{2+} ion, at saturation, by each carboxyl group is in agreement with the expected stoichiometry and suggests the accessibility of all carboxyl groups to Cu^{2+}. We have also obtained similar kinetic and isothermal data of Cu^{2+} adsorption by the variation 1 spheres under similar conditions. Because of the less open structure of the PAA domains, ~170 min was required to reach the saturation uptake of ~80 mg Cu^{2+} for each gram of microspheres.

The spheres containing PAA channels or layers, once dispersed by mechanical agitation, do not settle completely in water for 2–3 days. Such spheres also sequestered Pd^{2+} and Mn^{2+} from water. They should uptake other multivalent cations as well. Thus, they may be used in the "expensive" reclamation of water contaminated with heavy metals. More practically, one should use the PAA-lined channels or layers to produce nanosized catalysts, semiconductors, or magnetic particles.

Conclusion

We have prepared block copolymer microspheres with intricately segregated internal domains. The structure of such spheres resemble those of silica particles prepared by Yang et al.,[9] Fowler et al.,[10] or Lu et al.[11] Alternatively, the microspheres resemble diblock microdroplets prepared by Thomas et al.[12] from an aerosol technique or the meso-sized crystal-like structure of hexagonally packed hollow hoops prepared by Zhang et al.[13] by solution self-assembly of a diblock copolymer. This approach should be applicable to the preparation of various hydrophobic di-, tri-, or multiblock copolymers. One can also imagine the preparation of microspheres from copolymers containing exclusively hydrophilic blocks using the inverse water-in-oil emulsion method.

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