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Four-Phase Triple Coaxial Cylindrical Microdomain Morphology in a Linear Tetrablock Quaterpolymer of Styrene, Isoprene, Dimethylsiloxane, and 2-Vinylpyridine

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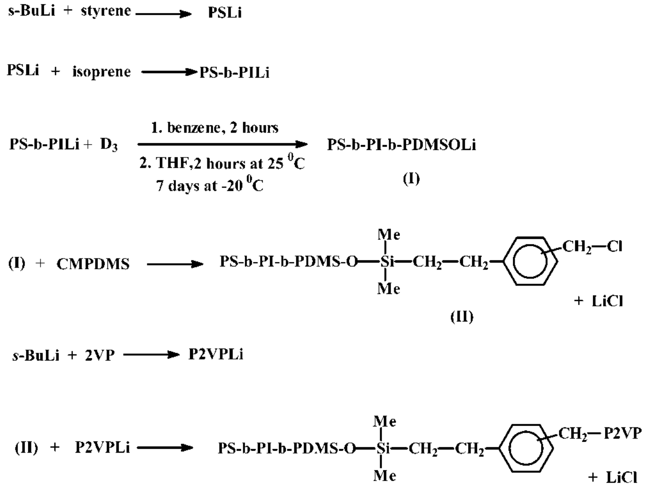
It is well-known that addition of a third block component to a diblock copolymer tremendously increases the variety of microdomain morphology, as reported by many researchers for various triblock terpolymers.[1−7] What do we expect if one more block component is added to a triblock terpolymer? Will it further increase the variety of the microdomain morphology, or will it change the morphology in a different way from that observed in triblock terpolymers? To our knowledge, no investigation on the microdomain morphology of tetrablock quaterpolymer has been reported yet.

Tetrablock quaterpolymers are just the first members of the big family of multicomponent multiblock copolymers (MMCP). These materials have the potential to generate a variety of well-controlled multiphase microdomain structures with nanosized structural units in bulk, thin films or to provide supramolecular structures with a mesoscopic length scale. In principle, they will be able to undergo order−order transition and order−disorder transitions leading to even more rich varieties of the microdomain structures, whose potential applications cannot be easily imagined on the basis of contemporary state of art. They could be used, for example, as multifunctional sensors or as multiselective catalysts for sequential or simultaneous chemical reactions of various kinds.

Transmission electron microscopy (TEM) of ultrathin sections is a common technique widely employed to observe microdomain structures in diblock or triblock copolymers as well as in triblock terpolymers. In most cases, one or more selective staining agents are necessary for observation under TEM to give a contrast among the microdomains composed of different components, because most polymers do not have any contrast to the others by themselves. Therefore, the constituent polymers in triblock terpolymers studied so far have been selected carefully so that the three microphases have different contrast and can be distinguished by TEM. The constituent polymers chosen in our tetrablock quaterpolymer were polystyrene (PS), polyisoprene (PI), poly(dimethylsiloxane) (PDMS), and poly(2-vinylpyridine) (P2VP). Because the four components are connected in this order (PS-*b*-PI-*b*-PDMS-*b*-P2VP), the four microphases can be clearly distinguished by TEM when the two-step selective staining was applied.

Scheme 1



The synthesis of PS-*b*-PI-*b*-PDMS-*b*-P2VP was based, on one hand, on recent advances in the controlled high-vacuum anionic polymerization of hexamethylcyclotrisiloxane[8,9] (D_3) and, on the other hand, on the selective linking of PDMSLi with the chlorosilane group of the heterofunctional linking agent chloromethylphenylethenyl dimethylchlorosilane (CMPDMS).[10] The basic reactions for the synthesis are given in Scheme 1.

The synthetic procedure was monitored by size exclusion chromatography (SEC) (Figure 1). The final product was purified from the excess of the P2VP, intentionally added for completion of the reaction and from the P2VP dimer, produced by reaction of P2VPLi with the remained quantity of the coupling agent, by repeated fractionation with the toluene/methanol system. The intermediate and final products were extensively characterized by SEC, membrane osmometry (MO), and ^{1}H NMR spectroscopy. The results are given in Figure 1.

The film specimen of PS-*b*-PI-*b*-PDMS-*b*-P2VP was obtained by casting 7 wt % polymer solution in toluene at room temperature over 1 week. The cast film was further dried under vacuum at room temperature overnight. Then a part of the as-cast film was annealed at 150 °C for 12 h under vacuum.

The as-cast and annealed film specimens were then subjected to ultramicrotoming into ultrathin sections of ca. 50−80 nm thickness with glass knives by using a Reichert Ultracut N ultramicrotome with an FC-4E cryo-sectioning unit. Sectioning was performed at −80 °C. The ultrathin sections were collected on 600 mesh copper grids without supporting film and brought back to room temperature. Osmium tetraoxide (OsO_4) and methyl iodide (CH_3I) were used as the staining agents for TEM observation. OsO_4 staining was performed by exposing the grids with the ultrathin sections in a glass bottle to OsO_4 vapor over 2% aqueous solution of OsO_4 for about 1 h at room temperature. OsO_4 has been reported to stain PI very dark and P2VP slightly dark.[4] The OsO_4-stained ultrathin sections on the grids were then stained with CH_3I vapor in a glass bottle for about 6 h at room temperature. CH_3I is supposed to stain only P2VP dark.

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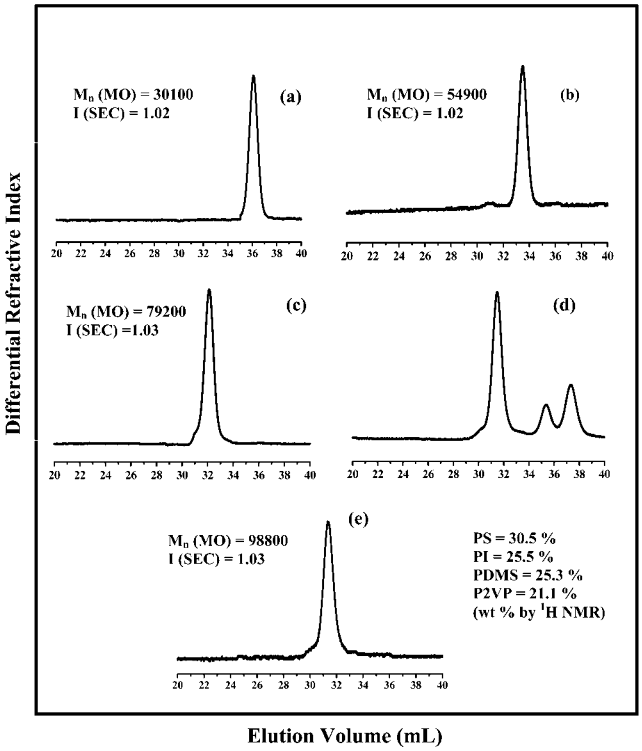

Figure 1. Size exclusion chromatograms of the PS block (a), PS-*b*-PI diblock copolymer (b), PS-*b*-PI-*b*-PDMS triblock copolymer (c), the raw products (d), and the fractionated tetrablock quaterpolymers (e).

The unstained specimen and stained specimens were subjected to TEM observation. A JEOL JEM2000FX was used for TEM observation. The accelerating voltage used was 120 kV throughout the observation. The TEM images were recorded with photographic films, digitized with a scanner, and visualized with Adobe Photoshop.

Parts a (unstained), b (stained), and c (stained) of Figure 2 are the transmission electron micrographs of PS-*b*-PI-*b*-PDMS-*b*-P2VP cast from toluene solution and annealed at 150 °C for 12 h. Even the unstained specimen gives a good contrast for TEM observation due to the Si atoms contained in PDMS component as shown in Figure 2a. Figure 2a is considered as a cross-sectional image of a cylindrical structure cut normal to the cylindrical axis, because other areas of the ultrathin section show stripe patterns. The cylinders are packed in a hexagonal array. Only the periphery of the cylinders appears dark, suggesting that the PDMS component forms layerlike domains around the cylinders (called hereafter “cylindrical shell”). The outsides of the shells seem to have hexagonal shapes. The cores of the cylinders appear less dark, but darker than the matrix, implying that they are composed of a different component from PDMS. The cores of the cylinders seem to have round shape.

Figure 2b shows a TEM image of the specimen stained with OsO_4. The PI domains stained very dark with OsO_4 appear to have a form of hexagonal cylindrical shell, similar to those observed for the PDMS domains in Figure 1a, and also form layerlike structure, both inside and outside being hexagon in this case. Close observation of the TEM image informs us the existence of less dark layers inside of the PI shells, suggesting that the PDMS shells observed in Figure 2a exist inside the PI shells. The contrast obtained by Si atoms in PDMS is much less than that obtained by Os atoms in the PI stained with OsO_4. The cores of the cylinders are bright, implying that they are composed of a different component than PI or PDMS. According to the sequence of PS-*b*-PI-*b*-PDMS-*b*-P2VP, the cores of the cylinders must be composed of P2VP, and the bright matrix must be the PS microphase. Now the volume fraction of the “three-phase” cylinders is dominating that of the matrix phase, and their hexagonal shape is clear.

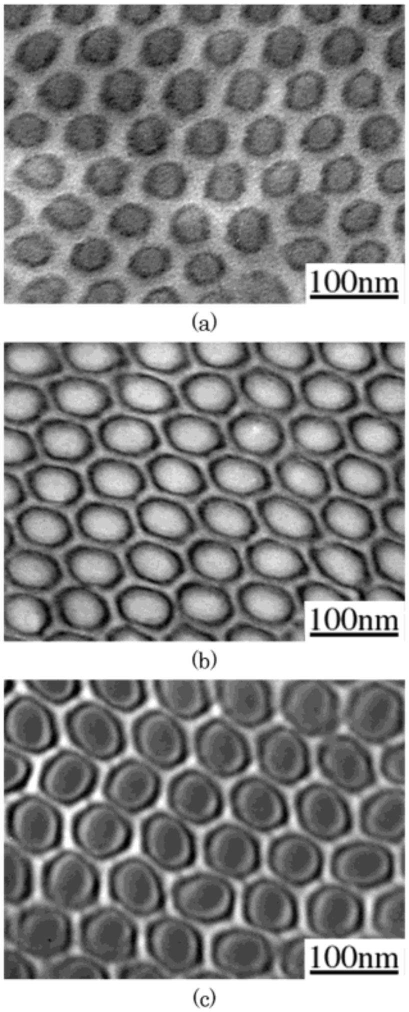

Figure 2. (a) Electron micrograph of the annealed PS-*b*-PI-*b*-PDMS-*b*-P2VP without staining, (b) stained with OsO_4, and (c) stained first with OsO_4 and subsequently with CH_3I.

Figure 2c is a TEM image of the specimen stained first by OsO_4 and subsequently by CH_3I. In addition to the cylinders appeared in Figure 2b, the cores of the cylinders stained by CH_3I appear very dark as well, exhibiting the structure of the triple coaxial cylinders. Now it is unequivocally clarified that the cores of the cylinders stained by CH_3I are composed of P2VP and that the bright matrix is the PS microphase.

Consequently, four phases of the microphase-separated structure in the PS-*b*-PI-*b*-PDMS-*b*-P2VP tetrablock quaterpolymer are unequivocally confirmed. The PI, PDMS, and P2VP microphases form triple coaxial cylinders with a hexagonal shape packed in a hexagonal array in the PS microphase, which forms the honeycomb-shaped matrix, as shown in Figure 3. The diameter of the coaxial cylinder is ca. 60 nm, and the distance between the cylinder axes is ca. 70 nm.

In the as-cast specimen, a four-phase structure was observed, similar to that of the annealed specimen.

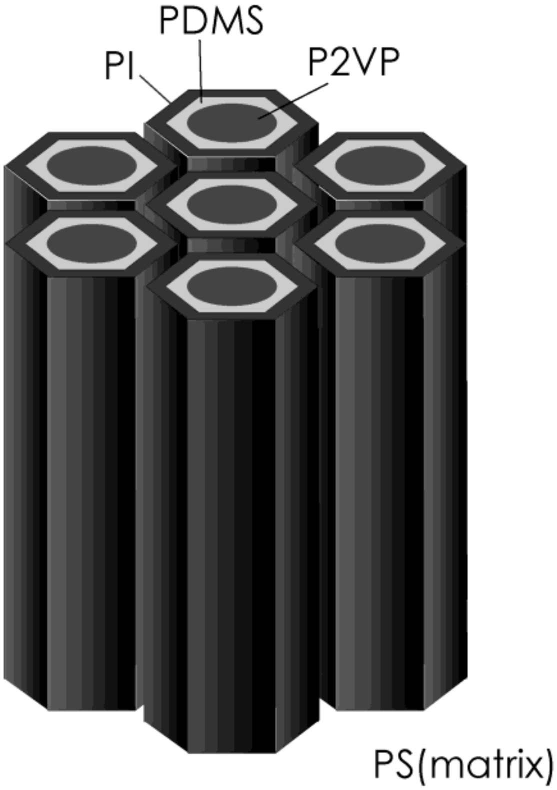

Figure 3. Schematic illustration of the model for the hexagonal triple coaxial cylinder structure observed in PS-*b*-PI-*b*-PDMS-*b*-P2VP.

However, the cylindrical structure of the as-cast specimen is more irregular than that of the annealed specimen, and some distortion of the hexagonal shape of the cylinder was observed. The distortion is considered to result from the strain induced by the casting process; i.e., the film was cast in a Petri dish so that shrinkage of the film due to the solvent evaporation occurred only along the thickness direction.

Usually, it is not easy to obtain an equilibrium microdomain structure in solids or films for a triblock terpolymer or tetrablock quaterpolymer with relatively high molecular weight, because a nonselective and good solvent for all the component polymers does not exist for most cases. In fact, various microdomain morphologies were observed in the films of PS-*b*-PI-*b*-PDMS-*b*-P2VP cast from the solutions in various solvents although the results are not shown here.[11] Nevertheless, the hexagonal coaxial cylinders are considered to be close to the equilibrium morphology. This is because the regularity of the cylindrical structure increases with annealing, whereas the other morphologies tended to change dramatically and their regularity to be even lost upon annealing. This is best interpreted as a consequence of the nonequilibrium morphologies in the as-cast films being observed on a path way approaching toward equilibrium morphologies.

Hexagonal coaxial cylindrical microdomain morphology has been observed for a triblock terpolymer consisting of PS, PI, and P2VP by Gido et al.[12] The explanation for the hexagonal shape in the outside of the PI cylinder shells was given in their paper. They attributed the shape to the optimum packing of the block chains having their one ends at the centers of the cylinders and the other ends at the nearly equal distance from the centers. As another important physical factor, we may think of the optimum packing of the matrix forming PS blocks chains whose phase volume is small compared with the volume of the three-phase cylinders.

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