Observation of Four-Phase Lamellar Structure from a Tetrablock Quarterpolymer of the ABCD Type

A. Takano,*,† K. Soga,† T. Asari,† J. Suzuki,‡ S. Arai,§ H. Saka,⊥ and Y. Matsushita†

Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan; The Computing Research Center, High Energy Accelerator Research Organization, 1-1 Oho, Tsukuba 305-0801, Japan; Center for Integrated Research in Science and Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan; and Department of Quantum Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

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Introduction. Block copolymers with incompatible components are known to form microphase-separated structure in the condensed system by combination of intramolecular phase separation and self-assembling nature.[1−4] For example, diblock copolymers of the AB type[5,6] or triblock terpolymer of the ABA type[7] show various two-phase structures, while triblock terpolymers of the ABC type also reveal a variety of three-phase structures.[8−12]

Microphase-separated structure for a four-component pentablock quintopolymer of the ABA′CA type, where A denotes polyisoprene (I) and A′ denotes polybutadiene (B), was investigated, and essentially three-phase structure was observed by TEM[13] since polyisoprene and polybutadiene are partially compatible with each other so that two polymer chains could be mixed up in addition to the technical reason that the I-rich phase and B-rich phase were not distinguished. Furthermore, recently coaxial cylindrical microdomains from three components in the matrix of a fourth one were observed for a tetrablock quarterpolymer of the ABCD type.[14] Then, what kind of structure can be formed from a tetrablock quarterpolymer of the ABCD type if polymer components A and D are compatible with each other? Poly(isoprene-*block*-styrene-*block*-2-vinylpryidine-*block*-4-trimethylsilylstyrene) (ISPT) is the present case since I and T are compatible.[15]

There are two choices to show self-assembled periodic structure. Assume lamellar structures for simplicity. One is actually a three-phase structure if the A block and D block belonging to different molecules can be mixed together, which leads to form the third single (A + D) phase in addition to B and C phases.[16,17] Consequently, the quarterpolymer is aligned in a head-to-tail manner, and so it forms an asymmetric three-phase structure whose repeating unit is −(DA)BC−, as schematically shown in Figure 1a. The other one consists of a head-to-head alignment of ABCD molecules for the sake of segregation between A block and D block chains. As a result, they produce a symmetric four-phase structure whose repeating unit is −(ABCDCB)−, which is also shown in Figure 1b.

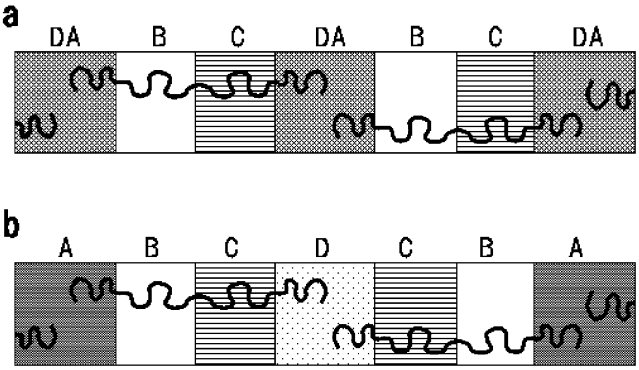

Figure 1. Schematic drawings of two possible alignments of ABCD tetrablock quarterpolymer in lamellar microdomains: (a) −(ABCD)$_n$− and (b) −(ABCDCB)$_n$−.

The equilibrium microphase-separated structure of ISPT has been observed in this study to conclude either one-way or two-way alignment can be attained for this copolymer. In the latter case, furthermore, the key technology for confirmation is the recognition of four different phases, especially in transmission electron microscopy.

Experimental Section. a. Sample Preparation. The tetrablock quarterpolymer was synthesized on the basis of anionic polymerization. First, the triblock terpolymer of poly(isoprene-*block*-styrene-*block*-2-vinylpryidine) (ISP) was prepared by a three-step sequential monomer addition in tetrahydrofuran with cumylpotassium as an initiator at −78 °C and kept as a living polymer under vacuum. Second, poly(4-trimethylsilylstyrene) having a 1,1-diphenylethylene type vinyl group at one end (T) was synthesized also in tetrahydrofuran with *sec*-BuLi followed by end-capping with 1,1-diphenylethylene, subsequently terminating by 1-[3-(chloropropyldimethylsilylphenyl)-1-phenyl]ethylene.[18] A living polymer of ISP was coupled with end-functional T, resulting in producing an ISPT tetrablock quarterpolymer. The desired ISPT quarterpolymer was isolated from the crude coupling product by size-exclusion chromatography (SEC) fractionation using a HPLC system of Tosoh Co.

b. Molecular Characterization. The number-average molecular weight (M_n) was obtained by a Hewlett-Packard high-speed membrane osmometer type 502 in toluene at 37 °C. Apparent molecular weight hetrogeneities, M_w/M_n, were determined by the SEC system of Tosoh Co. with a RI-8012 differential refractive index detector, a UV-8011 ultraviolet spectroscopic detector, and a set of three G4000HHR columns with 300 mm length and 7.8 mm i.d. ^{1}H NMR spectra were measured with a Varian Unity Inova 500 MHz NMR spectrometer at 500 MHz to obtain the composition of the block copolymer samples. Chemical shifts were referred to chloroform in chloroform-*d*.

c. Transmission Electron Microscopy (TEM). The sample film was obtained by solvent casting from a dilute solution of tetrahydrofuran and dried and annealed at 150 °C for 2 days under vacuum. The sample film was stained with osmium tetroxide and cut into ultrathin sections with thickness of ca. 50 nm by an

* To whom correspondence should be addressed.
† Department of Applied Chemistry, Nagoya University.
‡ High Energy Accelerator Research Organization.
§ Center for Integrated Research in Science and Engineering, Nagoya University.
⊥ Department of Quantum Engineering, Nagoya University.

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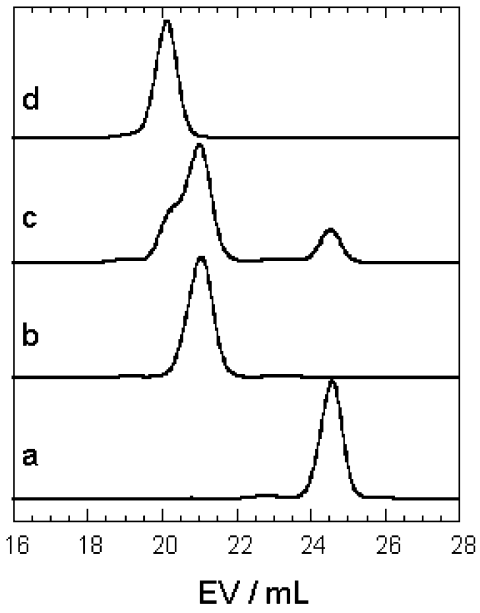

Figure 2. GPC chromatograms of (a) T, (b) ISP, (c) as-coupled product in between T and ISP, and (d) the fractionated product.

ultramicrotome, Ultracut UCT of LEICA. The microphase-separated structures were observed by a transmission electron microscope (Hitachi model H-800) under an acceleration voltage of 100 kV. Elemental mapping images to search the T phase were observed by a transmission electron microscope (Hitachi model H-9000) under an acceleration voltage of 300 kV with an imaging filter (Gatan, model 678), which was positioned at the end of the TEM.[19,20] To obtain the elemental mapping for silicon atoms, the three-window method was adopted.

d. Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) was performed by using a SAXS apparatus at the synchrotron radiation facility, installed in beamline 15A at the Photon Factory in Tsukuba, Japan. The wavelength of the monochromated beam was 0.150 nm; a point-collimated beam with size of 0.4 mm × 0.7 mm was irradiated on the cut and stacked film specimen along the direction parallel to the film surface.

Results and Discussion. a. Sample Preparation and Characterization. Figure 2 compares SEC chromatograms of the T polymer (a) and that of the ISP triblock terpolymer (b) as precursors. Both polymers have unimodal and symmetrical curves, and they suggest narrow molecular weight distributions. The chromatogram in Figure 2c shows the coupling product of the T polymer with living ISP triblock terpolymer. A large shoulder of ISPT tetrablock quarterpolymer appeared at the higher molecular weight side of the ISP triblock terpolymer peak. Therefore, SEC fractionation of the coupling product was performed to isolate the ISPT tetrablock quarterpolymer sample. The SEC chromatogram of the fractionated product is shown in Figure 2d, which gives a unimodal and symmetrical curve, reflecting a narrow molecular weight distribution.

The molecular characteristics of these polymers are listed in Table 1. Although the molecular weight of the fractionated quarterpolymer sample was not determined directly, the number-averaged molecular weight was estimated to be 133K from M_n of ISP triblock terpolymer precursor, 110K, which was measured by osmometry, and the sum of weight fractions of three components,

Table 1. Molecular Characteristics of Obtained Polymers

sample	$10^{-4}M_n$ [a]	M_w/M_n [c]	vol fraction[d] $\phi_I:\phi_S:\phi_P:\phi_T$
ISP	11.0	1.03	
T	3.0	1.02	
ISPT	13.3[b]	1.03	0.25:0.23:0.32:0.20

[a] Determined by osmometry. [b] Estimated from M_n(ISP) by osmometry and ϕ_{ISP} by ^{1}H NMR. [c] Apparent molecular weight distribution determined by SEC. [d] Determined by ^{1}H NMR.

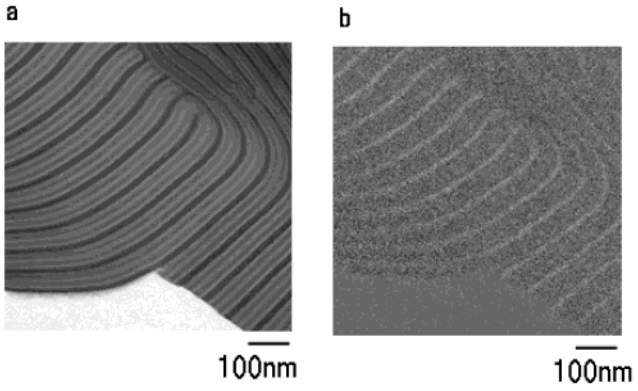

Figure 3. Transmission electron micrographs of the ISPT tetrablock quarterpolymer: (a) bright-field image and (b) elemental mapping image for silicon atoms.

0.82. The latter value was calculated from the measured volume fractions in Table 1 and the bulk densities of four polymer components, i.e., 0.926, 1.05, 1.14, and 0.930 for homopolymers I, S, P, and T, respectively. This value, 133K, is very close to the sum of measured M_n, 140K, that is, 110K for ISP triblock terpolymer and 30K for end-functionalized poly(4-trimethylsilylstyrene). This result shows that the fractionated product is composed mainly of the ISPT tetrablock quarterpolymer, though it may contain a small amount of the ISP triblock terpolymer.

b. Morphological Investigation. Figure 3a shows an example of a bright field transmission electron micrograph of the ISPT tetrablock quarterpolymer. Obviously, the sample possesses lamellar structure as if it includes three phases, whose repeating unit is −black−white−gray−white−gray−white−. Since the sample was stained with osmium tetroxide, each black stripe represents the I phase, the white one the S or T phase, and the gray one the P phase.[10] To confirm the correspondence of the white region in the middle of the black region in TEM to the exact polymer phase, an advanced TEM observation was carried out by way of silicon mapping using the energy-filtered mode.[19,20] Figure 3b shows an energy-filtered silicon-mapped image for the same sample location as in Figure 3a. By careful comparison of two figures, one notices that each white phase sandwiched with two gray phases in Figure 3a corresponds to the brighter phase in Figure 3b, which associates with the T phase because it should give a brighter image by silicon mapping.[18] Thus, the fourth phase, poly(4-trimethylsilylstyrene), was clearly distinguished from the polystyrene phase by this procedure. By combining the information in Figure 3a,b, we are able to assign the structure of this copolymer as a four-phase six-layer lamellar structure as shown in Figure 1b, which is the first observed structure for the multicomponent polymeric material.

In addition, Figure 4a shows a small-angle X-ray scattering intensity curve. Many peaks can be seen periodically along with the horizontal axis **q** (= 4π sin

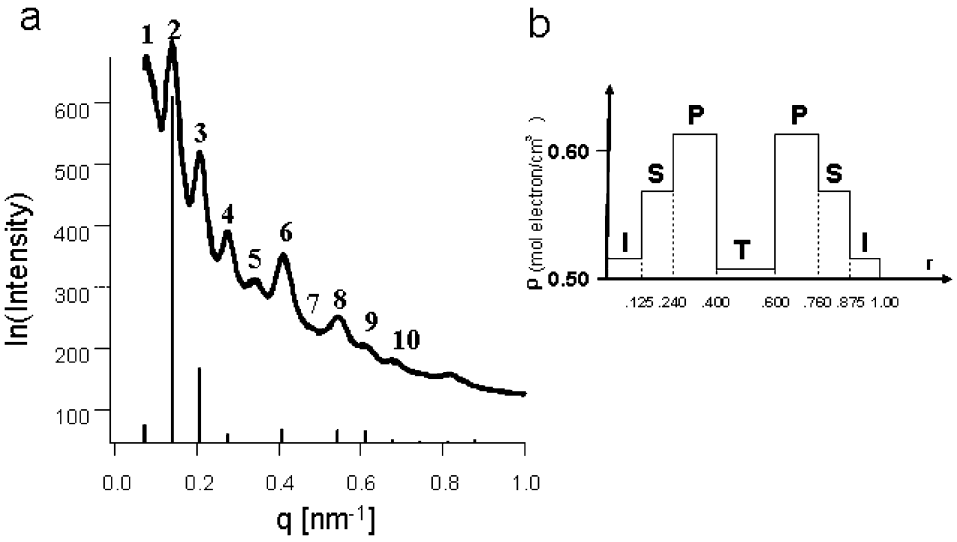

Figure 4. (a) SAXS diffraction pattern of ISPT tetrablock copolymer. Vertical bars express the calculated intensities for a lamellar structure aligned as $-(ISPTPS)_n-$. The integers at the top of the observed intensity correspond to the Miller index h. (b) Simplified representation for electron density profile of ISPT tetrablock quarterpolymer in a lamellar structure. Electron density values are 0.517, 0.565, 0.607, and 0.507 mol electron/cm^3 for ρ_I, ρ_S, ρ_P, and ρ_T, respectively.

θ/λ), which is the scattering vector, where λ and 2θ are the wavelength of X-ray and the scattering angle, respectively. From this figure, one notices the first peak is very weak, which we have never experienced so far for diblock copolymers and triblock terpolymers. Figure 4b exhibits the electron density profile assuming the cross section of the lamellar structure. At the bottom of Figure 4a, the relative diffracted intensities are shown as vertical bars, which are associated with the square of the structure factor at several (h00) diffraction planes in actually integer order calculated from the electron density profile in Figure 4b and the volume fractions of component polymers in Table 1. The calculated ones well explain the observed relative intensity heights up to at least the tenth one. This result is quite consistent with that from transmission electron microscopy. The latter information in the reciprocal lattice space is another strong evidence to confirm four-phase structure.

Thus, four-phase six-layer lamellar structure has been observed very clearly for four-component polymeric material for the first time by both TEM observation including energy-filtered mode and small-angle X-ray scattering experiment.

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