Preparation and Characterization of a Styrene−Isoprene Undecablock Copolymer and Its Hierarchical Microdomain Structure in Bulk

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ABSTRACT: A two-component multiblock copolymer with undecablock—two of them on both chain ends are long and nine of them are short—was successfully prepared by anionic polymerization using the six-step sequential monomer addition technique. Polymer components are polystyrene (S) and polyisoprene (I), its total molecular weight is 275K, and the overall S/I volume ratio is 0.70/0.30. Microphase-separated structure of the copolymer was observed by transmission electron microscopy and small-angle X-ray scattering, and it was confirmed that the copolymer forms a complex lamellar structure; its long period is 45 nm, which is composed of one thick lamellar domain formed by long polystyrene chains and I−S−I three thin lamellar domains, the length of the short period for I−S lamellae being about one-third of the longer period. This fact shows short block chains at the center favorably adopt a loop conformation over a bridge one. This unique lamellar structure having two length scales must be the first experimentally observed simple hierarchical structure for the block copolymer where the component polymers are connected by covalent bonds.

I. Introduction

Morphological features of block copolymers have been extensively investigated for the past four decades, and this field has been kept interesting and is still developing.[1−3] For example, as for the simplest two-component block copolymers of the AB type, it is well-established that they form self-organized structures such as spherical, cylindrical, and lamellar microdomain structures, etc., depending on their A/B volume fraction ratios. In recent years, the gyroid structure, which appears in narrow composition range in between cylindrical structure and lamellar one, was confirmed to be a thermodynamically stable structure,[4,5] it being attractive in application field since both two domains are three-dimensionally continuous.

In addition to a simple AB system, somewhat complex systems such as ABA triblock copolymers,[6−9] three-component ABC triblock copolymers,[10−15] star-shaped molecules of the $(AB)_n$ type,[16,17] $(AB)_n$ two-component multiblock copolymer system,[18] two-component pentablock copolymer of the ABABA type,[19] and heptablock copolymer of the ABABABA type[20] have been widely studied, and many static and dynamic structures and the related properties have been observed depending on their molecular architectures. Furthermore, very characteristic structures from ABC star-branched polymers have been studied by Hadjichristidis et al.[21,22] and also by Takano et al.[23,24] However, most of the copolymers show single periodicity except several peculiar examples, which showed hierarchical morphology.[13,15] Block copolymer blend systems such as an ABC/AC triblock/diblock blend[25] and an ABC-1/ABC-2 triblock copolymer blends[26,27] with different molecular structures gave new types of self-assembly manners; that is, the former show noncentrosymmetric superlattice structure, while the latter exhibits unique hierarchical structure. Furthermore, block copolymer having semicrystalline polymer components showed complex structure with quite different length scale periodicity.[28,29]

It is known that polymeric materials tend to form hierarchical structures, and the study on hierarchy of block copolymers was introduced by ten Brinke et al.[30−32] They prepared a graft copolymer by introducing side groups onto polymers by noncovalent hydrogen bond. That is, poly(4-vinylpyridine) (P4VP) and pentadecylphenol (PDP) was combined, where a hydroxyl group in PDP plays the role of proton donor and a nitrogen atom on a pyridine ring is a proton acceptor. Therefore, PDP can be easily grafted as short side chains on a P4VP block chain of poly(styrene-*block*-poly(4-vinylpyridine)). The morphology of this three-component system was observed, and it was confirmed that this molecule shows two different lengths scale periodicity at the same time; i.e., one is the normal microdomain spacing from PS-*b*-P4VP, and the other one is subspacing from the P4VP−PDP complex. Asari et al. have recently found very interesting hierarchical structures[33] with two kinds of periodicity for a complex blend system of the AB/CD type including hydrogen-bonding interaction, while Adams et al. also reported on diblock copolymers having liquid crystalline side chains.[34] In their researches, however, hierarchical periodicity was formed in perpendicular direction to each other in addition to the fact that the periodic length is short since the molecular weight of the base block copolymer is low.[35]

The materials with two quite different periodicity along the same axis can be conceived to be a useful photochromic crystal.[36] So as to form such periodic structure, a complex block copolymer with high molecular weight and having different block lengths is desirable. A theoretical work treated this problem using a self-consistent theory for a linear−alternating nonablock copolymer system, and the structures with two length scale periodicity were predicted.[37] In this paper, there-

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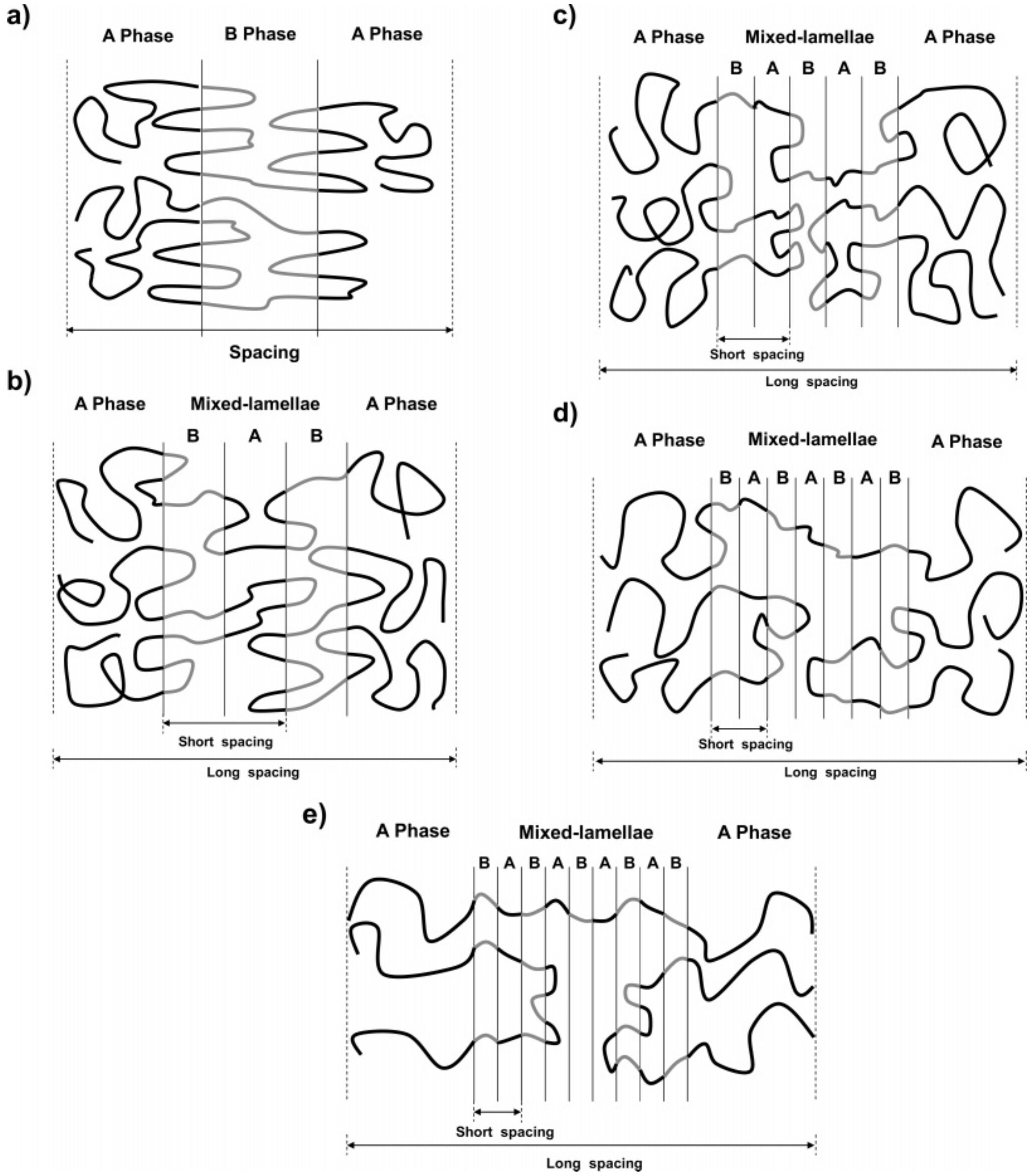

Figure 1. Schematic illustration of possible self-assembled structures of undecablock copolymers. The numbers of thin microdomains included in a repeating unit are (a) 1, (b) 3, (c) 5, (d) 7, and (e) 9.

fore, we introduce a two-component undecablock copolymer, having two long chains on both ends and nine short chains in the middle to form hierarchical structure having two length scale periodicity along the same direction. Its possible conformations in lamellar two-phase structures are schematically drawn in Figure 1. Five microphase-separated structures are probable to be formed; the number of their sublayers are 1, 3, 5, 7 and 9. We regard the structures shown in Figure 1b−e to have two periodicities, whose long period is the longer lamellar distance and the shorter one includes a pair of A−B thin lamellae.

II. Experimental Section

Materials. A styrene−isoprene undecablock copolymer composed of nine short blocks and two long polystyrene blocks on both ends was synthesized by a six-step alternative anionic polymerization in tetrahydrofuran (THF) at −78 °C with naphthalene−potassium as a bifunctional initiator. The details of the purification methods of monomers and solvent and the polymerization reaction were reported in a previous paper.[38] The appropriate amounts of isoprene and styrene monomers in ampules were added alternatively to the reaction vessel by a break-seal method to produce I, SIS, ISISI precursors, etc. Small amounts of tri-, penta-, hepta-, and nonablock copolymers were isolated as precursors in the course of polymerization for later characterization.

Characterization. The molecular weight distribution of undecablock copolymer and all precursors was estimated by a size exclusion chromatography (SEC) system, HLC-8020 of Tosoh Corp. The details of the experimental conditions were described earlier.[38] The purity of the undecablock copolymer and all precursors was estimated by temperature gradient interaction chromatography (TGIC). The TGIC experiments were carried out on a typical isocratic HPLC system equipped with a C18 bonded silica gel column (Hypersil C18, 100 Å pore, 150 × 4.6 mm, 3 μm particle size). The mobile phase used was a mixture of CH_2Cl_2 and CH_3CN (Kishida Chemical, HPLC grade, 75/25 in volume), and the flow rate was 0.5 mL/min. The column temperature was varied in a preprogrammed manner by circulating a fluid through a column jacket from a bath/circulator (HAAKE, P2, Germany). The TGIC chromatograms were recorded with a UV absorption detector, UV-8020, of Tosoh operating at a wavelength of 254 nm. Weight-average molecular weights of copolymers were determined by a multiangle laser light scattering (MALLS), DAWN EOS enhanced

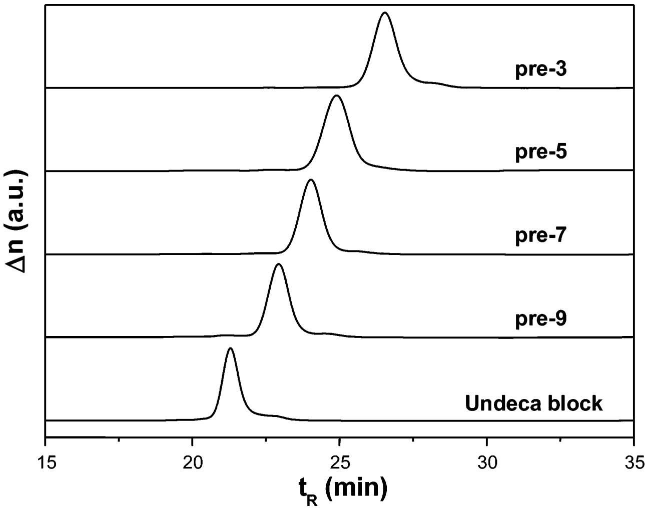

Figure 2. Comparison of SEC chromatograms of five multiblock copolymers.

optical system of Wyatt Technology. Reflective index increments, $\partial n/\partial c$, of the component polymers, i.e., $(\partial n/\partial c)_{PS}$ and $(\partial n/\partial c)_{PI}$, were measured by using both homopolymers. Overall $\partial n/\partial c$ of every precursors and multiblocks were estimated from eq 1 assuming the additivity and monodispersity.

$$(\partial n/\partial c)_{\mathrm{multi}} = (\partial n/\partial c)_{\mathrm{PS}} w_{\mathrm{PS}} + (\partial n/\partial c)_{\mathrm{PI}} w_{\mathrm{PI}} \qquad (1)$$

where w_i (i means PS or PI) denotes weight fraction of each polymer component. Equation 1 is known to be valid approximately if the molecular weight distribution indices of polymers are small enough.[39] Chemical compositions of four precursors and the final undecablock copolymer and the microstructures of their polyisoprene blocks were measured by ^{1}H NMR, Varian INOVA 500 MHz.

Morphological Observation. Sample films of four precursors and the undecablock copolymer for morphological observations were obtained by solvent-casting from 5 wt % dilute solutions of tetrahydrofuran. The film of 50/50 blend of nonablock/undecablock was also prepared for comparison. The sample films were dried under vacuum at room temperature and were subsequently annealed at 150 °C for 4 days.

For transmission electron microscopy (TEM) experiments, the sample films were embedded in a epoxy resin and cured at 80 °C for 12 h. Ultrathin sections were cut from the embedded specimens using an ultramicrotome, Reica Ultracut FCS, and a diamond knife at room temperature. To enhance contrast, the ultrathin sections of the sample films were stained with osmium tetroxide. The transmission electron microscope instrument used was a Hitachi H-800, operated under the acceralation voltage of 100 kV.

Small-angle X-ray scattering (SAXS) measurements were performed to observe microphase-separated structures. The instrument used was the apparatus installed in the beamline 15A at Photon Factory in Tsukuba equipped with an X-ray imaging plate. The sample-to-detector distance adopted was 2400 mm, and the wavelength of the incident X-ray beam was 0.1503 nm. X-ray beam was irradiated from the edge direction, where incident X-rays are parallel to the film surface.

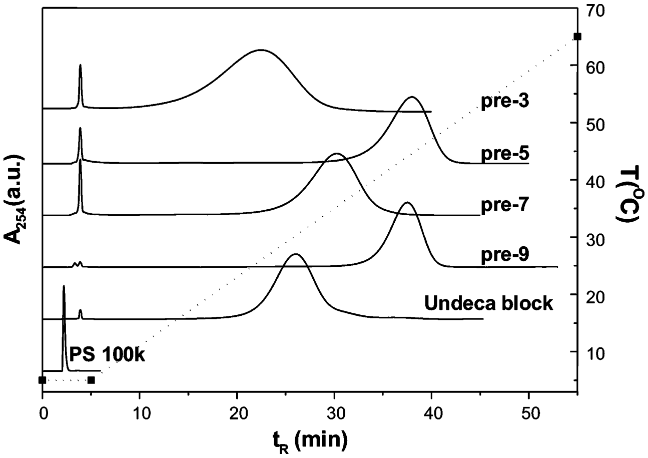

Figure 3. Comparison of TGIC chromatograms of five multiblock copolymers and a PS homopolymer.

III. Results and Discussion

Figure 2 compares SEC chromatograms of the undecablock copolymer and four precursors. From Figure 2, the peak top is shifted to the higher molecular weight side from top to bottom, showing successful monomer addition reactions. Very small tails were recognized on all the SEC chromatograms at low molecular weight region; therefore, the purity was carefully determined by TGIC.

Figure 3 shows a TGIC chromatogram of the undecablock copolymer, together with those of four precursors and a polystyrene homopolymer with molecular weight of 100K. Under the experimental conditions adopted in the present study, polystyrene homopolymer elutes in SEC regime, while polyisoprene homopolymer does not elute due to the strong interaction of polyisoprene with stationary phase. Generally speaking, TGIC retention increases with the molecular weight of polymer sample. However, for the present multiblock copolymers treated, TGIC retention was controlled by chemical composition. Namely the TGIC retention of multiblock copolymers decreased with the increase of PS content. Consequently, the TGIC retention time for undecablock copolymer was different from those of four precursor polymers, as is clearly shown in Figure 3. By examining the TGIC chromatogram in this figure, we determined that the total amount of precursor polymers included in the undecablock copolymer as polymer contaminates is estimated to be 5.5%.

Table 1 shows the molecular characteristics of all precursors and the undecablock copolymer. From Table 1, it is apparent that the molecular weight of the precursors is increasing from top to bottom, where the step sizes in molecular weight are relatively small up to the nonablock precursor, pre-9, as designed, indicating that alternating two-component multiblock sequences have been prepared, while the molecular weight suddenly jumps up to about double from nonablock to

Table 1. Molecular Characteristics of Multiblock Copolymers

sample		$M_w \times 10^{-4}$ [a]	increment $M_w \times 10^{-4}$	M_w/M_n [b]	Φ_S [c]
pre-3	SIS	4.14		1.06	0.63
pre-5	ISISI	7.71	3.57	1.05	0.38
pre-7	SISISIS	10.2	2.49	1.04	0.55
pre-9	ISISISISI	14.4	4.20	1.08	0.42
undecablock copolymer	SISISISISIS	27.5	13.1	1.04	0.70

[a] Determined by multiangle laser light scattering. [b] Determined by GPC (THF). [c] Determined by ^{1}H NMR.

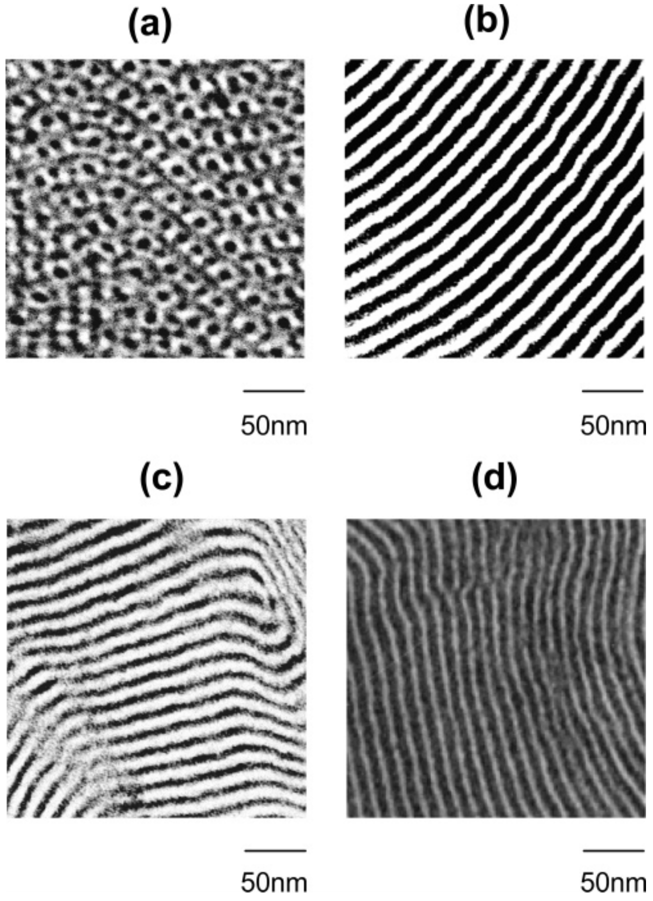

Figure 4. Transmission electron micrographs of multiblock copolymers: (a) pre-3, (b) pre-5, (c) pre-7, (d) pre-9.

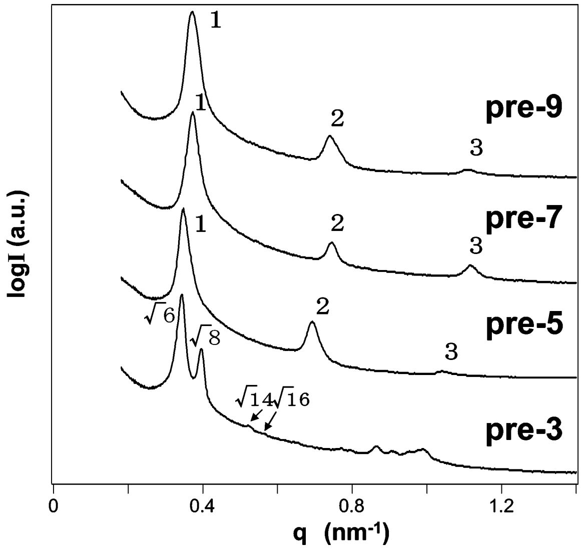

Figure 5. Comparison of SAXS diffraction patterns for tri-, penta-, hepta-, and nonablock copolymers.

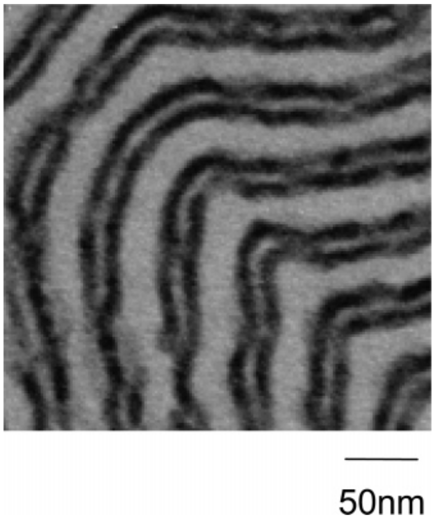

Figure 6. A typical bright field TEM image of the undecablock copolymer.

the final undecablock copolymer also just as designed. Accordingly, polystyrene content is oscillating; it finally reaches to 0.70. Furthermore, the molecular weight distribution of all the polymers is reasonably narrow. Fractions of microstructures of polyisoprene blocks in precursors and the final block copolymers estimated by ^{1}H NMR were found to be similar among samples and are as follows: 1,4-addition, 3%; 1,2-addition, 40%; 3,4-addition, 57%. Thus, we confirmed that an undecablock copolymer having nine short block chains at the center of the molecule and two long polystyrene block chains on both ends has been prepared quite successfully.

Figure 4 shows transmission electron micrographs of four precursors. The complex but periodic structure is shown in Figure 4a; this must be one shot of a bicontinuous gyroid structure, the details of which will be given below. The other three precursors, i.e., pre-5, pre-7, and pre-9, evidently exhibit alternating lamellar structures, as recognized in Figure 4b–d.

Figure 5 compares small-angle X-ray scattering profiles of four copolymers as precursors studied. At the bottom in Figure 5, one notices several peaks at the relative magnitudes of scattering vectors of $6^{1/2}$, $8^{1/2}$, $14^{1/2}$, $16^{1/2}$, etc., in the scattering profile of the triblock copolymer precursor, pre-3. These values are the typical series of reflections from bicontinuous gyroid structure, and the scattering result is consistent with that observed for transmission electron microscopy. The scattering profiles of the other three precursors have integer numbered peaks, and obviously they are representing lamellar structures. Their domain spacings D were estimated by applying the magnitude of scattering vector $|q|$ ($= 4\pi \sin \theta/\lambda$) to Bragg's condition, $D = 2\pi/|q|$, where 2θ is the scattering angle and λ is the wavelength of X-rays. Domain spacings obtained for pre-5, pre-7, and pre-9 are 18, 17, and 17 nm, respectively. Thus, domain spacing decreases with increasing the number of blocks, and it reaches a constant value as was reported previously.[18]

On the other hand, the undecablock copolymer shows very characteristic morphology as shown in Figure 6. This structure can be conceived to include lamellar microdomain structure composed of one thick lamella from long polystyrene blocks and three thin lamellae; two of them are polyisoprene microdomains, and the one in the middle is a polystyrene microphase.

Furthermore, the diffracted pattern for the undecablock copolymer and that for pre-9 are compared in Figure 7. The scattering profile of the undecablock copolymer includes three peaks shown at their relative location of 1:2:3, and the peak height of the second one is apparently low. The scattering curve for pre-9 at the middle in Figure 7 exhibits three distinct peaks designated as $\underline{1}$, $\underline{2}$, and $\underline{3}$. One notices the magnitudes of $|q|$ for the former peak series are much smaller than those of the latter, indicating the tremendous increase in

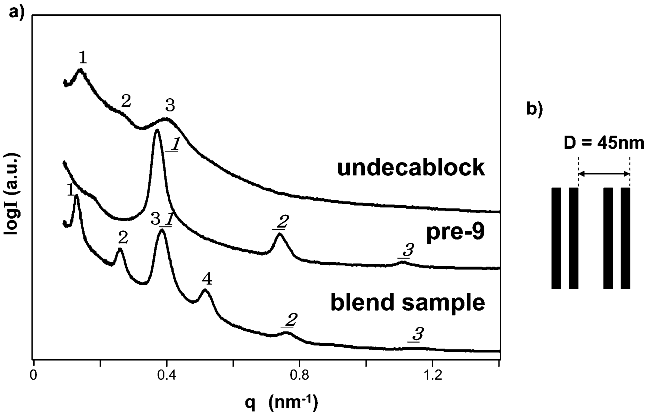

Figure 7. (a) Comparison of SAXS profiles of undecablock and nonablock copolymers and their 50/50 blend. (b) A schematic image for the cross section of the structure of undecablock copolymer.

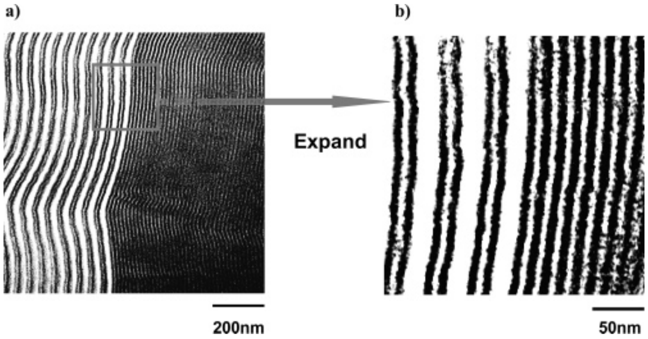

Figure 8. Transmission electron micrographs of the 50/50 blend sample from undecablock and nonablock copolymers.

domain spacing. The estimated longer domain spacing is 45 nm, though all the peaks are broad comparing with the pattern for pre-9 reflecting that the degree of lamellar orientation parallel to the film surface is relatively low for the present large undecablock molecules. Unfortunately, the shorter spacing was hard to be estimated directly from the scattering curve because of weak signals at higher *q* values; it was estimated as approximately one-third of the longer spacing from TEM image in Figure 6. Figure 7 also compares the profile from the 50/50 blend of pre-9/undecablock at the bottom. It is evident that the scattering curve includes two kinds of peak series: one from undecablock copolymer designated as 1, 2, 3, and 4 and the other from pre-9 pointed out by *1*, *2*, and *3*. Here we notice that peaks 3 and *1* overlap to produce one large peak and, furthermore, that the bottom curve includes the fourth peak assigned as "4", which is missing at the top curve, reflecting that the higher orientation of lamellae parallel to the film surface is achieved for the blend.

Figure 8 shows transmission electron micrographs of this blend sample. Figure 8a is the view for a wide area, and the image on the left side is identical to that in Figure 6 for undecablock copolymer itself, but it is clear that the structure in Figure 8a is highly ordered compared with the one for pure undecablock copolymer. Figure 8b is just an enlarged image for the section surrounded by a square designated in Figure 8a, and this view evidently shows a macrophase-separated structure between microphase-separated structures of undecablock and nonablock.

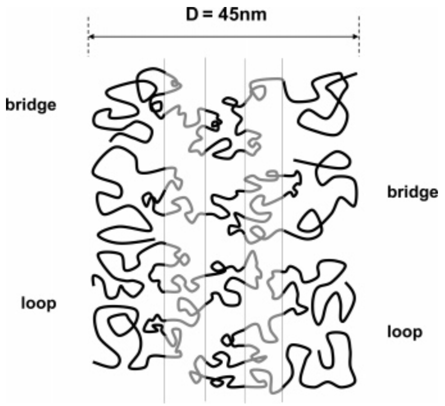

Figure 9. Schematic illustration of possible conformations of undecablock copolymer molecules in a hierarchical structure. The solid thick lines are for polystyrene, whereas thin lines are for polyisoprene.

We would discuss the reason for the formation of the present hierarchical structure with only three thin lamellar layers. The possible conformation of this undecablock copolymer is shown in Figure 9. The population of chain conformations which fit to three-layered structure is slightly larger than that for five-layered structure, since every short polystyrene chains in a undecablock polymer are permitted to dissolve into larger domain composed of long polystyrene chains with all loop conformation, as shown in Figure 9. As a result, the number of loop conformation must be slightly larger than that of bridge one in the shorter hierarchical level; however, it must be independent of the loop/bridge ratio in the longer level for whole the undecablock copolymer chain. Furthermore, the a priori condition that the number of short chains per unit volume must be constant among different lamellae to keep the segment density constant is a severe and dominant factor for the present system to inhibit the multilayered structures more than five. This condition becomes more severe with increasing the number of layers.

In conclusion, a large molecular weight undecablock copolymer, which has two long polystyrene chains at both ends and includes nine short multiblocks inside, has been successfully synthesized. From a morphological observation using TEM and SAXS, the hierarchical lamellar structure with two different periodic distances within one repeating unit cell has been produced, which is the first experimentally observed result in polymer morphology. The better lamellar orientation was achieved by blending a nonablock center unit with an undecablock copolymer, and it could be a useful optical material if we can scale up the lamellar domain spacing some more up to several hundred nanometers.

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