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Observation of Cylinder-Based Microphase-Separated Structures from ABC Star-Shaped Terpolymers Investigated by Electron Computerized Tomography

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ABSTRACT: Characteristic cylindrical microphase-separated structures have been found for three ABC star-shaped terpolymers. The samples are composed of polystyrene (S), polyisoprene (I), and poly(2-vinylpyridine) (P); their volume ratios of I:S:P are about 1:1:0.7, 1:1:1.2, and 1:1:1.9, respectively, three components being connected at one branch point. From three-dimensional morphological observation by TEM combined with electron computerized tomography, a terpolymer with volume ratio of 1:1:0.7 shows honeycomb-type microdomain structure, i.e., (6^3), having three kinds of hexagonal cylinders arranged hexagonally with junction points being arrayed one-dimensionally at the intersection of three domains, while others show characteristic cylindrical structures with mainly 4-fold, (4.8^2), and 6-fold, (4.6.12), symmetry. It has been clarified, however, that many defects exist in the regular microdomain structures of all three terpolymers.

Introduction

It is well-known that block and graft copolymers consisted of incompatible components form regular self-assembled structure, so-called microphase-separated structure in bulk.[1−4] Various kinds of block polymers such as AB-,[5,6] ABA-,[6] $(AB)_n$-,[7] ABC-,[8,9] and ABCD-type[10] linear block polymers were prepared, and their self-assembled structures have been investigated. Especially, the microphase-separated structures of AB diblock copolymers have been extensively studied, and it has been clarified that they give various morphologies such as spherical, cylindrical, bicontinuous, and lamellar structures depending on their compositions. Furthermore, it has been also confirmed that several linear copolymers with different architectures, i.e., ABA, $(AB)_n$, and ABC type, show essentially similar morphological change with composition. It should be noted that the common feature in molecular structure for these polymers is that two adjacent polymers being linked at one junction point. If we restrict the discussion within linear block polymers, it might be very hard to design new morphologies. To overcome this limitation, a new molecular design will be required. One of the possible candidates is an ABC star-shaped terpolymers in which three different polymers are connected at one junction point. Microphase separation from the three component polymers in the ABC star-shaped terpolymer requires a one-dimensional spatial arrangement of the connecting points; therefore, this copolymer in microphase-separated structure must be highly frustrated in bulk.

Several groups have reported on preparation methods and the morphological features of ABC star-shaped terpolymers. Fujimoto et al. synthesized the ABC star-shaped terpolymers consisting of poly(dimethylsiloxane) (PDMS), polystyrene (PS), and poly(*tert*-butyl methacrylate) (PTBMA) utilizing the macromonomer technique, with nonpolymerizable macromonomers having 1,1-diphenylethylene (DPE) on one chain end.[11] Using three PDMS−PS−PTBMA star-shaped terpolymers with arm-length ratio of about 1:1:1, Okamoto et al. reported that the samples form three-dimensional continuous structure with 3-fold symmetry, but a specific microdomain model was not proposed.[12] Iatrou et al. synthesized a ABC star-shaped terpolymer consisting of PS, polyisoprene (PI), and polybutadiene (PB) using chlorosilane chemistry, while Hadjichristidis et al. reported the morphology of the PS−PI−PB, that is, PS cylinders in matrix of mixture of PI and PB.[13] Sioura et al. synthesized four ABC star-shaped terpolymers consisting of PS, PI, and poly(methyl methacrylate) (PMMA) also using chlorosilane chemistry and reported that all samples form three-phase, two-dimensionally periodic microstructure of inner PI columns with surrounding PS annuals in a matrix of PMMA, where the connecting points did not arrange one-dimensionally.[15−17] Hückstädt et al. prepared 12 ABC star-shaped terpolymers consisting of PS, PB, and poly(2-vinylpyridine) (P2VP) using the DPE macromonomer technique. They reported on the characteristic cylindrical structures with 4-fold or 6-fold symmetry.[18] Furthermore, Bellas et al. synthesized a ABC star-shaped terpolymer consisting of PS, PI, and PDMS using chlorosilane chemistry,[19] while Yamauchi et al. investigated its morphology by TEM observation of selective staining technique using the energy-filtering TEM method in addition to the conventional TEM.[20] Furthermore, they employed electron computerized tomography with both the energy-filtering TEM technique and the conventional one, and they observed cylindrical structure with mainly 4-fold symmetry by constructing the three-dimensional images of the sample.

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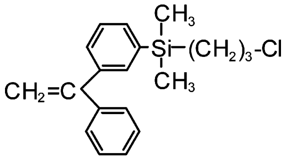
On the other hand, Gemma et al. have reported on microphase-separated structures of the ABC star-shaped terpolymers with the arm-length ratio for A:B:C of 1:1:X ($0.17 \le X \le 25$) using the computer simulation method and predicted that three components basically form polygonal and cylindrical microdomain structures where junction points were arranged on a linear line if X is relatively low, i.e., $0.37 \le X \le 2.25$.[21,22]

Throughout those experimental works mentioned above, however, no systematic works on 1:1:X series with respect to sample composition have been carried out, so force consistency between experimental results and theoretical ones concerning the assembling manners of cylindrical structures has not been clarified yet.

Therefore, the composition dependence of morphology for ABC star-shaped terpolymers by preparing a series of samples with compositions of 1:1:X, where X equals 0.7, 1.2, and 1.9, has been investigated in this study. To carry out this study successfully, it is important to adopt a selective staining method in which three phases can be observed simultaneously in one-shot image, and furthermore an electron computerized tomography technique was introduced to observe three-dimensional structure accurately.

Experimental Section

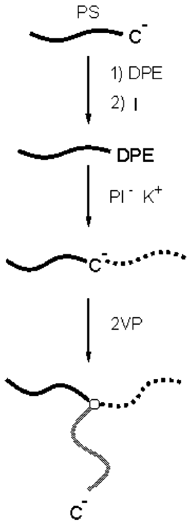
Materials. *sec*-Butyllithium was purchased from Asia Lithium Co. Ltd. and was diluted with purified *n*-heptane. Cumylpottasium was synthesized by the reaction of cumylmethyl ether and potassium–sodium alloy in THF at room temperature in vacuo for 8 h. Concentrations of those two initiators were determined by titration with standard HCl solution. Tetrahydrofuran (THF) used also as a solvent for polymerization, three monomers, i.e., styrene, isoprene, and 2-vinylpyridine, and also 1,1-diphenylethylene (DPE) were purified with the same manners as reported previously.[9,10] 1-[3-(3-Chloropropyldimethylsilyl)phenyl]-1-phenylethylene (**I**) was prepared by the reaction of 1-(3-bromophenyl)-1-phenylethylene and 3-chloropropyldimethylchlorosilane and was purified in the same manners as reported previously.[10] Methanol was dried over calcium hydride.



I

Synthesis of ABC Star-Shaped Terpolymers. ABC star-shaped terpolymers were synthesized via three steps as shown in Scheme 1. All operations were carried out in sealed glass apparatuses with break-seals under a pressure of 1×10^{-3} Pa or lower. First, styrene was polymerized with *sec*-butyllithium in THF at −78 °C for 1 h to give polystyryllithium, and then it was end-capped with DPE at the ratio of [DPE]/[Li] = 4/1, followed by termination with **I** at the ratio of [**I**]/[Li] = 4/1 at room temperature. By this procedure, a polystyrene macromonomer having a DPE type vinyl group (PS) was prepared. The polymer obtained was purified by precipitation from THF solution into an excess amount of methanol three times; a part was isolated as a precursor for later use. After being freeze-dried, PS was transferred into a vacuum apparatus and diluted with purified THF, and a THF solution of 1,4-dilithio-1,1,4,4-tetraphenylbutane was added to the THF solution of PS until a very faint red color was remained. Second, polyisoprenylpottasium, PI$^-$, was prepared by polymerization of isoprene with cumylpottasium in THF at −78 °C for 24 h. A small amount of living polymer solution was separated as an aliquot and terminated with methanol. Third, a controlled amount of PI$^-$ solution was allowed to react with the PS solution at the molar ratio of [PS]/[PI$^-$] = 1.01 at −40 °C for 7 days to give polystyrene–polyisoprene diblock copolymer having a carbanion at the linking point. The living diblock copolymer solution was separated into several ampules with break-seals, small amount of aliquot of the living polymer solution being isolated as an aliquot for later characterization. Finally, a controlled amount of 2-vinylpyridine monomer in THF was added to the living diblock copolymer, and polymerization of the monomer was carried out at −78 °C. After being quenched with methanol, the obtained polymer was precipitated in water and freeze-dried.

Scheme 1



Fractionation. In the course of syntheses of the ABC star-shaped terpolymers, small amount of PSs and deactivated diblock copolymers were included in the resultant as-polymerized product. To remove those undesirable polymers from the reaction mixture, fractionation by gel permeation chromatography (GPC) was carried out at room temperature using the preparative GPC system consisting of a system controller (SC-8020), a computer-controlled pump (CCPP-M), an automatic sample injector (AS-8071), a fraction collector (FC-8020), and a refractive index detector (RI-8020) of Tosoh Ltd. equipped with a set of two G4000H$_{HR}$ columns of Tosoh Ltd., which are 300 mm in length and 21.5 mm in inner diameter. All runs for GPC fractionation were made in THF containing 0.1% triethylamine as an eluent. The concentrations of the polymer solutions were ca. 0.3% w/v.

Molecular Characterization. The weight-average molecular weight of PS was determined by light scattering with a Dawn-EOS multiangle laser light scattering apparatus (Wyatt Technology Co.) in THF at 35 °C. Compositions of the component polymers in star-shaped terpolymers were determined by ^{1}H NMR with a JEOL EX-400 NMR spectrometer at 399.65 MHz. The chemical shift was referred to chloroform in chloroform-*d*. Apparent molecular weight heterogeneities, M_w/M_n, of precursors and the final products were determined by GPC with a set of three G4000H$_{HR}$ columns of Tosoh Ltd. with 300 mm length and with 7.8 mm inner diameter.

Morphological Observation. Films used for morphological observation were cast from ca. 2% THF solutions of samples for a few days under a nitrogen gas atmosphere. The cast films were dried at room temperature for 6 h under vacuum, followed by annealing at 140 °C for a week in a vacuum oven. Small pieces of film samples, typically with size of ca. 7 mm × 0.7 mm × 0.2 mm, were stained with an osmium tetroxide aqueous solution at 60 °C for 10 h. The stained films were cut into ultrathin sections with ca. 50 nm thickness using an ultramicrotome, Reica Ultracut FCS, at room temperature with a diamond knife (Diatome cryo-T). The microphase-separated structures of the sections were observed by a transmission electron microscope (Hitachi: H-800) operated at an accelerating voltage of 100 kV.

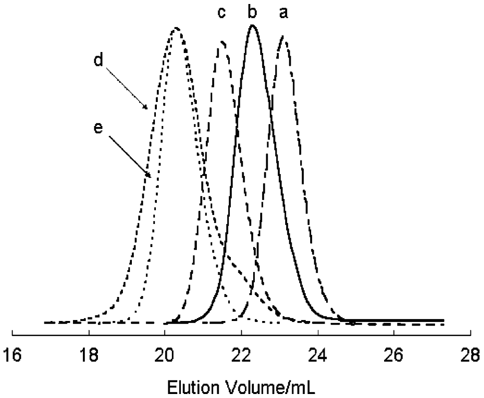


Figure 1. GPC chromatograms of (a) PS, (b) PI, (c) coupling product from PS-DPE and PI$^-$, (d) as-polymerized product of 2-vinylpyridine from living polystyrene–polyisoprene diblock copolymer, and (e) the fractionated product.

Table 1. Molecular Characteristics of ABC Star-Shaped Terpolymers and Component Polymers

sample	$10^{-4}M_n$	M_w/M_n [c]	ϕ_A:ϕ_B:ϕ_C [d]
PS–DPE	4.92[a]	1.04	
PS–PI diblock	9.44[b]	1.05	1:1.04:0
SIP star-0.7	13.4[b]	1.04	1:1.08:0.71
SIP star-1.2	15.8[b]	1.05	1:1.03:1.19
SIP star-1.9	19.9[b]	1.04	1:1.08:1.92

[a] M_n value was estimated from weight-average molecular weight, M_w, measured by light scattering and molecular weight heterogeneity, M_w/M_n, measured by GPC. [b] Estimated from M_n value of PS-DPE and weight fractions converted from mole fractions determined by ^{1}H NMR as shown in the last column of this table. [c] Determined by GPC. [d] Determined by ^{1}H NMR.

To investigate three-dimensional structures, electron computerized tomography was adopted in this work. For this method, a transmission electron microscope (FEI:TECNAI F30) was used, it being operated at an accelerating voltage of 120 kV.[23] A series of a total 71 TEM images were collected, that is, 51 images within tilt angle φ of $-50° \leq \varphi \leq 50°$ with 2° step, 10 images within tilt angle φ of $-60° \leq \varphi < -50°$, and another 10 images within $50° < \varphi \leq 60°$ with 1° guaranteed step by an automatic computer-controlled sample stage. Three-dimensional reconstruction image was given by using a three-dimensional volume modeling software, IMOD (Boulder Laboratory), and a three-dimensional visualization and modeling software, AMIRA (TGS Inc.).

Results and Discussion

Preparation of ABC Star-Shaped Terpolymers. Figure 1 shows a GPC diagram of a series of synthetic steps for an ABC star-shaped terpolymer. Curve a in Figure 1 shows a GPC chromatogram of the PS. It is a unimodal and nearly symmetric curve representing a fairly narrow molecular weight distribution. Table 1 lists the molecular characteristics of PS. The functionality of DPE-type vinyl group in the macromonomer was confirmed to be almost quantitative.[24] Curve b in Figure 1 shows a GPC chromatogram of the PI precursor, which is also a unimodal curve showing a reasonably narrow molecular weight distribution. Curve c in Figure 1 shows a GPC chromatogram of a coupling product from PS and PI$^-$, that is, polystyrene-*block*-polyisoprene diblock copolymer. The main peak in GPC curve of the coupling product was shifted to the higher molecular weight region, which is nearly a single peak with a tiny amount of shoulder from either homopolymer. Thus, an almost exact stoichiometric reaction between PS and PI$^-$ took place in the coupling reaction. Curve d in Figure 1 shows a GPC chromatogram of an as-polymerized product of 2-vinylpyridine from living polystyrene–polyisoprene diblock copolymer. The main peak in the GPC curve of an as-polymerized product was shifted to the higher molecular weight region; however, it has a shoulder at 21.6 min, which corresponds to the peak of diblock copolymer. This is probably because of impurity which comes from heat-seals when the living diblock copolymer solution was separated into amples with break-seal. Curve e in Figure 1 shows a GPC chromatogram of an ABC star-shaped terpolymer purified by GPC fractionation. It is a sharp and symmetric curve reflecting a narrow molecular weight distribution. Table 1 lists the molecular characteristics of the three ABC star-shaped terpolymers, which are coded SIP star-0.7, SIP star-1.2, and SIP star-1.9, respectively, where numerical values correspond to the volume ratio of poly(2-vinylpyridine) relative to polystyrene and polyisoprene. The volume fractions of component polymers were calculated by ^{1}H NMR charts with bulk densities of polymers, i.e., 1.05, 0.926, and 1.14 g/cm^3 for polystyrene, polyisoprene, and poly(2-vinylpyridine), respectively. Thus, we concluded that polymers obtained from the synthetic procedure adopted in this study are well-defined ABC star-shaped terpolymers with almost the same volume fraction of polystyrene and polyisoprene, but with three different volume fractions of poly(2-vinylpyridine)s as designed.

Morphological Observation. Figure 2 compares TEM images of the three ABC star-shaped terpolymers. These images shows very small areas (250 nm × 250 nm) and relatively well-oriented parts. Since the samples were stained with osmium tetroxide, the white part represents polystyrene phase, the gray part the poly(2-vinylpyridine) one, and the black part the polyisoprene one.[8,9] In Figure 2a, SIP star-0.7 shows honeycomb-type microdomain structure where three kinds of microdomains mutually form hexagonal sections though each domain was deformed from regular hexagon. This type of microphase-separated structure with 3-fold symmetry and with high regularity has been observed for the first time in this study.

Gemma et al. reported on the prediction of morphology for ABC star-shaped terpolymers with arm-length ratio N_A:N_B:N_C = 1:1:X, with $0.17 \leq X \leq 25$ and with equal interactions among three components by computer simulation, and it was predicted that characteristic cylinder-based microphase-separated structures appeared in relatively narrow range in terms of X ($0.37 \leq X \leq 2.25$).[22] For expressing polygonal cross sections of periodic cylindrical structures as in Figure 2, we adopted the manner of tiling pattern used in a book of Grunbaum and Shephard,[25] where a set of integers is employed to express the type of a vertex formed by polygons. Thus, for the honeycomb-type structure from three components, (6^3) or (6.6.6) is assigned for example. As a matter of fact, they predicted that the (6^3) phase would appear at $0.80 \leq X \leq 1.2$ regions. To the contrary, honeycomb-type structure was observed for a sample with $X = 0.7$ in our experiment. This discrepancy is probably because the segment–segment interactions among three components could be considerably different from one another.

In Figure 2b, SIP star-1.2 shows a characteristic cylindrical structure with 4-fold symmetry; that is, microdomains of polyisoprene and poly(2-vinylpyridine) form octagonal sections, and a microdomain of polysty-

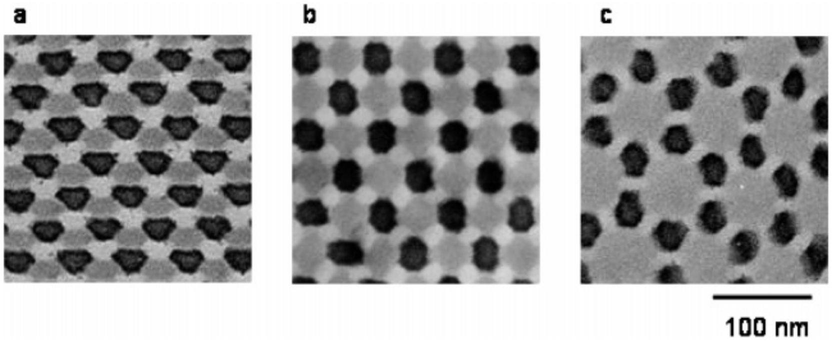


Figure 2. Transmission electron micrographs of (a) SIP star-0.7, (b) SIP star-1.2, and (c) SIP star-1.9.

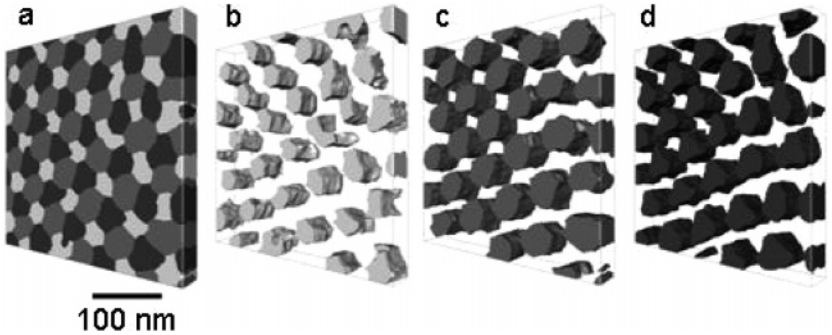


Figure 3. Three-dimensional images of the SIP star-0.7 of (a) three phases, (b) P phase, (c) I phase, and (d) S phase.

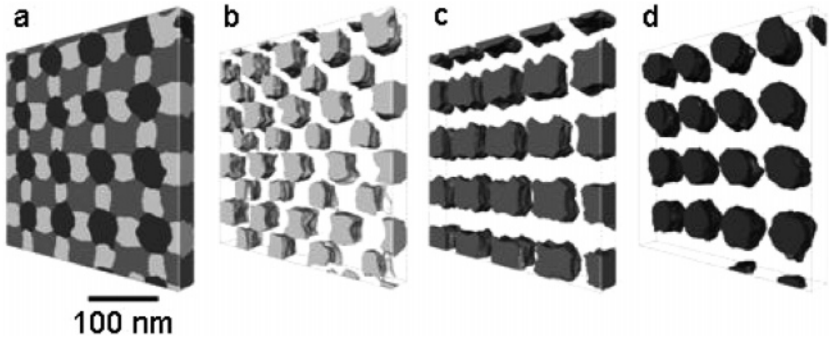


Figure 4. Three-dimensional images of the SIP star-1.2 of (a) three phases, (b) P phase, (c) I phase, and (d) S phase.

rene reveals square section, which is assigned as (4.8^2) or (4.8.8) structure, though each domain was also deformed from a regular polygon. According to the prediction by Gemma et al., (4.8^2) phases would appear at the $0.38 \leq X \leq 0.7$ region. Apparently, this is contradictory to the present experimental result for SIP-1.2 again. This may be also probably due to the difference in segment−segment interaction among three components.

In Figure 2c, SIP star-1.9 shows an another characteristic cylindrical structure with 6-fold symmetry; that is, microdomains of poly(2-vinylpyridine), polyisoprene, and polystyrene formed dodecagonal, hexagonal, and square sections, respectively, which is assigned as (4.6.12) structure. This result is consistent with the prediction by Gemma et al.[22]

To obtain three-dimensional microdomain structures precisely, electron computerized tomography was adopted. Three-dimensional reconstructed images of SIP star-0.7, SIP star-1.2, and SIP star-1.9 are shown in Figures 3, 4, and 5, respectively; the thicknesses of the reconstructed images are approximately 25−30 nm. In these images, the white part shows polystyrene phase, the gray part the poly(2-vinylpyridine) one, and the black part the polyisoprene one, respectively, which correspond to the contrast of TEM images where samples were stained with osmium tetroxide. Figure 3a shows a reconstructed image of SIP star-0.7 with three phases, while parts b, c, and d of Figure 3 show reconstructed images of the poly(2-vinylpyridine) phase, polyisoprene one, and polystyrene one only, respectively. Each phase looks like hexagonal cylinders arranged hexagonally representing (6^3) structure. Figure 4a shows a reconstructed image of SIP star-1.2 with three phases, while Figures 4b−d also separately show either one of three component phases. From these figures, polyisoprene and poly(2-vinylpyridine) phases both look like octagonal cylinders arranged on a square lattice, while the polystyrene one forms square cylinders arranged hexagonally, corresponding to (4.8^2) structure. Figure 5a shows a reconstructed image of SIP star-1.9 from three phases, while Figures 5b−d separately show either one of three phases. The poly(2-vinylpyridine) phase is forming dodecagonal cylinders arranged hexagonally, whereas the cylinders are surrounded by six hexagonal cylinders of polyisoprene and also by six tetragonal cylinders of polystyrene, representing the (4.6.12) structure. Summarizing the feature of these three structures observed in this work, all are classified as single junction point line class,[22] where vertices of each structure are all

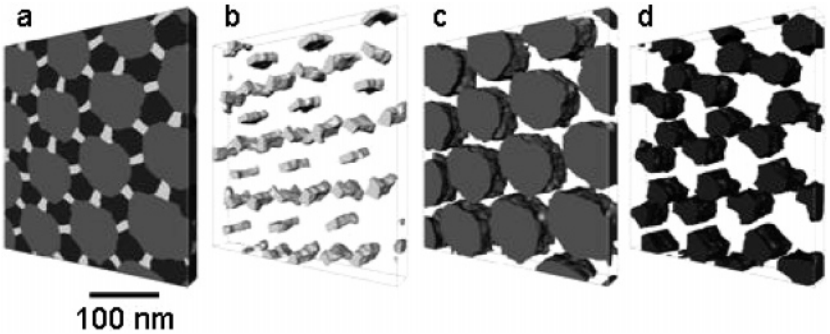


Figure 5. Three-dimensional images of the SIP star-1.9 of (a) three phases, (b) P phase, (c) I phase, and (d) S phase.

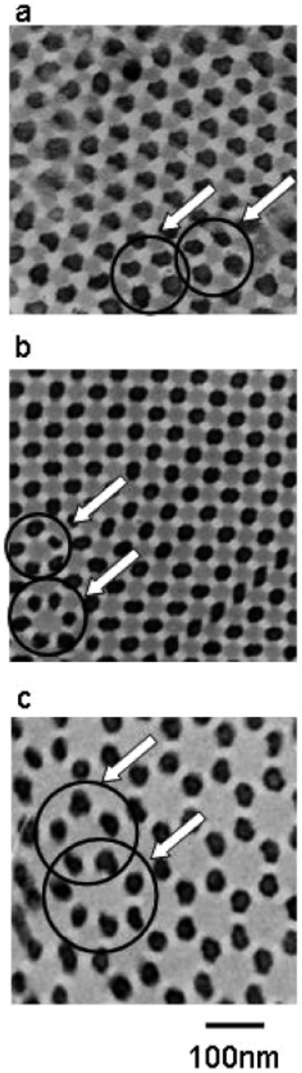


Figure 6. Transmission electron micrographs of (a) SIP star-0.7, (b) SIP star-1.2, and (c) SIP star-1.9, where locations of defects are indicated by circles and arrows.

under the same circumstance. Thus, it was confirmed that ABC star-shaped terpolymers form characteristic cylinder-based microphase-separated structures when the volume ratio of poly(2-vinylpyridine), *X*, is in the range of $0.7 \leq X \leq 1.9$ relative to polystyrene and polyisoprene, both being set to unity.

Furthermore, if we observe the microphase-separated structures of three SIP star-shaped terpolymers in TEM images more carefully, it is easy to find out many defects in the regular microdomain structures of all three terpolymers. Figure 6 shows TEM images for three SIP star-shaped terpolymers, in which locations of defects are indicated by circles and arrows. For example in Figure 6b, well-ordered (4.8^2) structure with 4-fold symmetry covers almost all area in this micrograph; however, cylindrical intersections with 5-fold or 6-fold symmetry designated by circles can be seen. Essentially the same kinds of defects can be also found in Figures 6a,c. Comparing the regularity of cylindrical structures in between SIP star-shaped terpolymers and conventional two-component block copolymers such as polystyrene-*block*-polyisoprene diblock copolymers, we notice that the regularity in formers is definitely poorer than that in latters. This seems to be due to the difference in rate of structural formation between ABC star-shaped terpolymers and two-component linear block copolymers. Namely during formation of microphase-separated structures, connecting points of the AB diblock copolymers can move two-dimensionally on interface, while connecting points of the ABC star-shaped terpolymers can move only on one-dimensional line, which are schematically described and compared

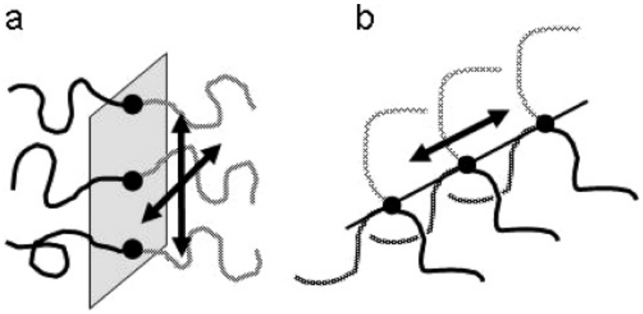


Figure 7. Schematic drawings of mobility of connecting points of (a) AB diblock copolymers and (b) ABC star-shaped terpolymers.

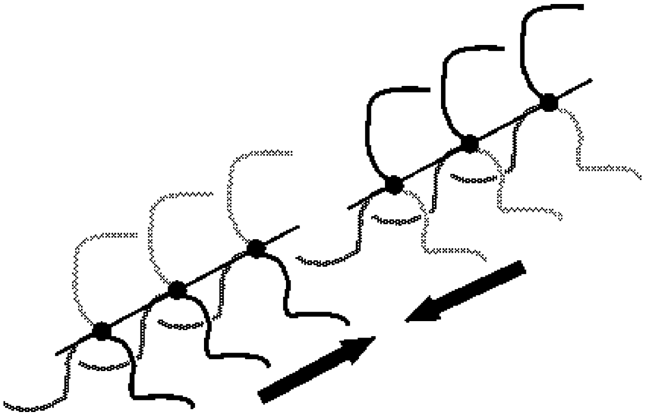


Figure 8. Schematic drawings of encounter of two cylinders with reflection symmetry.

in Figure 7. Thus, it is conceived that two-component block copolymers can attain stable structures more quickly than ABC star-shaped terpolymers. Furthermore, when two cylinders with reflection symmetry are encountered each other, they cannot connect smoothly; this can cause defects quite easily as schematically described in Figure 8. It seems to be actually impossible to accomplish these kinds of defects, once the defects are generated, even though sample films are heated at higher temperature for a long period.

In conclusion, well-defined SIP star-shaped terpolymers consisting of polystyrene (S), polyisoprene (I), and poly(2-vinylpyridine) (P) were successfully prepared by anionic living polymerizations, which have volume ratios of S:I:P are about 1:1:0.7, 1:1:1.2, and 1:1:1.9. It has been found that by morphological investigations three SIP star-shaped terpolymers form characteristic cylinder-based microphase-separated structures having (6^3), (4.8^2), and (4.6.12) phases depending on their volume ratio of poly(2-vinylpyridine), X, that is, 0.7, 1.2, and 1.9, while those of polystyrene and polyisoprene both being set to unity. However, it has been confirmed that many defects exist in the regular microdomain structures of all three terpolymers.

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