

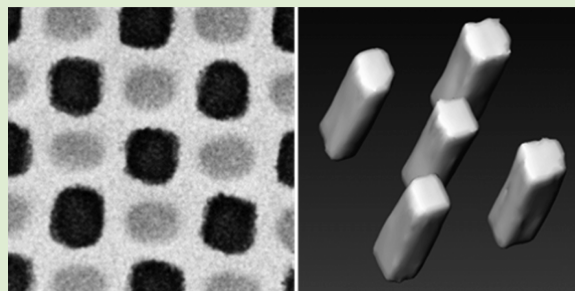
Formation of Tetragonally-Packed Rectangular Cylinders from ABC Block Terpolymer Blends

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Supporting Information

ABSTRACT: Effect of composition distribution of ABC linear terpolymers on the formation of periodic structures was investigated. Five poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (ISP) triblock terpolymers with almost constant molecular weights of ca. 130k and with similar center-block fraction at around 0.55, were blended variously. It has been found that tricontinuous gyroid structures gradually transform into a cylindrical structure whose rectangular cylinders are packed tetragonally if composition distribution increases. Further experiments by 3D-TEM observation on binary equimolar mixtures of two molecules with similar molecular weights of 122k and 124k, giving the average composition of $\varphi_1/\varphi_S/\varphi_P = 0.23/0.59/0.18$, has verified to show more evident rectangular-shaped cylinders with 4-fold symmetry. This new structure, having periodic surfaces with nonconstant mean-curvature, could be formed due to the systematic localization of component polymer chains along the domain interfaces.



Monodisperse block copolymers with incompatible components are known to form self-assembled periodic microphase-separated structures and a large number of studies have been carried out by both experimentally^{1–4} and theoretically.^{5–7} Common feature of traditionally-known simple structures such as spherical, cylindrical, and lamellar structures consist in the fact that their polymer/polymer interfaces possess constant mean-curvature surfaces.

Lately somewhat more complex structures were found such as bicontinuous gyroid structures for AB diblock copolymers,^{8,9} tricontinuous gyroid structures,^{10,11} a hexagonal core-shell morphology,¹² and a core-shell gyroid structure¹³ for linear three-component triblock terpolymers of the ABC type; furthermore, the very periodic cubic structure in (AB)_n-star¹⁴ and hierarchical structures in three-component multiblock terpolymers¹⁵ have been known to show new morphological features. All these structures show periodic morphologies with mesoscopic length scales; however, in some cases, such as gyroid structures, their mean curvatures are not really constant as precisely reported for a two-component system.¹⁶

If diblock copolymer systems possess certain polydispersity, generally speaking, it still conforms simple and periodic structures as the result of spontaneous and uniform mixing of different chains. Hashimoto et al. studied the morphologies of binary mixtures of poly(styrene-*b*-isoprene) (SI) with different composition,¹⁷ while Hillmyer et al. investigated polydispersity effect on morphology of poly(ethylene-*alt*-propylene)-block-poly(DL-lactide) (PEP-PLA).¹⁸ Moreover, Noro et al. reported the effects of composition distribution on morphologies of poly(styrene-*b*-2-vinylpyridine) (SP) diblock¹⁹ and poly(2-vinylpyridine-*b*-styrene-*b*-2-vinylpyridine) (PSP) triblock co-

polymer systems, and found small but quantitative effects.²⁰ Thus, only light effects due to molecular weight or composition distribution of samples were recognized for two-component copolymer systems.

On the other hand, however, the situation is fairly different for linear ABC triblock terpolymer system, since they possess central B chains that have to show more restricted bridge type conformation in contrast to tail type ones for all AB diblock copolymer chains. This structural feature is known to make morphological variation, in short, symmetric triblock terpolymers tend to form tetragonal lattices instead of hexagonal ones.^{21,22} As a more perturbed system, periodic undulated lamellar structure has been clearly observed for the poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (ISP) triblock terpolymer system with constant composition but wide molecular weight distribution.²³ Moreover, polydispersity effects in poly(isoprene-*b*-styrene-*b*-ethylene oxide) (ISO) triblock terpolymer were observed by X-ray experiments.²⁴ The main purpose of the present work is the creation of morphologies having nonconstant mean-curvatures (non-CMC) with mesoscopic length scales induced by composition distribution. It can be introduced by blending several block terpolymers with the same chain lengths but have different compositions. New rectangular-shaped cylinders with 4-fold symmetry have been found if composition distribution exceeds the critical value.

Received: December 21, 2013

Accepted: January 16, 2014

Published: January 17, 2014

Figure 2 compares morphologies of five parent block copolymers. Since the samples were stained with OsO_4 and I_2

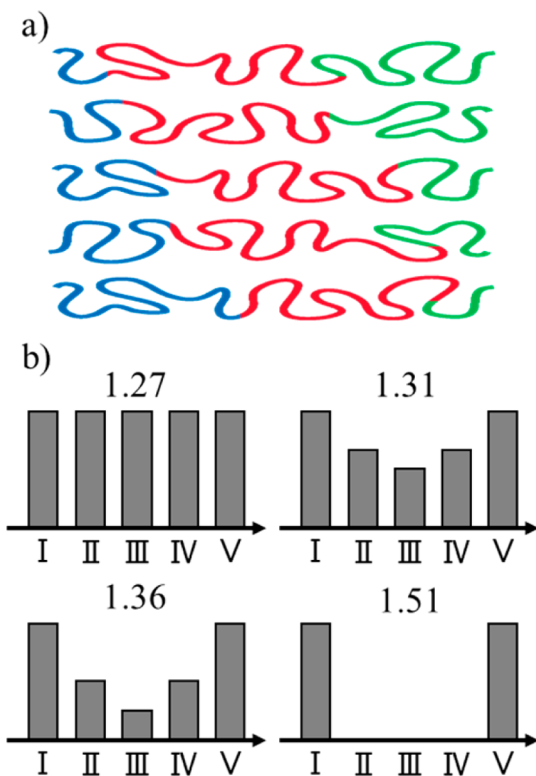


Figure 1. (a) Schematic representation of the five ISP triblock terpolymers investigated. Blue, red, and green chains represent I, S, and P, respectively. (b) Blend manners of five parent triblock terpolymers and the composition distribution indices, defined as those of polyisoprene blocks, of the blend.

for the TEM observations, the black, white, and gray domains represent I, S, and P phases, respectively. The ISP-I ($\varphi_I/\varphi_S/\varphi_P = 0.08/0.52/0.40$) in Figure 2a is a sphere-in-lamella structure, in which the minor component polyisoprene (I) stays as isolated spheres at the center of lamellae formed by polystyrene (S). This result is quite reasonable since this sample has highly asymmetric composition. The structure with essentially the same feature is seen in Figure 2e for ISP-V ($\varphi_I/\varphi_S/\varphi_P = 0.39/0.56/0.05$), though it is somewhat hard to recognize the isolated P phase. Alternatively, the ISP-III ($\varphi_I/\varphi_S/\varphi_P = 0.24/0.55/0.21$) in Figure 2c shows the tricontinuous gyroid structure, which is consistent with the previous result for symmetric block copolymer series.²⁴ Two intermediate samples, the ISP-II and -IV, also show gyroid structures nevertheless the volume ratios of two end blocks, I/P for -II and P/I for -IV, are approximately three for two samples.

Figure 3 displays structures of these blends. Figure 3a,b for blends with distribution indices of 1.27 and 1.31 show gyroid structures, which are essentially the same as that in Figure 2c. In Figure 3c, two totally different images can be clearly recognized in the TEM shot, one is gyroid network structure shown at the upper half of the figure, the other is much simpler one shown in the lower half of the figure. We notice that the fraction of this simpler structure, having two isolated domains aligned tetragonally in an alternating manner, increases with increasing CDI as is seen in Figure 3d, which is actually binary mixture of the ISP-I and -V. This seems to be a periodic structure, whose

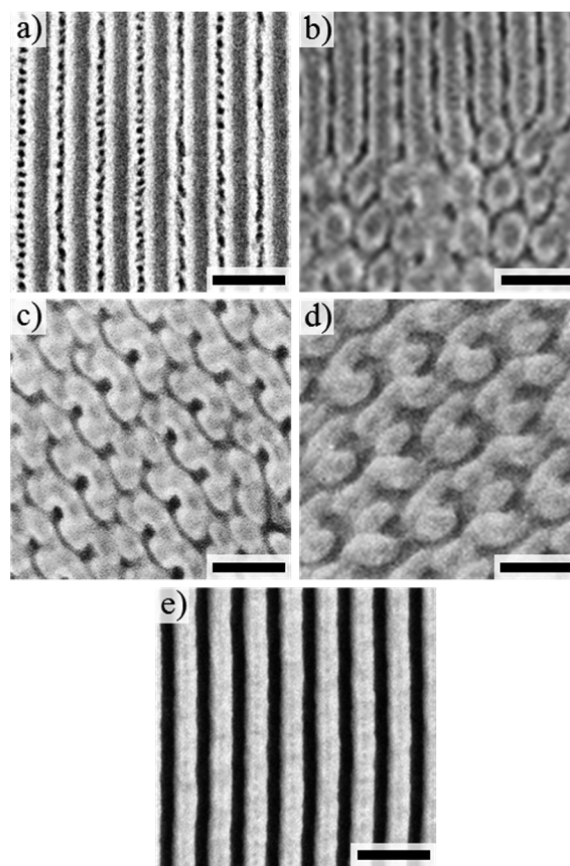


Figure 2. Comparison of microphase-separated structures for the five parent triblock terpolymers. Samples are (a) ISP-I, (b) ISP-II, (c) ISP-III, (d) ISP-IV, and (e) ISP-V, respectively. Scale bars all represent 100 nm.

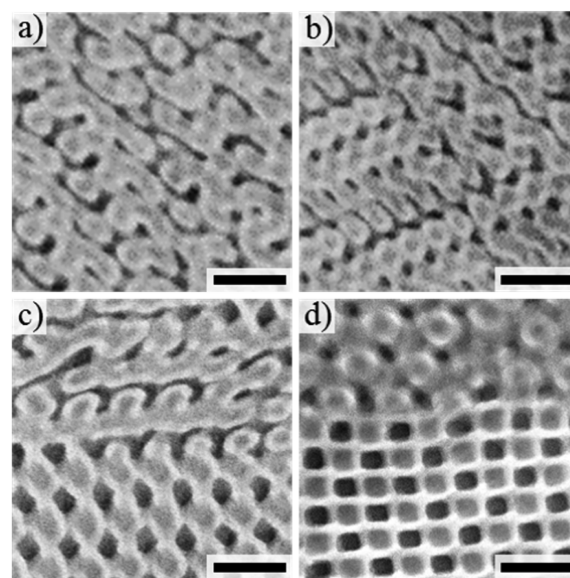


Figure 3. TEM images of the blend samples with various composition distribution index (CDI), which are (a) 1.27, (b) 1.31, (c) 1.36, and (d) 1.51, respectively. Scale bars all represent 100 nm.

isolated domains look rectangular shape instead of commonly-known round one. However, at the same time it has been confirmed by both TEM and SAXS experiments that the morphology of this binary blend is not simple but still includes

two structures, that is, tetragonally-packed isolated domain structure and gyroid structure (Figure S1).

Then another binary blend with different center block fraction was prepared to investigate whether this unusual structure is a quite stable one or not (In short, ISP-V ($\phi_I/\phi_S/\phi_P = 0.39/0.56/0.05$) and ISP-VI ($\phi_I/\phi_S/\phi_P = 0.06/0.62/0.32$. Its TEM image is in Figure S2.) were mixed to give equimolar blend with the composition of $\phi_I/\phi_S/\phi_P = 0.23/0.59/0.18$. From Figure 4a, which is a TEM image of this binary blend,

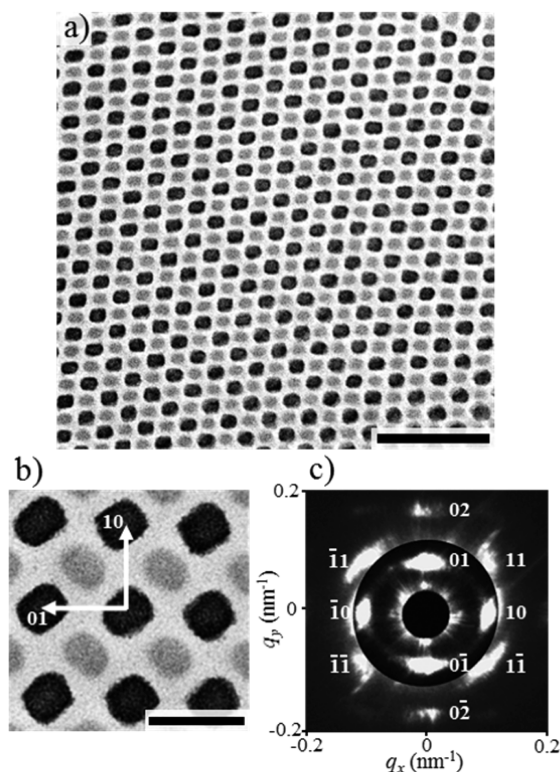


Figure 4. (a) Typical TEM image over a wide range of the binary blend from ISP-V and ISP-VI. Scale bar represents 200 nm and (b) a TEM image at higher magnification (scale bar: 50 nm). (c) A microbeam SAXS diffraction pattern from the same binary blend sample.

one clearly recognizes tetragonally-packed cylindrical structure has been formed over a wide range. Figure 4b shows a TEM image at higher magnification, which looks like rectangular cross-section of tetragonally-aligned black (I) and gray (P) cylindrical domains appear alternatingly. Figure 4c displays a two-dimensional microbeam SAXS diffraction pattern for this blend, which clearly exhibits 4-fold symmetry pattern with its domain distance of 43 nm. This value is consistent with the observed one, 46 nm, by real space image in Figure 4b.

Furthermore, Figure 5a displays a TEMT image constructed, where I domains are penetrating through S matrix, so that we can conclude that the present structure is tetragonally-arranged cylindrical structure whose domain interfaces are rectangular shape not round one. Obviously this I/S interface, probably also P/S one, have the feature of non-CMC, which is seldom observed for monodisperse system but can happen for copolymer system with relatively high molecular weight distribution²³ or complex blends with particular interaction such as hydrogen bonding between two chemical components as one block of copolymers.^{27,28} Figure 5b,c schematically

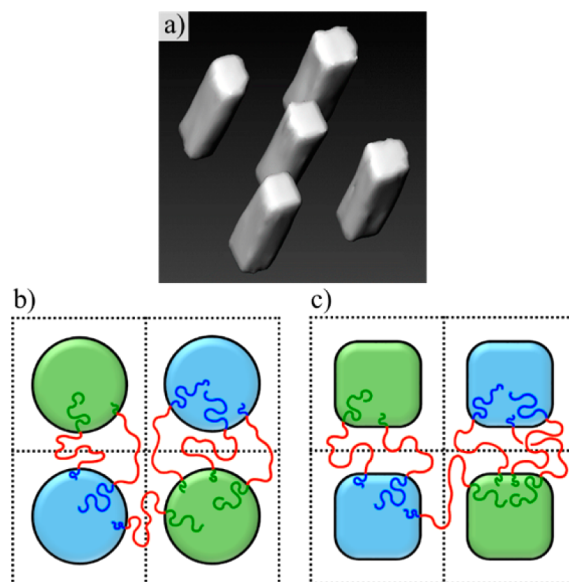


Figure 5. (a) TEMT image constructed from 101 TEM images. I cylinders stained with OsO_4 are picked and highlighted. (b, c) Compare schematic illustrations of possible arrangement of cylinders. When the binary chains with a big difference in block chain lengths are dispersed uniformly in round-shape cylinders, the conformational entropy loss of three chains could be large as shown in (b). In order to reduce this frustration, two chains might be localized, and hence, unusual rectangular-shaped cylinders could be formed as shown in (c).

displays possible arrangement of component polymers. Figure 5b is a well-known round-shaped cylinders arranged tetragonally, while Figure 5c shows rectangular cylinders also arranged tetragonally with block chains. Comparing these two figures, we notice the conformational entropy losses of two end blocks, that is, I and P chains in independent cylinders, as well as center S chains in matrix could be considerably large for Figure 5b arrangement. In Figure 5c, on the other hand, conformational entropy losses for I, P, and S chains are recovered due to unusual rectangular shape of cylinders by sacrificing the placement entropy of junction points from different molecules.

Thus, we can create cylindrical structure with rectangular shape, whose surface has the feature of non-CMC. Combining the present result and the previous one, which is the study on molecular weight distribution, we can safely say that the triblock terpolymer systems with fairly wide molecular or composition distribution tend to produce new surfaces with non-CMC to release the stress on chains by localizing each chain at proper seat. This is the inherent feature of an ABC triblock terpolymer system that can never happen on diblock copolymer systems.

EXPERIMENTAL SECTION

Polymer samples, poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (ISP), were synthesized by three-step anionic polymerizations in tetrahydrofuran (THF) at -78°C from cumyl-potassium as an initiator.²⁵ Six samples were prepared and their molecular characteristics are listed in Table 1. As the first step, five samples from ISP-I through ISP-V, their molecular characteristics are compared in Figure 1a, were mixed at dilute solution states in THF to give blends with various composition distributions. The blend manners of five samples are schematically drawn Figure 1b, where the numbers at the top of bar graph indicates the composition distribution index (CDI) of blend samples. Here the molecular weight distribution of polyisoprene block is chosen as CDI assuming five parent polymers are perfectly monodisperse. The

Table 1. Molecular Characteristics of the Poly(isoprene-*b*-styrene-*b*-2-vinylpyridine) (ISP) Parent Triblock Terpolymers Used in This Study

sample name	M_n^a	φ_I^b	φ_S^b	φ_P^b	M_w/M_n^c
ISP-I	126000	0.08	0.52	0.40	1.03
ISP-II	124000	0.13	0.55	0.32	1.05
ISP-III	161000	0.24	0.55	0.21	1.07
ISP-IV	145000	0.34	0.55	0.1	1.04
ISP-V	124000	0.39	0.56	0.05	1.06
ISP-VI	122000	0.06	0.62	0.32	1.02

^aDetermined by osmometry. ^bDetermined by ¹H NMR spectroscopy and the densities of I, S, and P at room temperature (ρ_I : 0.926, ρ_S : 1.05, ρ_P : 1.14). ^cEstimated from a SEC chromatogram whose elution volumes were calibrated with polystyrene standards.

average volume fractions in blends are all similar as $\varphi_I/\varphi_S/\varphi_P = 0.25/0.54/0.21$, because the symmetric blends were prepared. It should be noted that a monodisperse ISP triblock terpolymer with this composition, for instance, the parent block copolymer ISP-III, show tricontinuous gyroid structure.²⁶

Sample films were obtained by casting solvent very slowly for three days and films were thermally treated at 150 °C for longer than four days. Transmission electron microscopy (TEM) experiments were carried out for ultrathin sections stained with OsO₄ and I₂ by the TEM apparatus JEM-1400 of JEOL Ltd. Small angle X-ray scattering (SAXS) experiments were also performed using the micro beam SAXS apparatus installed at the SPring-8 facility in Hyogo, Japan. X-ray beam was irradiated from the direction parallel to the film surface.

To investigate three-dimensional microdomain structures, a transmission electron microscopy tomography (TEMT) experiment was carried out using a JEM-1400 of JEOL Ltd., being operated at an acceleration voltage of 120 kV. A series of a total of 101 TEM images were collected with tilt angles ranging from -50° to +50° in 1° increment. The series of TEM images were aligned by the fiducial marker method using the Au nanoparticles as the marker. The three-dimensional reconstruction image was given by using a reconstruction software, Composer, and a visualization and modeling software, Visualizer, both of JEOL System Technology Co., Ltd.

■ ASSOCIATED CONTENT

Supporting Information

SAXS pattern and TEM image. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

TEMT experiments were carried out under the kind guidance of Mr. Kazumi Kobayashi (JEOL), and the authors deeply appreciate his kind support. This work was financially supported by Kakenhi (25248048), from MEXT; Y.M. is grateful for their support. Y.A. was financially supported by the Program for Leading Graduate Schools "Integrative Graduate Education and Research in Green Natural Sciences", MEXT, Japan. Microbeam SAXS measurements were performed under the approval of Spring-8 (Proposal No. 2009B1631). SAXS measurements were carried out at Photon Factory (PF), Institute of Materials Structure Science, High Energy Accelerator Research Organization, Japan (No. 2013G737).

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