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Preparation and Morphology of Ring-Shaped Polystyrene-*block*-polyisoprenes

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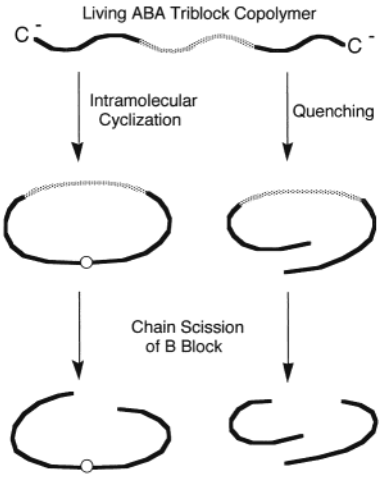
ABSTRACT: Three polystyrene-*block*-polyisoprene-*block*-polystyrenes (SIS) with different compositions were prepared and cyclized by the coupling reaction between two end groups on the same molecules. Ring-shaped polystyrene-*block*-polyisoprenes (SI) were isolated from the coupling products by GPC fractionation. They were ozonized in order to decompose the polyisoprene blocks selectively referring to the linear molecule. GPC analysis of the decomposed products obtained by ozonolysis quantitatively confirmed that the fractionated products include ca. 90% ring molecules. The morphological transition of the ring-shaped block copolymers depends on composition in essentially the same manner as that of the linear triblock copolymers, whereas the domain spacings of SI ring-shaped block copolymers were all smaller than those of the corresponding SIS linear triblock copolymers, which is attributed to looped chain conformation.

Introduction

Ring polymers are interesting materials that should have quite different properties from those of the corresponding linear ones. Ring polymers are usually prepared by coupling bifunctional polymers with bifunctional coupling agents. Polystyrenes,[1−6] poly(2-vinylpyridine)s,[7,8] polybutadiene,[9] and poly(tetrahydrofuran)s,[10,11] for example, have been synthesized by this method. α,ω-Hetro-bifunctional polymers have been also used for the synthesis of ring polymers.[12−15] In these studies, their ring structures were characterized by their comparing of chain dimensions to those of linear polymers; however, that provides indirect evidence only. Although NMR analysis of linking points should provide direct evidence for ring structures, it is not applicable to high molecular weight polymers.[12,13] Although careful characterization of a sample by pyrolysis−gas chromatography/mass spectroscopy (Py-GC/MS) by detecting a trace amount of linking group in the sample has provided direct evidence of the ring structure, it is not applicable to high molecular weight polymers, and the applicable polymer species for Py-GC/MS are limited.[8]

We recently proposed a new approach for proving the cyclic structure of a homopolymer.[16] Scheme 1 illustrates this method using a ring-shaped block copolymer composed of two components. An AB ring block copolymer is synthesized by intramolecular cyclization from an ABA triblock copolymer. If the B blocks are decomposed, the molecular weight of the resulting linear A block from the former should be double that of the latter. The difference in molecular weights of the two decomposed products will be distinguishable by GPC; therefore, the content of ring molecule in the polymer sample can be estimated quantitatively. Polymers such as 1,4-polyisoprene with carbon−carbon double bonds in the main chain are suitable for the B block, since the carbon−carbon double bonds of polydienes are easily decomposed by ozonolysis.[17]

Scheme 1



The microphase-separated structures of ring-shaped copolymers are also quite interesting. Since the ring-shaped copolymers have no chain ends and have a looped chain conformation instead, their chain conformations in the microphase-separated structures should be topologically quite different from linear block copolymers. Recently, ring-shaped polystyrene(PS)-*block*-poly(dimethylsiloxane) (PDMS) was synthesized by coupling a linear living triblock copolymer precursor with $Cl_2Si(CH_3)_2$,[18,19] while ring-shaped PS-*block*-poly(2-vinylpyridine) (P2VP) copolymers were prepared by the same method from Li−P2VP-*block*-PS-*block*-P2VP−Li and 1,4-bis(bromomethyl)benzene.[20] Lecannec et al. subsequently investigated the morphology of these two ring-shaped copolymer systems,[21] though they did not report the purity of the ring-shaped samples; the samples did not have narrow molecular weight distributions ($M_w/M_n \geq 1.17$).

This study reports the synthesis of a telechelic ABA triblock copolymer of polystyrene and polyisoprene as

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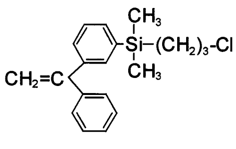
A and B, respectively, and the synthesis of AB ring copolymer using the telechelic ABA triblock copolymer by a coupling reaction, followed by purification using GPC fractionation. Finally, the amount of ring-shaped molecules in the sample was determined accurately by combining ozonolysis and GPC measurements, which we will call ozonolysis−GPC analysis. The morphology of the ring-shaped diblock copolymers and linear triblock copolymers will also be compared.

Experimental Section

Materials. The initiator, potassium naphthalenide, was synthesized by the reaction between potassium (Soekawa Pure Chemicals Co. Ltd., 99%) and naphthalene (Aldrich Co. Ltd., 99%) in THF at room temperature in vacuo for 5 h.[22] The concentration of the initiator was determined by titration with standard HCl solution. Tetrahydrofuran (THF, Hayashi Pure Chemicals Co. Ltd., 99.5%) was dried with sodium metal, distilled in vacuo with sodium anthracenide, and then purified by distillation from a mixture of α-methylstyrene tetramer−sodium dianion. Benzene (Kishida Reagents Chemicals Co. Ltd., 99%) was dried over calcium hydride under reduced pressure, purified by distillation with the addition of *n*-BuLi. Styrene (Kishida Reagents Chemicals Co. Ltd., 99.5%) was dried over calcium hydride under reduced pressure, purified by distillation with octylbenzophenone−sodium.[23,24] Isoprene (Kishida Reagents Chemicals Co. Ltd., 98%) and 1,1-diphenylethylene (DPE, Hokko Chemicals Co. Ltd., 95%) were dried over calcium hydride under reduced pressure, purified by distillation with *n*-BuLi. 1-[3-(3-Chloropropyldimethylsilyl)-phenyl]-1-phenylethylene (**I**) was synthesized from 1-(3-bromophenyl)-1-phenylethylene (**II**) and 3-chloropropyldimethylchlorosilane (**III**) (Shin-etsu Silicone Co. Ltd.).[25] **II** was prepared by reaction of 3-bromoacetophenone (Aldrich Co. Ltd., 99%) with phenylmagnesium bromide followed by hydrolysis and dehydration in 65% yield. **II** (88 g, 0.34 mol) dissolved in THF (250 mL) was added dropwise to magnesium turnings (9.5 g, 0.40 mol) under nitrogen gas at 65 °C for 2 h to give the Grignard reagent. After filtration, **III** (60 g, 0.35 mol) was added to the Grignard reagent and stirred at 20 °C for 12 h. Fractional distillation of the product at 160−163 °C under 133 Pa gave 94 g (0.30 mol) of **I** in 87% yield from **II**. The product was confirmed to be **I**: 400 MHz ^{1}H NMR ($CDCl_3$): δ 0.21 (s, 6H, CH_3Si), 0.78 (t, 2H, $-CH_2-Si$), 1.70 (quint, 2H, $C-CH_2-C$), 3.40 (t, 2H, $Cl-CH_2-$), 5.40 (d, 2H, $CH_2{=}C$), 7.20−7.46 (m, 9H, $C_6H_4 + C_6H_5$). Purification of **I** was carried out in an all-glass apparatus equipped with break-seals under a pressure of 1×10^{-3} Pa or lower. After being dried with calcium hydride, **I** (42 g, 0.13 mol) was transferred into a vacuum apparatus and purified by distillation in vacuo at a bath temperature of 150 °C. Finally, **I** was diluted to ca. 10% (v/v) with purified THF. Methanol was dried over calcium hydride.



I

Preparation of Linear Triblock Copolymer. A preparation of telechelic polystyrene-*block*-polyisoprene-*block*-polystyrene (SIS) triblock copolymers with DPE type vinyl groups on both ends is shown in Scheme 2. All the operations were carried out in sealed glass apparatus with break-seals under a pressure of 1×10^{-3} Pa or lower. One example for synthesis of a linear triblock copolymer was as follows; first, isoprene (5.0 g, 0.074 mol) was anionically polymerized in THF (200 mL) with 4.0 mL of THF solution of potassium naphthalenide (0.071 mol/L) at −78 °C for 24 h to give bifunctional polyisoprenyl potassium. Second, approximately 10% (v/v) of THF solution of styrene (5.6 g, 0.054 mol) was introduced to the living polymer solution and polymerized at −78 °C for 1 h. Third, 1.5 mL of THF solution of DPE (0.57 mol/L) was added to the solution of living polymer for end-capping in the molar ratio of $[\mathrm{DPE}]/[\mathrm{K}] \fallingdotseq 3/1$ for 1 h, followed by termination with 2.7 mL of THF solution of **I** (0.32 mol/L) in the molar ratio of $[\mathbf{I}]/[\mathrm{K}] \fallingdotseq 3/1$ at room temperature. The polymers obtained were purified by precipitation in an excess amount of methanol three times to remove the residual DPE and **I**. The other samples were also synthesized by the same manner using different amounts of monomers. Three SIS triblock copolymers with different compositions were encoded L-1, L-2, and L-3 as shown in Table 1. After being freeze-dried, the SIS triblock copolymers (2.0 g) were transferred into vacuum glass apparatuses and then diluted with purified THF (2 L) for cyclization reactions; that is, the polymer concentration for cyclization is ca. 0.1% (w/v).

Scheme 2

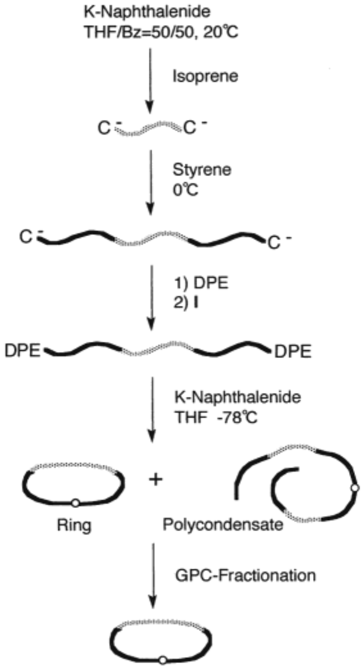


Table 1. Molecular Characteristics of Samples

	polyisoprene block	linear/ring block copolymer			
sample	$10^{-4}M_n$[a]	$10^{-4}M_n$[a]	M_w/M_n[b]	Φ_{PI}[c]	P[d]
L-1	0.7_9	6.0_7	1.0_7	0.14	
R-1	0.7_7	6.4_0	1.0_4	0.13	0.91
L-2	1.8_3	6.3_1	1.0_8	0.31	
R-2	1.6_2	6.0_0	1.0_5	0.30	0.91
L-3	2.7_6	6.0_0	1.0_7	0.49	
R-3	2.8_6	6.2_2	1.0_5	0.49	0.90

[a] Estimated from ^{1}H NMR. [b] Determined by GPC. [c] Volume fractions of polyisoprene blocks estimated from ^{1}H NMR and the bulk densities of component polymers (see text). [d] Ring molecule content determined by ozonolysis−GPC analysis.

Cyclization Reaction of Linear Triblock Copolymer. Cyclization reaction between two end vinyl groups within a SIS triblock copolymer was carried out in the same manner as reported previously,[16] as shown in Scheme 2. Potassium naphthalenide was used again as the linking agent, and 4.0 mL of THF solution of potassium naphthalenide (0.071 mol/L) was introduced into 2 L of THF solution (0.1% (w/v)) of the linear triblock copolymer described above in the molar ratio of $[\mathrm{DPE}]/[\mathrm{K}] \fallingdotseq 5$ at −78 °C and stirred for 2 days. After being quenched with dried methanol, the obtained polymer was precipitated into an excess amount of methanol.

Fractionation. In the course of the cyclization reaction, the high molecular weight polycondensation products were formed in addition to cyclic products. The cyclic polymer was isolated by GPC fractionation at room temperature using a fully automatic instrument of Tosoh Ltd. type HLC-837 equipped with a pair of columns GMH6 (bead size is 13 μm and pore sizes are 10^2−10^6 Å) of Tosoh Ltd.; the column size is 300 mm in length and 21.5 mm i.d. Chloroform was used as an eluent; the flow rate was 10 mL/min, at room temperature, for all runs. The concentrations of the polymer solutions were ca. 0.2% (w/v). The fractionated polymers were coded R-1, R-2, and R-3, which correspond to L-1, L-2, and L-3, respectively.

Molecular Characterization. Apparent molecular weights and molecular weight heterogeneities, M_w/M_n, were determined by GPC System of Tosoh Ltd. with a RI-8012 differential refractive index detector, a UV-8011 ultraviolet spectroscopic detector, and a series of two G4000HXL columns (bead size is 5 μm, pore size is 10^4 Å) and two GMHXL columns (bead size is 9 μm, pore sizes are 10^2−10^6 Å) with 300 mm length and 7.8 mm i.d. each. THF was used as an eluent, and the flow rate was 1 mL/min, at room temperature. Standard polystyrenes were used for a calibration. ^{1}H NMR spectra were measured with a JEOL EX-400 NMR spectrometer at 399.65 MHz to obtain the number-average molecular weight, M_n, and composition of the block copolymer samples. Chemical shifts were referred to chloroform in chloroform-*d*. In the ^{1}H NMR spectrum of the SIS triblock copolymers, M_ns were estimated from comparison of signals of vinyl protons from the DPE group (5.4 ppm) on both chain ends, vinyl protons of polyisoprene (4.7−5.2 and 5.6−6.0 ppm), and phenyl protons of polystyrene (6.4−7.3 ppm). Quantitative introduction of **I** onto bifunctional living polymer was confirmed previously.[25] Accordingly, M_ns of the ring-shaped sample were also estimated from comparison of signals of methyne protons (3.8 ppm) at the connected part, vinyl protons of polyisoprene, and phenyl protons of polystyrene.

Ozonolysis. Ozonized oxygen was generated by a ceramic ozonizer model KA-10 of Koyo Iron Works and Construction Co. Ltd. To cleave the carbon−carbon double bonds in the polyisoprene chain, ozonized oxygen (ca. 2%) was bubbled into dichloromethane/methanol (95/5 vol/vol) solutions of linear triblock copolymers and also into those of the fractionated polymers at −78 °C for 30 min with a flow rate of ca. 300 mL/min.

Morphological Observation. Films used for morphological observation were cast from ca. 5% (w/v) toluene solutions of samples and evaporated for a few days under nitrogen. The cast films were dried for 6 h and annealed at 150 °C for a week in a vacuum oven. The films were cut into ultrathin sections (50−80 nm thick) using an ultramicrotome, Reichert Ultracut N at room temperature. The sections were stained with osmium tetroxide vapor from 5% aqueous solution at room temperature for 12 h. The microphase-separated structures of the sections were observed by a JEOL transmission electron microscope JEM-2010 operated at an accelerating voltage of 120 kV.

Small-angle X-ray scattering (SAXS) was carried out using a M18XHF[22] of MAC Science Co. having Kratky camera system with a copper target X-ray source operated at 43 kV−390 mA. The monochromated Cu Kα line with λ of 0.154 nm was used for the measurements. A scintillation counter and a step-scanning goniometer were also provided.

Results and Discussion

Preparation of Linear Triblock Copolymer. Figure 1a shows a GPC chromatogram of an SIS linear triblock copolymer, L-2, as an example. It is a unimodal with a symmetrical curve and has a reasonably narrow molecular weight distribution. Table 1 lists the molecular characteristics of the three linear SIS triblock copolymers. The three copolymers have similar chain lengths of approximately 60K as designed and fairly narrow molecular weight distributions ($M_w/M_n \leq 1.08$), but different compositions. From the molar ratio determined by ^{1}H NMR measurements and the densities of the bulk polymers ($d_{\text{polystyrene}} = 1.05$ g/cm^3, $d_{\text{polyisoprene}} = 0.924$ g/cm^3), the volume fractions of polystyrenes in the SIS linear triblock copolymers were estimated to be 0.14 for L-1, 0.31 for L-2, and 0.49 for L-3, whereas all the polyisoprene chains of three samples contained 3% 1,4 and 97% 1,2 or 3,4 linkages.

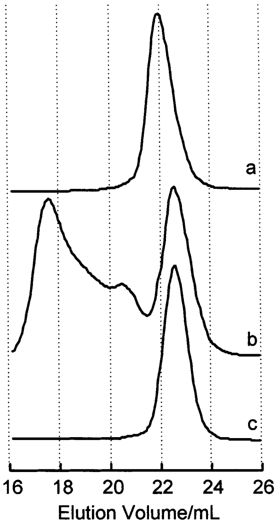


Figure 1. GPC chromatograms of (a) a as-polymerized product of linear triblock copolymers, L-2, (b) the crude product after cyclization, and (c) the fractionated ring molecule, R-2.

Preparation of Ring-Shaped Copolymer. Figure 1b shows a multipeak GPC chromatogram for the crude product after dimerization reaction between end vinyl groups within the SIS linear triblock copolymer, L-2. The polymers eluting in the range 16−20 mL are high molecular weight polycondensation products formed by intermolecular reactions, while the product eluting at around 22.5 mL is the desired ring copolymer produced by intramolecular reaction since the peak position is shifted considerably from that for linear counterpart in Figure 1a. The crude product was fractionated by GPC to isolate ring-shaped copolymer. Figure 1c shows the GPC chromatogram of the fractionated product, R-2. The chromatogram of the fractionated polymer is symmetric and unimodal and has a relatively narrow molecular weight distribution. The number-average molecular weights and polystyrene volume fractions of the fractionated products, together with those of the parent linear triblock copolymers, were measured by NMR and are summarized in Table 1. The molecular weights of the fractionated products agree well with those of the parent linear triblock copolymers, and the compositions of the linear and corresponding ring-shaped copolymers are almost the same.

Ozonolysis−GPC Analysis. Ozonolysis−GPC analysis was employed to prove the ring architecture of the fractionated samples and determine the ring molecule contents in the samples. Figure 2a compares the RI-detected GPC chromatogram of the product decomposed by ozonolysis of the parent linear triblock copolymer, L-3, with that of the parent triblock copolymer before ozonolysis. The apparent molecular weight of the decomposed polymer has decreased considerably, while maintaining low polydispersity. GPC analysis using RI and UV detectors simultaneously confirms that the RI/UV peak area ratio for the product eluting at around 24.7 mL agrees well with that of the polystyrene homopolymer, which means that the decomposed product consists overwhelmingly of polystyrene and hence contains little polyisoprene fragment. The GPC curve of the decomposed product appeared in the range 23−

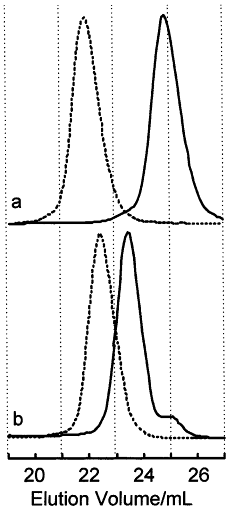


Figure 2. Comparison of GPC chromatograms before and after decomposition by ozonolysis: (a) a parent linear triblock copolymer (broken line), L-3, and the corresponding decomposed product (solid line); (b) a fractionated sample (broken line), R-3, and its decomposed counterpart (solid line).

27 mL and is unimodal, with a narrow molecular weight distribution. Its apparent molecular weight by GPC is 16.2K, which is close to the M_n of one polystyrene (S) block chain in the SIS linear triblock copolymer, 16.3K.

Figure 2b shows the GPC chromatogram of the ozone-decomposed polymer of the fractionated product and that of the polymer before ozonolysis, R-3. The peak of the former at around 22−26 mL is bimodal, and the peak molecular weights of the main peak and its shoulder are 33.5K and 16.8K, respectively. The existence of a peak whose molecular weight is 33.5K, which is almost twice that of the latter, is direct evidence of forming cyclic structure, as described in Scheme 1. The purity of the ring-shaped molecule was estimated to be 0.90 by comparing the peak area for the main peak and the much smaller shoulder. Thus, the ring polymer contents in the fractionated products, *P*, have been quantitatively determined from the area ratio of the two peaks in the chromatograms, which are also listed in Table 1. All of the fractionated products contain an extremely high amount of ring molecules.

Comparison of Morphology between Linear SIS Triblock Copolymers and Ring SI Copolymers. Figure 3 compares TEM images of the linear SIS triblock copolymers and the corresponding SI ring-shaped block copolymers. The ring molecules and corresponding SIS linear triblock counterparts have similar microphase-separated structures. Their structures are PI spheres in the PS matrix for L-1 ($\Phi_{PI} = 0.13$) and R-1 ($\Phi_{PI} = 0.14$) as shown in Figure 3a,b, PI cylinders in the PS matrix for L-2 ($\Phi_{PI} = 0.30$) and R-2 ($\Phi_{PI} =$

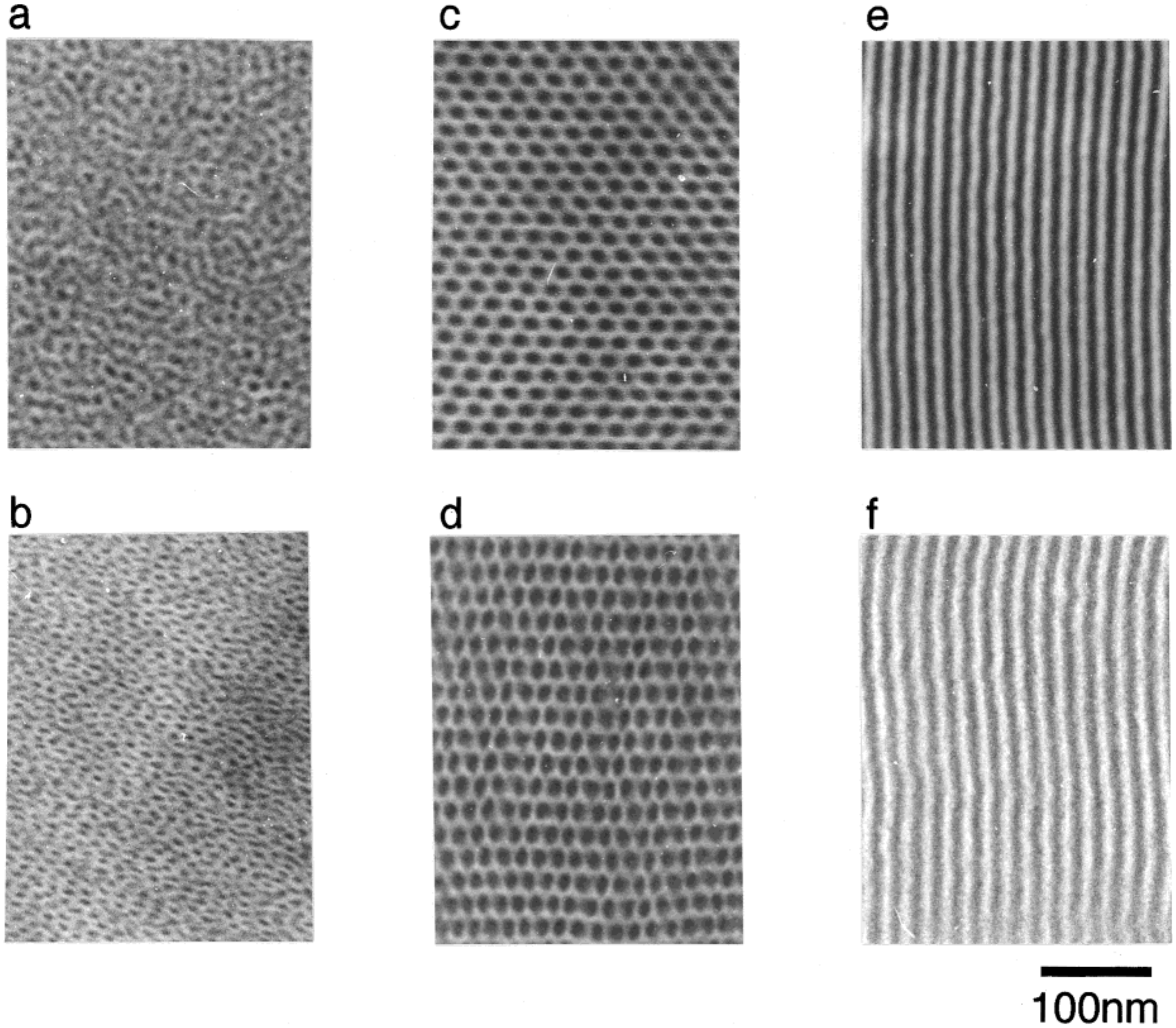


Figure 3. Electron micrographs of the linear triblock copolymers and the fractionated ring molecules: (a) L-1, (b) R-1, (c) L-2, (d) R-2, (e) L-3, and (f) R-3.

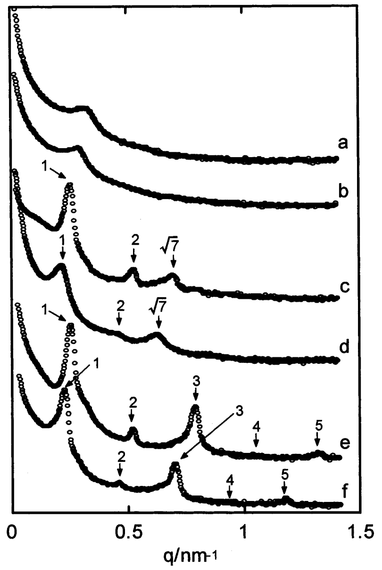


Figure 4. SAXS diffraction patterns of the linear triblock copolymers and the fractionated ring molecules: (a) L-1, (b) R-1, (c) L-2, (d) R-2, (e) L-3, and (f) R-3.

Table 2. Domain Spacings of Samples

sample	structure	q_1/nm^{-1}	D/nm
L-1	sphere	0.30$_8$	25.$_0$
R-1	sphere	0.32$_9$	23.$_4$
L-2	cylinder	0.23$_7$	30.$_6$
R-2	cylinder	0.26$_9$	27.$_0$
L-3	lamella	0.23$_2$	27.$_1$
R-3	lamella	0.26$_7$	23.$_5$

0.30) in Figure 3c,d, and alternating lamellar structures from PI and PS for L-3 ($\Phi_{PI} = 0.49$) and R-3 ($\Phi_{PI} = 0.49$) in Figure 3e,f.

Figure 4 compares SAXS intensity profiles of the SIS linear triblock copolymers and the corresponding SI ring-shaped block copolymers. The two curves for the samples L-1 ($\Phi_{PI} = 0.13$) and R-1 ($\Phi_{PI} = 0.14$) in Figure 4a,b show only one peak each at q of 0.308 and 0.329 nm^{-1}, respectively, where q ($=4\pi \sin \theta/\lambda$) is the magnitude of the scattering vector, λ is the wavelength of X-ray, and 2θ is the scattering angle, in which B consists of spherical structures with a fairly low ordering of spheres; this is quite consistent with the TEM results. The two curves for the samples L-2 ($\Phi_{PI} = 0.30$) and R-2 ($\Phi_{PI} = 0.30$) in Figure 4c,d exhibit three reflection peaks each at the relative ratio of 1, $\sqrt{4}$, and $\sqrt{7}$ in terms of q. This diffraction pattern is consistent with hexagonally packed cylinders arranged in a matrix, since the peak $\sqrt{3}$ should be suppressed because of the scattering form factor from the hexagonal cylinders whose volume fraction is around 0.30.[26] The curves for the samples L-3 ($\Phi_{PI} = 0.49$) and R-3 ($\Phi_{PI} = 0.49$) in Figure 4e,f show the multireflection peaks at the ratio q_n/q_1 of 1, 2, 3, 4, and 5, which indicate the alternating lamellar structures. The even number order peaks for L-3 and R-3 are very low because of the form factors from lamellar structure with a thickness ratio of 0.49/0.51 for two phases which correspond to the volume fractions of the present samples (Table 1). Thus, all SAXS results are quite consistent with the TEM results.

Table 2 compares the domain spacings D for an SI ring-shaped block with those of the corresponding SIS triblock copolymers, which have been precisely evaluated by applying Bragg's condition to the magnitude of the scattering vectors at the first peak potitions in the SAXS profiles. D can be represented by $(3/2)^{1/2}2\pi/q$, $(4/3)^{1/2}2\pi/q$, and $2\pi/q$ for spherical, cylindrical, and lamellar structures, respectively. The domain spacings of the SI ring-shaped block copolymers are all smaller than those of the SIS triblock copolymers. This may be attributed to the difference in their chain conformations in bulk. Both block chains of an SI ring-shaped molecule must have a looped conformation. The chain elongation along the direction normal to the microdomain interface must therefore be suppressed relative to those of two block chains in a linear counterpart, which has free ends.

In conclusion, well-defined ring-shaped polystyrene-*block*-polyisoprenes were prepared by anionic living polymerization followed by intramolecular cyclization reactions between two end groups. Ring-shaped diblock copolymers were isolated from the coupling product by GPC fractionation. To confirm the ring structure quantitatively, the strategy in Scheme 1 was attempted. Linear triblock copolymers and the cyclized and fractionated products were ozonized to decompose the polyisoprene chains. GPC analysis of the decomposed products by ozonolysis demonstrated that the fractionated products include ca. 90% ring molecule. Morphological investigations confirmed that the morphological transition of the ring-shaped block copolymers varies with composition in essentially the same manner as that of the linear triblock copolymers; moreover, the domain spacings of the SI ring-shaped block copolymers are smaller than those of the SIS triblock copolymers, which can be attributed to the looped chain conformation of the ring molecules.

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