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Preparation, Characterization, and Nanophase-Separated Structure of Catenated Polystyrene−Polyisoprene

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ABSTRACT: A catenated copolymer consisting of cyclic polystyrene (PS) with short poly(2-isopropenylnaphthalene) (PIPN) segments and cyclic polyisoprene (PI) were prepared by living anionic polymerization. The molecular weight of catenated copolymer is 37 kDa. Naphthalene side groups attached to the PIPN segments in the cyclic P(IPN-*b*-S) were radical-anionized by a reaction with potassium in THF, and telechelic PI was successfully cyclized by a pair of coupled reactions at two close radical-anionized sites on the cyclic chain under dilute conditions. Formation of the catenated copolymer consisting of cyclic P(IPN-*b*-S) and cyclic PI was confirmed by size-exclusion chromatography using a UV detector with a wavelength of 320 nm for preferential detection of naphthalene moieties. After isolation of the catenated copolymer by fractionation, it was confirmed by transmission electron microscopy that the topologically linked polymers exhibit a nanophase-separated structure in bulk.

Introduction

Cyclic polymers have attracted the interest of many researchers because of their lack of chain ends. Hence, many investigations of cyclic polymers have been performed both theoretically[1–4] and experimentally.[4–12] As a result, several meaningfully different solution properties of cyclic structures including chain dimensions in solution[13] and bulk properties such as glass transition temperatures[14–16] and diffusion constants[17] have been identified.

Catenated polymers are more advanced research objectives because of their topologically self-constrained structures. In general terms, synthesis and characterization of a catenated polymer represent a very difficult and painstaking process. Several successful examples of low molecular weight compounds are known in which the desired molecules were obtained from template synthesis by using a metal complex[18,19] and $\pi-\pi$ stacking.[20] However, examples of preparation and characterization of catenated polymers with molecular weight greater than 10 kDa are extremely difficult and have not been reported yet.

On the other hand, block copolymers with incompatible components are known to form nanophase-separated structures in concentrated solutions or in bulk due to the direct constraint of covalent bonds.[21–25] Also, syntheses and nanophase structures of cyclic diblock copolymers have been reported.[26,27] It is worthwhile to consider the phase structure of a complex catenated polymer with two incompatible components that cause the "molecule" to be in a strong segregation regime in the condensed state. Although Hogen-Esch and co-workers have reported the synthesis of a catenated copolymer,[28] information regarding the yield, chain conformation, and phase structure in bulk was not provided.

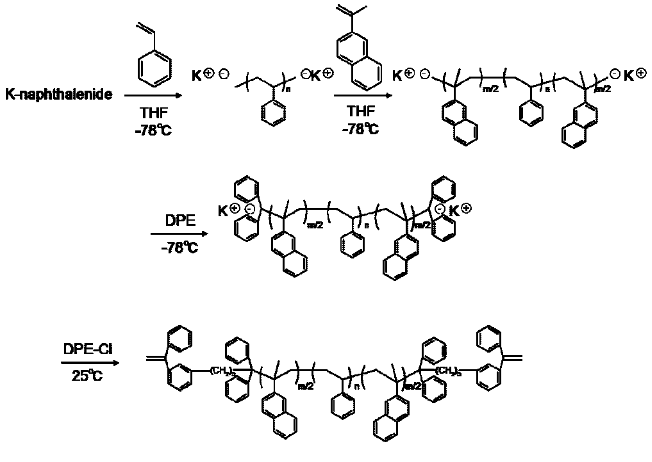
In this work, we have attempted to synthesize a catenated copolymer in a "one-to-one" reaction and finally succeeded in preparation of a polystyrene−polyisoprene catenated copolymer, although the yield was quite low. As a strategic method for an effective catenated ring-closure reaction, we aimed to carry out an intramolecular coupling reaction of the second polymer that has a reactive double bond on both ends at radical anionized reaction sites on the first cyclic polymer. Polystyrene was chosen as a first polymer species, and several naphthalene side groups were introduced into the polystyrene chain to produce radical anions. Polyisoprene was selected as a second polymer species.

Experimental Section

Materials. The details of purification procedure of solvents and monomers were the same as reported previously.[29,30] Potassium naphthalenide was used as an initiator and end-to-end coupling reagent in this study. This compound was synthesized by a reaction of naphthalene and potassium in tetrahydrofuran (THF) at room temperature in vacuo. 2-Isopropenylnaphthalene (IPN) was distilled with 2-isopropylnaphthalene as an azeotropic mixture using triphenylmethyllithium as a purification agent.

Synthesis of Cyclic P(IPN-*b*-S). A telechelic P(IPN-*b*-S-*b*-IPN) triblock copolymer with 1,1-diphenylethylene (DPE)-type functional groups on its chain ends was synthesized using a two-step living anionic polymerization followed by a two-step chemical modification of the chain ends. Scheme 1 shows a brief synthetic method of telechelic P(IPN-*b*-S-*b*-IPN). The details of the polymerization procedure of telechelic polystyrene were reported previously.[22–24] All the operations were carried out under a vacuum of 10^{-5} Torr

Scheme 1. Synthetic Scheme of a Telechelic P(IPN-*b*-S-*b*-IPN) Copolymer End-Capped with DPEs



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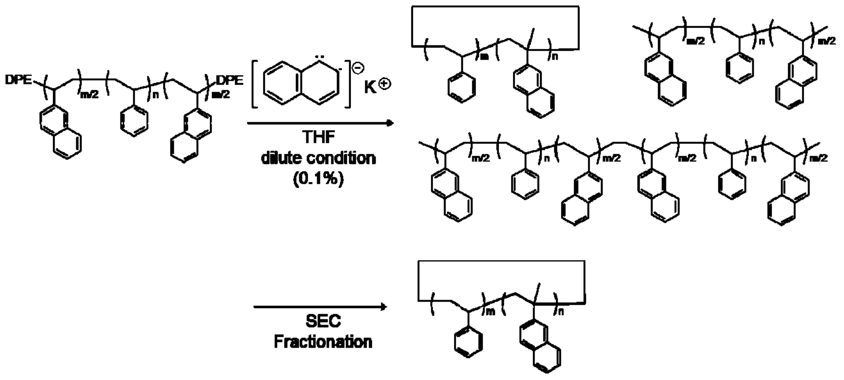
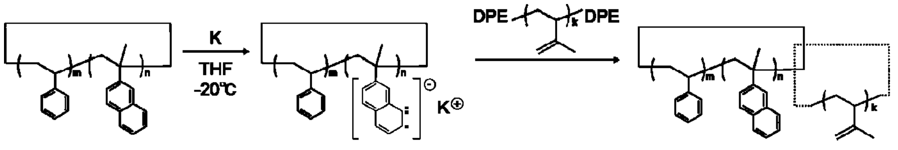
Scheme 2. Synthetic and Separation Scheme of a Cyclic P(IPN-*b*-S) Copolymer



Scheme 3. Synthetic Image of a Catenated Copolymer (Solid Line: PS; Dotted Line: PIPN; Dashed Line: PI)



or lower in a glass apparatus. Styrene was anionically polymerized with potassium naphthalenide using as an initiator in THF at −78 °C, followed by addition of IPN into a solution of bifunctional living polystyryl anions. The bifunctional living polymer was end-capped with DPE and addition of 1-[3-(3-chloropropyldimethylsilyl)phenyl]-1-phenylethylene (DPE-Cl), resulting in introduction of vinyl-type functional groups on both chain ends.[27] The polymer solution was precipitated into an excess amount of methanol to remove excess DPE (which had been added on purpose) and other chemical residues and subsequently freeze-dried.

The telechelic triblock copolymer was cyclized with potassium naphthalenide in a highly dilute solution of THF (ca. 0.1%) as shown in Scheme 2 for about 12 h. After being quenched with methanol, the polymer was precipitated into an excess amount of methanol repeatedly to exclude naphthalene residues produced during the course of the coupling reaction. To remove undesirable polymer products such as intermolecular condensation products and noncyclized linear polymers, separation of cyclic polymers was carried out using a preparative SEC system. THF was used as an eluent, and the concentration of polymer solution was about 0.7% (w/v). 2.3 g of the cyclic P(IPN-*b*-S) was obtained from the crude product with 8.3 g.

Telechelic PI with DPE-type vinyl groups was synthesized by the essentially same process as the synthesis of P(IPN-*b*-S-*b*-IPN) triblock copolymer for 2 h at −78 °C. The polymer solution was precipitated into excess methanol to remove DPE and other residues, followed by drying under vacuum. The telechelic PI was then transferred into a vacuum apparatus and diluted to 9.5% (w/v) with purified THF. A THF solution of 1,4-dilithio-1,1,4,4-tetraphenylbutane was then added until the faint red color of the dilithio compound remained. The microstructure of PI were confirmed by ^{1}H NMR, and it estimated that the ratio of 1,2-, 3,4-, 1,4-sutructures is 23:72:5.

Synthesis of Catenated PS-PI. Synthesis of a catenated copolymer was carried out as shown in Scheme 3. 0.5 g of cyclic P(IPN-*b*-S) diblock copolymer was radical-anionized with potassium metal in THF at −20 °C. The THF solution of 0.7 g of telechelic PI purified previously was added into the dilute radical-anionized P(IPN-*b*-S) solution. An overall polymer concentration of ~0.3% mixture was left for 12 h without stirring. Methanol was added to quench the DPE anions, and the reaction product was precipitated into excess methanol three times to remove DPE and other chemical residues, followed by filtration and drying of the product under vacuum.

Separation and Molecular Characterization of Catenated PS-PI. Separation of the catenated PS-PI was carried out in two steps. In the first step, solvent fractionation was performed in *n*-hexane two times to remove excess PI homopolymers. In the second step, SEC separation was conducted with THF as an eluent at a flow rate of 5 mL/min to remove P(IPN-*b*-S) residues. The concentration was ~0.5%. The SEC system was equipped with three columns (one TSK-gel G4000H_{HR} and two G3000H_{HR} columns of Tosoh) at a column temperature of 40 °C. Finally, 10 mg of sample was obtained (0.8% yield).

The apparent number-average molecular weights (M_n) of precursor polymers and the catenated copolymer as well as the polydispersity indices (PDI) were determined by SEC. All the SEC measurements were carried out by using THF as an eluent at a column temperature of 40 °C with the wavelength set at 254 and 320 nm. Absolute molecular weights of precursor polymers were measured by the light scattering method in THF at 35 °C with a Wyatt Technology DAWN EOS. ^{1}H NMR measurements were performed to determine the microstructure of the polyisoprene and

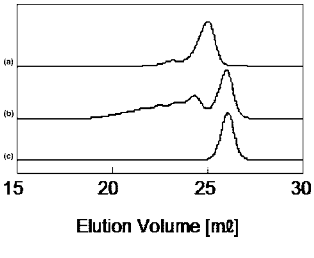


Figure 1. SEC chromatograms obtained in THF of (a) telechelic P(IPN-*b*-S-*b*-IPN), (b) cyclization product obtained from (a), and (c) SEC-fractionated product from (b).

Table 1. Molecular Characteristics of the Polymers Prepared

sample	M_n[a] [kDa]	M_w/M_n[a]	M_w[b] [kDa]	molar ratio[c]
telechelic P(IPN-*b*-S-*b*-IPN)	14.7	1.03	1.75	
cyclic P(IPN-*b*-S)	11.3	1.02	1.96	S:IPN = 0.93:0.07
telechelic PI	20.1	1.07	1.72	
catenated PS-PI	36.8	1.03		S:I = 0.49:0.51

[a] Determined by SEC based on a calibration curve using polystyrene standards. [b] Determined by light scattering. [c] Estimated by ^{1}H NMR.

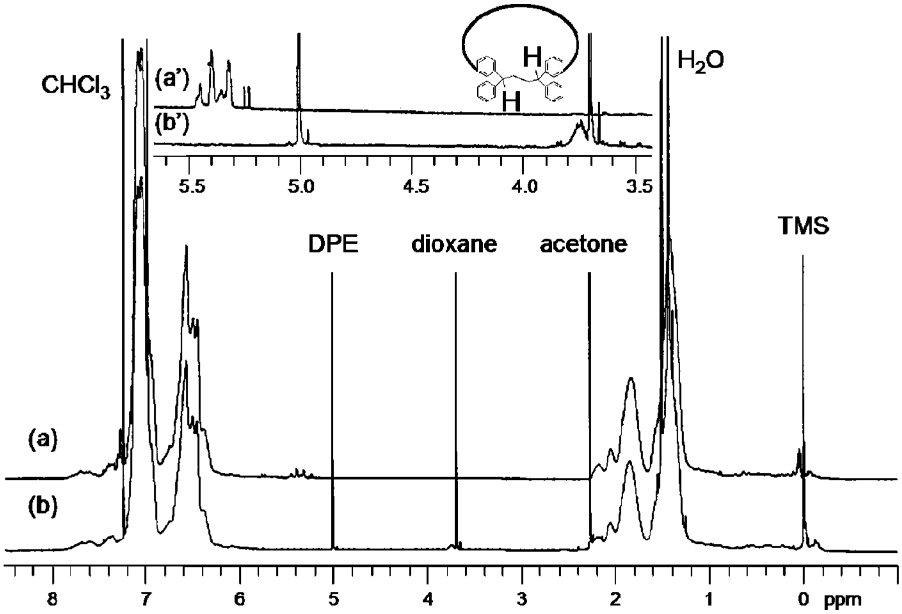


Figure 2. 500 MHz ^{1}H NMR spectra of (a) linear telechelic P(IPN-*b*-S-*b*-IPN) and (b) cyclic P(IPN-*b*-S). (a′) and (b′) are enlarged ones from (a) and (b), respectively. Solvent used is $CDCl_3$. The DPE-type double bonds disappeared, and the 2H protons peaks newly appeared in 3.75 ppm by coupling reaction.

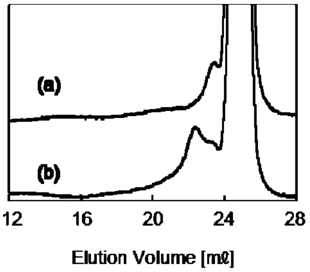
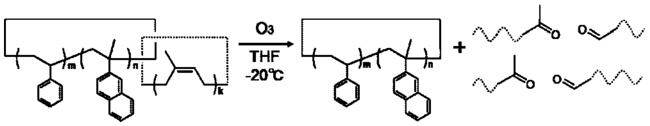


Figure 3. SEC chromatograms in THF of (a) radical-anionized and inactivated cyclic P(IPN-*b*-S) precursor and (b) catenation reaction product.

Scheme 4. Degradation Reaction Scheme of PI in a Catenated Copolymer by Ozonolysis



to confirm a ring structure of cyclic polystyrene with the Varian UNITY-INOVA-500 MHz at 20 °C in $CDCl_3$.

Ozonolysis was conducted to confirm that cyclic P(IPN-*b*-S) does not make covalent bond after catenation reaction. Ozone was generated for cleavage of C−C double bonds in the PI with a ceramic ozonizer model KA-10 from Koyo Iron Works and Construction Co., Ltd. Ozonized oxygen (ca. 2%) was blown into dichloromethane/methanol (95/5) solutions of the fractionated catenated product for 5 min at a flow rate of 60 mL/min.

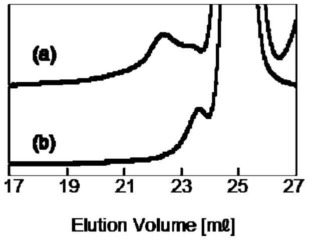


Figure 4. SEC chromatograms of the catenated reaction products before (a) and after (b) ozonolysis. The eluent is THF.

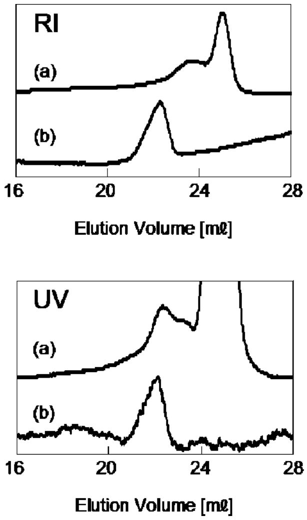


Figure 5. SEC chromatograms of catenated PS-PI before (a) and after (b) fractionation detected with RI and UV detectors, respectively. The eluent is THF.

Films used for morphological observation were cast from chloroform solutions. The cast films were dried for 6 h and annealed at 150 °C for 2 days under vacuum. The films were cut into sections (50 nm thick) using an ultramicrotome, Reica Ultracut UCT, at room temperature. The sections were stained with osmium tetroxide vapor from 5% aqueous solution at 70 °C temperature for 15 min. The nanophase-separated structures of the sections were observed by transmission electron microscopy (TEM) using a Hitachi H-800 operated at an accelerating voltage of 100 kV.

Results and Discussion

Figure 1 compares RI-detected SEC chromatograms of the telechelic P(IPN-*b*-S-*b*-IPN) triblock copolymer (a), the crude cyclization reaction product (b), and the fractionated cyclic P(IPN-*b*-S) (c). It is obvious from the chromatogram in Figure 1b that the polymers eluting in the range of 17−24 mL are high molecular weight polycondensation products formed by inter-

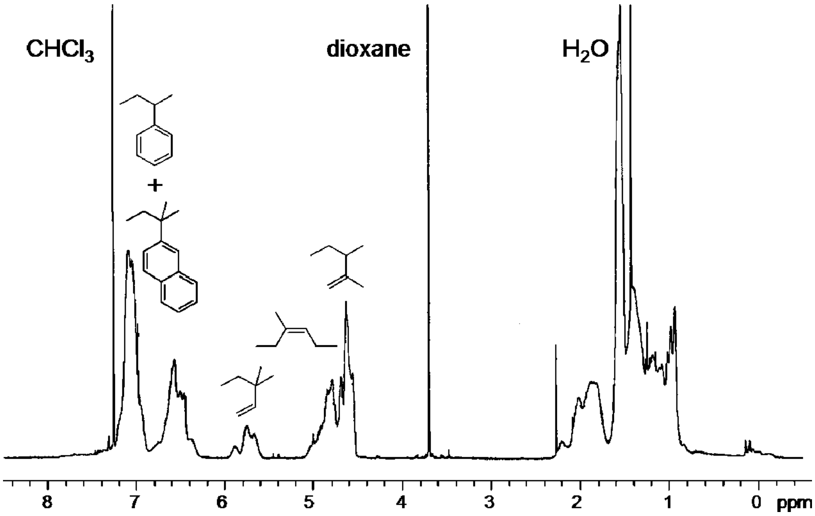


Figure 6. A 500 MHz ^{1}H NMR spectrum of the catenated PS-PI copolymer in $CDCl_3$. The molar ratio of each polymer is estimated from the peaks derived from PI double bond (4.5−6.0 ppm) and IPN-S aromatic ring (6.3−7.8 ppm).

molecular reactions, while the product eluting at around 26.0 mL is the desired cyclic copolymer produced by an intramolecular reaction. The main peak position is shifted considerably from that of the noncyclic P(IPN-*b*-S) counterpart, as shown in Figure 1a. The crude reaction product was fractionated by SEC to isolate the cyclic copolymer, and Figure 1c shows the chromatogram of the fractionated product. The peak of the fractionated polymer is unimodal and symmetric and has a relatively narrow molecular weight distribution. Table 1 lists molecular characteristics of the polymers. Figure 2 compares ^{1}H NMR spectra of the linear precursor P(IPN-*b*-S-*b*-IPN) (a) and the fractionated polymer (b) in which the appearance of protons (2H at 3.75 ppm) can be seen which are introduced by the coupling reaction of the DPE-type double bond. The part in the middle range and enlarged at the top of the figure and the corresponding ones are designated as (a′) and (b′). The disappearance of the DPE-type vinyl proton (4H at 5.3−5.5 ppm) in charts (b′) is also notable. Using these peak areas in the NMR spectra, the cyclic polymer content of the fractionated product is found to be over 90%. Furthermore, the P(IPN-*b*-S) copolymer consists of 93 mol % of PS and 7 mol % of PIPN (see also Figure 2).

Figure 3a shows a UV-detected SEC chromatogram ($\lambda = 320$ nm) of a quenched sample of radical-anionized cyclic P(IPN-*b*-S), while Figure 3b shows a SEC chromatogram of the catenated reaction product of the reaction between the radical-anionized cyclic P(IPN-*b*-S) and telechelic PI. It is apparent from Figure 3a that a part of the precursor appears at 24.9 mL, whose apparent molecular weight is 11 kDa. The precursor was dimerized by the reaction with potassium metal, resulting in that one additional peak appeared at 23.4 mL whose apparent molecular weight is 21 kDa. While the catenated reaction product contains about 8% of new product eluted at 18−23 mL (which evidently has a higher molecular weight than that of the dimerized precursor), the apparent molecular weight of the most distinct peak eluted at 22.3 mL is 35 kDa and its yield is ca. 3%. This may indicate the formation of catenated copolymers.

Only cyclic P(IPN-*b*-S) remains after degradation of PI component by ozonolysis. Therefore, the presence of catenated copolymer was confirmed to compare the change of elution curve before/after ozonolysis. Cleavage of C−C double bond and degradation in PI occurred as shown in Scheme 4 by ozonolysis. Figure 4 shows SEC chromatograms of catenation reaction products before (a)/after (b) ozonolysis. It was confirmed that the chromatogram after ozonolysis (Figure 4b) has almost the same peak shape as the peak of the radical-anionized cyclic P(IPN-*b*-S) before the catenation reaction (Figure 3a), which means that the new products eluted at 19−23 mL are not coupling products consisting of only cyclic P(IPN-*b*-S), but might instead be catenated copolymer series which decompose to reproduce cyclic P(IPN-*b*-S) through ozonolysis.

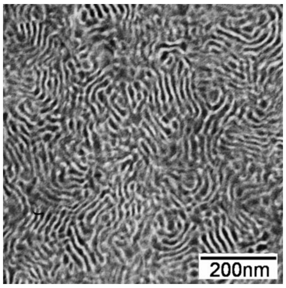


Figure 7. TEM image of the catenated PS-PI copolymer.

Figure 5 compares SEC chromatograms of the catenation reaction product before (a)/after (b) fractionation observed by RI and UV ($\lambda = 320$ nm) detectors. It is evident that the fractionated product has a higher apparent molecular weight than those of the component precursor polymers. (The apparent molecular weights of cyclic P(IPN-*b*-S), cyclic PI, and the fractionated product at their maximum peak height as determined by SEC were 11, 19, and 32 kDa, respectively.) These chromatograms provide strong support for the production of the catenated copolymer.

The ^{1}H NMR spectrum of the fractionated product is shown in Figure 6. It was confirmed that the fractionated product contains P(IPN-*b*-S) and PI by comparing peak areas at 4.5−6 ppm derived from PI double bond and 6.3−7.8 ppm from P(IPN-*b*-S) aromatic ring and that the molar ratio of P(IPN-*b*-S) to PI in the product is about 1:1, which is a reasonable value for the catenated copolymer as designed. Combining these results, we are convinced that the catenated PS-PI molecule has been prepared successfully as a result of our new synthetic strategy.

Figure 7 shows a TEM image of the catenated PS-PI. The lamellar structure has been clearly identified in the catenated complex molecule as a result of observation of definite nanophase separation. This nanophase separation may occur even though the two-component polymers are not connected directly, as long as they reside in the strong segregation region. Lamellar domain spacing of the catenated PS-PI was estimated

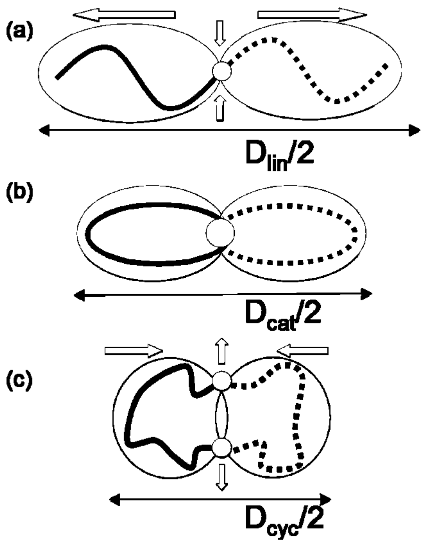


Figure 8. Schematic images for chain conformations in bulk and the domain spacings of (a) linear, D_{lin}, (b) catenated, D_{cat}, and (c) cyclic, D_{cyc}, copolymers.

to be 20 nm from the TEM image. Here we compare the lamellar domain spacings of a linear SI diblock copolymer,[22] a SI cyclic diblock copolymer,[26] and the catenated SI copolymer with the same molecular weight and composition. Considering the total molecular weight of 32 kDa of the present catenated copolymer, the domain spacings of the corresponding linear SI and cyclic SI copolymers are estimated to be 26 and 16 nm, respectively. Thus, the lamellar domain spacing of the catenated copolymer is smaller than that of the linear copolymer but larger than that of the corresponding cyclic copolymer at the same molecular weight. This result can be explained by comparing the chain conformations of the catenated copolymer with the linear and cyclic polymers in bulk. Figure 8 compares schematic images of possible conformations and domain spacings of three copolymers in the strong segregation region. The linear block copolymer chain is elongated along a direction perpendicular to the lamellar interface because it can adopt all possible tail conformations and has one free chain end, while the elongation of the cyclic molecule might be restricted due to its loop conformation which leads to smaller domain spacing. The present catenated copolymer does not have any junction points but is restricted topologically at the interface. The degree of restriction of the catenated copolymer should be between that of the linear and cyclic molecules, and therefore its chain could also be at an intermediate length, and these lead to the relationship $D_{\text{lin}} > D_{\text{cat}} > D_{\text{cyc}}$, where D_{lin}, D_{cat}, and D_{cyc} denote the domain spacings for linear, catenated, and cyclic copolymers.

Conclusion

As an alternative to a stochastic threading reaction, the synthesis of a catenated copolymer was successfully carried out by cyclization of a telechelic polymer on the first cyclic polymer carrying radical anions. Formation of the catenated polymer was clearly detected and produced in a much higher yield (5%) relative to previous synthesis attempts. The catenated polymer shows a definite nanophase-separated structure, and its domain spacing was found to be between the domain spacings of the corresponding linear and cyclic copolymers.

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