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Published in:
Journal of Chemical Physics

DOI:
[10.1063/1.1760514](https://doi.org/10.1063/1.1760514)

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Document Version
Publisher's PDF, also known as Version of record

Publication date:
2004

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Matsushita, Y., Iwata, H., Asari, T., Uchida, T., ten Brinke, G., & Takano, A. (2004). Chain elongation suppression of cyclic block copolymers in lamellar microphase-separated bulk. *Journal of Chemical Physics*, 121(2), 1129 - 1132. <https://doi.org/10.1063/1.1760514>

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Chain elongation suppression of cyclic block copolymers in lamellar microphase-separated bulk

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(Received 23 January 2004; accepted 19 April 2004)

Chain elongation suppression of cyclic block copolymers in microphase-separated bulk was determined quantitatively. Solvent-cast and annealed films are confirmed to show alternating lamellar structure and their microdomain spacing D increases with increasing total molecular weight M according to the relationship $D \propto M^{0.59}$, which agrees quite consistently with the theoretically predicted power law, i.e., $D \propto M^{3/5}$. This result is in contrast to the well-established issue for linear block copolymers, where the relationship $D \propto M^{2/3}$ has been confirmed to hold both experimentally and theoretically. This means that chain elongation of each component block is suppressed considerably, owing to their looped conformation in strongly segregated bulk. © 2004 American Institute of Physics. [DOI: 10.1063/1.1760514]

Block copolymers are fascinating research objectives in both the academic field and the application one, since they exhibit novel properties in condensed systems resulting from forming self-organized periodic structures, called microphase-separated structures.

Cyclic macromolecules have attracted many researchers' interest since they are conceived to be a kind of "model" polymers with no chain ends, so that it may influence on several properties of polymers considerably. Historically, theoretical works predicted the contracted chain conformation of cyclic molecules compared to linear homologs prior to experimental works.¹⁻³ Later Douglas and Freed predicted possible contraction in dilute solutions by applying renormalization group theory to cyclic molecules,⁴ while Cates and Deutsch predicted suppression of chain dimension of cyclic molecule in bulk.⁵ Furthermore, Marko predicted contraction of lamellar microdomain thickness for a ring-shaped block copolymer.⁶ On the other hand, enormous efforts have been dedicated to preparation and characterization of cyclic homopolymer molecules⁷⁻¹⁷ and also of cyclic block copolymers.¹⁸⁻²¹

Throughout these experimental studies, however, the direct evidence of cyclic structure was not shown; moreover, the purity of the cyclic molecules has not been determined quantitatively in most of the works. Among them, Ohtani *et al.* have proved the cyclic structure directly by using poly(2-vinylpyridine) with detectable junction point by pyrolysis gas chromatography/mass spectroscopy and determined the ring fraction,¹⁶ while Lee *et al.* determined the fractions of cyclic polystyrenes precisely by liquid chromatography at the critical condition method.¹⁷ Takano *et al.* have reported on preparation and characterization of cyclic

polystyrenes with short poly (2-tert-butyl-butadiene) sequence and proposed a novel method to prove the purity of cyclic molecule,²¹ while they also prepared polystyrene-block-polyisoprene cyclic copolymers with three different compositions and determined the purity of cyclic molecules included in the samples accurately.²⁰

Linear block copolymer is known to be elongated considerably along the direction normal to microdomain interface because of strong interaction in between incompatible polymer components.²²⁻²⁷ In contrast to linear homologs, chain elongation of cyclic block copolymers in bulk must be suppressed because they have to adopt looped conformation, their two junction points being tethered on the same microdomain interface. Magnitude of chain compression was calculated by Marko⁶ following the approach of Leibler,²⁸ assuming Gaussian chain correlation combined with random phase approximation in the strong segregation regime, where actually no chain contraction was predicted comparing domain spacing of AB cyclic copolymer with that of ABA triblock copolymer molecule with the same molecular weight and composition.²⁶ Lescanec *et al.* experimentally observed domain contraction for two kinds of cyclic block copolymers as a function of χN , where χ is the Flory-Huggins interaction parameter and N denotes total degree of polymerization.¹⁸ Recently shrinkage of microdomain was also reported for cyclic polystyrene-block-polyisoprene²² and also for cyclic polystyrene-block-polybutadiene²⁹ copolymers; however, suppression of microdomain has not been quantitatively clarified yet. Therefore, molecular weight dependence of the domain spacing of cyclic block copolymers was studied in comparison with the linear homologs to

TABLE I. Molecular characteristics of linear and ring block copolymers.

	$M_n \times 10^{-3}$	DP ^a	M_w/M_n	Purity (%)	Φ_s (%)	D (nm)
SII-5	31.5	378	1.07	...	50	14.4
SII-5	34.2	412	1.06	95	49	15.0
SII-6	69.4	822	1.06	...	53	25.4
SII-6	67.2	796	1.09	87	53	23.6
SII-7	101	1216	1.04	...	49	32.6
SIR-7	100	1184	1.04	79	53	28.9
SII-8	175	2081	1.06	...	52	46.4
SIR-8	186	2202	1.05	79	52	41.1

^aTotal degree of polymerization of samples calculated from molecular weights and volume fractions.

determine the degree of chain suppression exactly in this work using well-characterized samples.²⁸

Cyclic block copolymers from polystyrene (*S*) and polyisoprene (*I*) were prepared by two-step anionic polymerization of isoprene and styrene to produce *S-I-S* triblock copolymers followed by capping both chain ends with reagents having diphenylethylene group. Some amount of linear triblock copolymers were isolated as precursors to compare their structural feature with cyclic molecules later. Finally both ends were reacted with the aid of potassium naphthalenide under extremely diluted condition, and cyclic molecule obtained has been isolated by preparative size exclusion chromatography (SEC) as reported previously.²² Four copolymers with different molecular weight were prepared; their code names are $(SI)_c$ -I through $(SI)_c$ -IV. Number average molecular weights of $(SI)_c$ -I and -II were measured by membrane osmometry while those of $(SI)_c$ -III and -IV were determined by combining molecular weights of polystyrene blocks with their mole fractions. The former were estimated by SEC chromatograms of polystyrene after decomposing polyisoprene blocks by ozonolysis, while latter were measured by ¹H NMR. Using the same SEC chromatograms, the purity of cyclic molecule was estimated, which comprised coupled polystyrene sequence decomposed from cyclic molecule and small amount of short polystyrene blocks originally on both chain ends of unreacted *SIS* triblock copolymer whose molecular weight is half of the former.²² Molecular weights and compositions of linear triblock copolymers, whose code names are *SIS*-I through *SIS*-IV, were separately determined. Molecular characteristics of four pair of samples are listed in Table I. From this table, we notice that all the samples have almost the same polystyrene volume fraction ϕ_s of around 0.5 and also that the purity of cyclic molecules is not perfect but sufficiently high to discuss the structural feature of cyclic block copolymer molecule without affecting the results seriously.

Films for morphological observation were cast very slowly from dilute solutions of tetrahydrofuran for four days, followed by heating for a week at 150 °C, which is high enough above glass transition temperature of polystyrene. Microphase-separated structures were observed by transmission electron microscopy and by small angle x-ray scattering; the details of the experiments were reported previously.²²

As is schematically shown in Fig. 1, if small force *f* is applied to two opposite points of a block copolymer mol-

ecule, the total chain dimension *r* should be expressed as Eq. (1) (Ref. 30),

$$r \cong R_g^2 f / kT, \quad (1)$$

where R_g denotes radius of gyration of the molecule. The elastic energy F_e per block polymer chain equals *f* times *r* so that Eq. (2) holds,

$$F_e = fr \propto kTr^2/R_g^2. \quad (2)$$

Interfacial energy F_i can be described as

$$F_i = kT\gamma N/r, \quad (3)$$

where γ is the surface tension in between two component polymers and is assumed to be large enough to form microphase-separated structure since we are dealing with the system in the strong segregation regime. On the other hand, chain dimension of cyclic molecule can be predicted⁵ as a function of *N* as

$$R_g \propto N^{2/5}. \quad (4)$$

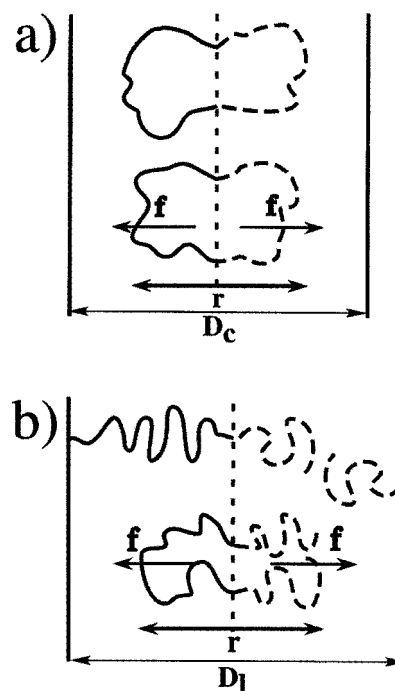


FIG. 1. Schematic comparison of chain elongation of block polymers in lamellar microdomain in between (a) a cyclic block copolymer and (b) a linear triblock copolymer.

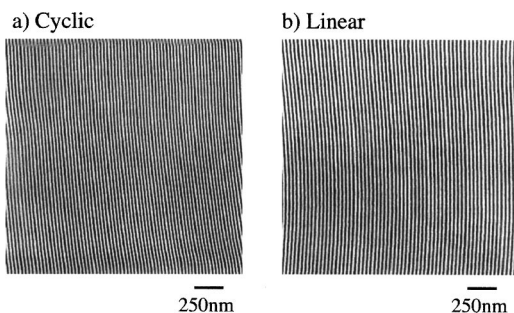


FIG. 2. Typical transmission electron micrographs from block copolymer films. Samples (a) $(SI)c$ -III and (b) SIS -III.

Introducing the relationship in Eq. (4) into Eq. (2) and replacing domain spacing D_c for cyclic block copolymer from chain displacement r because D_c should be proportional to r as shown in Fig. 1(b), total free energy F of forming lamellar structure can be described ignoring numerical prefactor as

$$F/kT \cong D_c^2/N^{4/5} + N/D_c. \quad (5)$$

Minimizing F with respect to D_c , we have the relationship

$$D_c \propto N^{3/5}. \quad (6)$$

The relationship in Eq. (6) should be compared with that for linear block copolymer, whose domain spacing D_ℓ can be expressed by Eq. (7), in the strong segregation regime,

$$D_\ell \propto N^{2/3}. \quad (7)$$

Cyclic block copolymers as well as the corresponding linear ones were confirmed to possess very periodic and qualitatively similar alternating lamellar structure from morphological observation as shown in Fig. 2. Figure 3 compares small-angle x-ray scattering (SAXS) diffraction patterns as an example obtained for one of the cyclic molecules

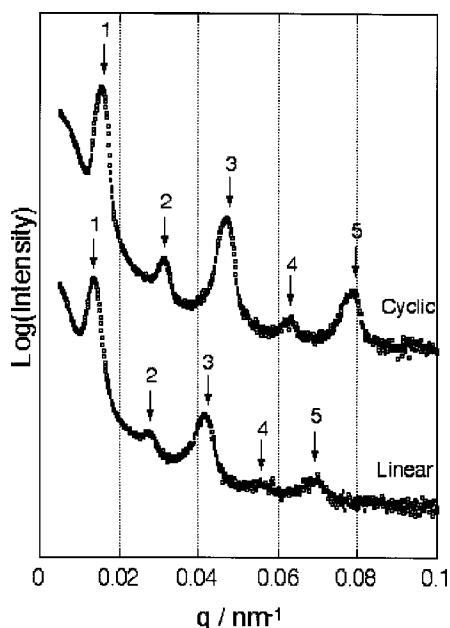


FIG. 3. Comparison of small angle x-ray scattering patterns. The top curve is for cyclic molecule and the bottom one is for a linear counterpart. Samples (a) $(SI)c$ -IV and (b) SIS -IV.

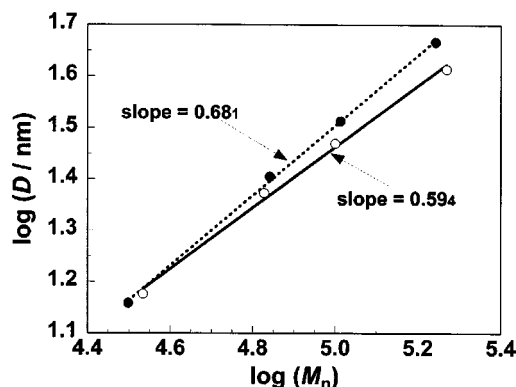


FIG. 4. Double logarithmic plots of domain spacing and total molecular weights of block copolymers. Open circles are the experimental data for cyclic block copolymers and the filled circles are for linear ones. The solid and the dotted lines are obtained by least square best fit to the data.

and the corresponding linear counterpart as a function of the magnitude of the scattering vector $q (= 4\pi \sin \theta / \lambda)$, where λ is the wavelength of x ray and 2θ is the scattering angle. It is obvious from this figure that the repeating distance for SI cyclic molecule estimated by the top curve is shorter than that for a SIS triblock copolymer obtained from the bottom one. Measured domain spacing D_c for cyclic copolymers together with those for linear counterparts, D_ℓ , are listed in Table I. From this table one notices that the ratio D_c/D_ℓ is 0.89 for sample pair IV whose χN is about 210 since total degree of polymerization is about 2100 and χ parameter for polystyrene-polyisoprene pair is 0.10 at room temperature.³¹ This result is consistent with the previously reported one,¹⁸ where the D_c/D_ℓ ratio is 0.91 for polystyrene-block-polydimethylsiloxane cyclic block copolymer with χN of 260.

Using this χ value and the total degree of polymerization in Table I, χN for $(SI)c$ was estimated to be ca. 40, this value is large enough compared with theoretically predicted critical value by Marko⁶ and Borsari³² independently for cyclic block copolymer molecules, ca. 18. Therefore, we can safely assume that all the samples form two-phase structures in the strong segregation regime.

Domain spacing values are plotted against total molecular weights of the samples double logarithmically in Fig. 4 together with those of the linear molecules. It is clear that the difference in D is getting larger with increasing molecular weight and the exponent α of the following equation:

$$D = kM^\alpha \quad (8)$$

for cyclic molecules is determined to be 0.594, while that for linear molecules is 0.681. The former value is quite consistent with the predicted one as shown in Eq. (6), while the latter agrees well with the well-known two-third power law as is in Eq. (7).³³ This means that the chain dimension along the direction perpendicular to lamellar microdomain interface for a cyclic molecule is meaningfully smaller than that of a linear triblock copolymer molecule with the same molecular weight. This could be attributed to the fact that two blocks of all the cyclic chains must have loop-type conformation in lamellar phase and hence the elongation along this direction can be suppressed as predicted because of the teth-

ering nature. However, it should be noted that the experimentally observed exponent 0.59_4 is still much larger than the exponent 0.5 in the radius of gyration (R_g)-molecular weight (M) relationship, $R_g \propto M^{1/2}$, for the unperturbed linear polymer chain.

From this fact, we understand that the polymer chain of cyclic block copolymer in microphase-separated bulk whose both ends are tethered on microdomain interface is still considerably elongated toward the direction normal to the interface because of segregation power in this regime. This relationship, $D = kM^{0.59_4}$, has been obtained by the counterbalanced effects of (a) block chain elongation due to interfacial segregation power and (b) chain contraction owing to elastic energy from chains whose both ends are tethered on the same microdomain interface.

ACKNOWLEDGMENTS

This work was partially supported by the Ministry of Education, Science, Sports and Culture, Grant-in-Aid program Nos. 12450383 and 13031040. This work was also done under support of Center of Excellence (COE) program entitled "The Creation of Nature-Guided Materials Processing" in the School of Engineering, Nagoya University, which has been assigned as one of the 21st century COE programs. Furthermore, this research was supported in part by a grant from Daiko Foundation. The authors are thankful for their financial assistance.

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