

FOCUS REVIEW

Direct observation and mutual diffusion of cyclic polymers

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A cyclic polymer is one of the ideal model polymers with which to investigate the effects of chain topology on the physical properties of polymers. In this review, I summarize my recent work demonstrating that the chain structure of cyclic polymers can be directly observed by atomic force microscopy (AFM) and that the mutual diffusion of cyclic polymers is faster than that of corresponding linear ones. For direct evidence of the cyclic structure, isolated molecules of cyclic poly(sodium styrenesulfonate), which was derived from cyclic polystyrene, were observed by AFM. The mutual diffusion of cyclic polystyrene/cyclic deuterated polystyrene was investigated as a function of temperature and molecular weight by dynamic secondary ion mass spectroscopy. For the molecular weight of 113k, the mutual diffusion coefficient of cyclic polystyrene, D_C , was approximately twofold larger than that of the corresponding linear polymer, D_L , at all temperatures. Under an iso-free volume condition, the D_C value was larger than the D_L value for all the molecular weights. These results clearly show that the chain topology strongly affects the molecular motion of the whole chain.

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INTRODUCTION

Cyclic polymers are attractive as counterparts to linear polymers from the viewpoint of both polymer chemistry and polymer physics. Many efforts have been made to synthesize and characterize cyclic polymers.^{1–20} The basic strategies for preparing cyclic polymers are end-to-end ring closure reactions: a coupling reaction between living polymers with functional groups on both ends and bifunctional linking agents^{5,7,9,10} or an intramolecular coupling reaction between chain ends of telechelic macromonomers.¹³ In both cases, the cyclization products include undesired linear precursors, dimers and trimers, among others. Hence, the main products should be separated out by using fractional precipitation, gel permeation chromatography and/or ultracentrifugation sedimentation, making use of the fact that the chain dimension of the cyclic polymers in solution is smaller than that of the linear counterpart at the same molecular weight.^{21,22} The purity of the cyclic polymers can be determined by nuclear magnetic resonance (NMR) and matrix-assisted laser desorption/ionization mass spectrometry if the molecular weight is small enough ($M_w < 10k$).^{7–9} Recently, liquid chromatography at the critical condition, based on a combination of entropic and enthalpic separations, was also developed and applied to the separation of cyclic polymers from a cyclic/linear mixture.^{23–26} This method has an advantage in comparison with NMR and matrix-assisted laser desorption/ionization mass spectrometry because liquid chromatography at the critical condition can be used for high- M_w samples and

facilitates the estimation of the purity of the cyclic polymers.²⁶ However, all the methods mentioned above provide us indirect information. In other words, there is no explicit evidence for the cyclic structure of the chain.

Great attention has also been paid to the physical properties of cyclic polymers as a counterpart to those of linear polymers. The difference between cyclic and linear polymers, in terms of molecular structure, is only the presence or the absence of chain ends. However, this small difference leads to various kinds of different physical properties, such as chain dimension in solution and bulk,^{5,21,27–31} glass transition temperatures,^{32–35} viscoelasticity,^{36,37} diffusion,^{38–43} microphase-separated structures⁴⁴ and crystallization^{45–47} among others. Hence, cyclic polymers are one of the ideal model polymers to use for understanding the effect of topology on the thermodynamics and molecular motion of polymers.

The number of experimental reports on the molecular motion of cyclic polymers is much less than that of computer simulation and theoretical studies on the topic^{48–60} because of the difficulty of synthesizing cyclic polymers, in particular, those with high molecular weight ($M_w > 10k$). In the later 1980s, some pioneering work on tracer diffusion³⁸ and zero shear viscosity³⁶ of cyclic polystyrenes was reported; the difference in the physical properties between the cyclic and linear polystyrenes was found in the reports, but it was unclear how much 'linear contamination' was included in the samples at that time. Kapnistos *et al.*³⁷ measured the stress

relaxation of cyclic polystyrenes with very high purity evaluated by liquid chromatography at the critical condition measurement and reported that the cyclic polystyrenes with M_w s of 198k and 161k, which were much larger than the entanglement molecular weight, M_e , for linear polystyrene, showed no obvious rubbery plateau, but showed a power-law stress relaxation. They claimed that entangled cyclic polymers exhibit completely different topological arrangements than their linear counterparts, such as the lattice animal conformation.^{37,48,49} However, the mutual diffusion of cyclic polymers with high purity so far has not been investigated.

In this review, ring-shaped structures of cyclic polymers were visually confirmed by atomic force microscopy (AFM). For the observation of isolated cyclic molecules, cyclic polystyrene was converted to cyclic poly(sodium styrenesulfonate) (c-PSS) to expand the molecule by introducing intramolecular charge repulsion. Then, the interdiffusion of cyclic polystyrene/cyclic deuterated polystyrene bilayer films was examined by dynamic secondary ion mass spectroscopy and compared with that of linear polystyrene/linear deuterated polystyrene bilayer films. The results clearly show that the effect of chain ends is significant for the molecular motion of the whole chain.

EXPERIMENTAL PROCEDURE

Materials

Monodisperse cyclic and linear polystyrenes (c-hPS, l-hPS) and their deuterated counterparts (c-dPS, l-dPS) were used in this study. Table 1 shows characteristics of the samples used in this study. The details of syntheses and characterization of the c-PSs are described elsewhere.²⁶ The purity of the c-PSs was confirmed to be >95% based on liquid chromatography at the critical condition measurements.²⁶ Weight-averaged molecular weights, M_w s, were evaluated by multi angle laser light scattering. N and N_e , listed in Table 1, are the degree of polymerization and a number of entanglement segments, respectively. The N_e s are calculated by M_w/M_e , where M_e for hPS is 13.3k (Fetters *et al.*⁶¹) (M_e for dPS is simply estimated to be a factor of 1.08, which is the weight ratio of monomeric units of styrene- d_8 /styrene- h_8 , 112/104). Glass transition temperatures, T_g s, of c-hPS, c-dPS, l-hPS and l-dPS were measured by differential scanning calorimetry. The T_g s of c-hPS and c-dPS were basically constant and independent of M_w , although the values were somewhat dispersed. This result was in contrast to the T_g of the linear PS, which decreased with decreasing M_w in the low- M_w region because of the excess free volume induced by the chain ends.

Table 1 Characteristics of polystyrenes used in this study

Sample code	M_w	N	N_e	M_w/M_n	T_g/K
c-hPS-109k	109k	1.05×10^3	8.2	1.02	376.0
c-dPS-117k	117k	1.04×10^3	8.2	1.02	373.6
l-hPS-115k	115k	1.11×10^3	8.6	1.04	376.0
l-dPS-127k	127k	1.13×10^3	8.9	1.04	378.9
c-hPS-42k	41.7k	4.01×10^2	3.1	1.02	370.6
c-dPS-50k	50.4k	4.50×10^2	3.5	1.02	372.8
l-hPS-44k	44.2k	4.25×10^3	3.3	1.03	375.6
l-dPS-52k	52.0k	4.64×10^2	3.6	1.04	374.5
c-hPS-15k	15.0k	1.01×10^2	1.1	1.02	377.0
c-dPS-12k	12.0k	1.07×10^2	8.4×10^{-1}	1.02	371.0
l-hPS-16k	16.0k	1.43×10^2	1.2	1.03	371.7
l-dPS-15k	15.2k	1.36×10^2	1.1	1.04	365.3
c-hPS-5k	4.8k	4.6×10^1	3.6×10^{-1}	1.02	377.1
c-dPS-6k	6.0k	5.4×10^1	4.2×10^{-1}	1.02	375.1
l-hPS-6k	6.0k	5.8×10^1	4.5×10^{-1}	1.04	365.9
l-dPS-8k	7.5k	6.7×10^1	5.2×10^{-1}	1.05	364.8

AFM observation

c-hPS-109k was sulfonated by Vink's method, followed by neutralization by treatment with sodium hydroxide.⁶² The degree of sulfonation of the c-PSS was determined to be 74% by inductively coupled plasma mass spectroscopy. The c-PSS solution was dropped onto mica and was successively blown out by a nitrogen gas stream; consequently, a few PSS molecules were adsorbed onto the mica substrate. The c-PSS molecules were observed by AFM with intermittent contact mode. AFM images were obtained by a SPA 300HV with an SPI3800 controller (Seiko Instruments Industry Co., Ltd., Chiba, Japan) at 293 K in air. The cantilever tip used for this observation was microfabricated from silicon, and its spring constant and resonant frequency were 33 N m^{-1} and 324 kHz, respectively.

Bilayer preparation

l-hPS/l-dPS and c-hPS/c-dPS bilayer films were prepared by the floating technique.^{63,64} The bottom dPS layer for the bilayer was prepared from a toluene solution onto a silicon wafer by spin coating. The thickness of this layer was approximately 200 nm. The dPS films were annealed at 393 K for 48 h under vacuum to remove the residual solvent and the strain imposed by the film preparation process. The top hPS film with the nearly same thickness was independently prepared in a similar manner. The perimeter of the hPS films was scored with a blade, and the films were successively floated off onto the water surface. Then, the hPS film was picked up onto the dPS film. The bilayers were annealed above T_g s under nitrogen atmosphere for sufficiently long times and successively immersed into liquid nitrogen to quench the interdiffusion. Table 2 lists the bilayer films used in this study. The M_w s of the bilayers were approximately the same, with the largest difference being 20%. The N_e values of the second lowest M_w samples, that is, the components of C-bilayer-3 and L-bilayer-3, were approximately unity.

Dynamic secondary ion mass spectroscopy (DSIMS)

The depth profiles of the bilayers were examined by DSIMS (SIMS 4000, Seiko Instruments Inc., Chiba, Japan, –Atomika Analysetechnik GmbH, Germany), where the incident beam of oxygen ions with 4keV and approximately 30 nA was focused onto a $200 \times 200 \mu\text{m}$ area of the specimen surface and the incident angle was 45° . A 20-nm-thick gold layer was sputter coated on the specimen surface to avoid charging of the specimen during the DSIMS measurement.

RESULTS AND DISCUSSION

Direct observation of single molecules of cyclic polymers

Figure 1 shows AFM images of isolated c-PSS molecules. All the molecules represent ring-shaped structures for c-PSS as shown in Figure 1a; the purity of the cyclic polymers was sufficiently high. The enlarged image and schematic representation of c-PSS are shown in Figures 1b and c, respectively.⁶⁵ The apparent contour lengths measured for c-PSS molecules ranged between 160 and 210 nm, whereas the length of a fully stretched PSS chain with a corresponding degree of polymerization was calculated to be 270 nm. Hence, the observed length for c-PSS molecules was apparently shorter than the expected one and the apparent length distribution for the molecules

Table 2 Bilayer films used in this study

Sample code	Top layer	Bottom layer
C-bilayer-1	c-hPS-109k	c-dPS-117k
L-bilayer-1	l-hPS-115k	l-dPS-127k
C-bilayer-2	c-hPS-42k	c-dPS-50k
L-bilayer-2	l-hPS-44k	l-dPS-52k
C-bilayer-3	c-hPS-15k	c-dPS-12k
L-bilayer-3	l-hPS-16k	l-dPS-15k
C-bilayer-4	c-hPS-5k	c-dPS-6k
L-bilayer-4	l-hPS-6k	l-dPS-8k

was broad. This was due to the incomplete sulfonation of c-PSS, which led to the detachment of the unsulfonated portion in the c-PSS from the substrate, resulting in the reduction of the projected contour length. There may have been several small kinks of chains perpendicular to the substrate, which were all ignored owing to limited resolution.⁶⁶

MUTUAL DIFFUSION

Time evolution of the interfacial thickness

Figure 2 shows a typical DSIMS profile of H⁻, D⁻ and C⁻ for a (l-hPS/l-dPS) bilayer film. Gold and l-dPS were also laminated onto the (l-hPS/l-dPS) bilayer film to achieve stable sputtering and prevent charging of the bilayer film. As the intensity of C⁻ was nearly constant throughout the bilayer, it is clear that the steady-state etching proceeded during the measurement. The abscissa of the etching time can be simply converted to the depth from the surface with the assumption of a constant sputtering rate through the bilayer, which was pre-examined using the dPS film with a known thickness. A measured concentration profile by DSIMS is generally broadened from an ideal one, owing to an instrument function mainly originated from an atomic mixing effect. The broadening of the measured DSIMS profile was subtracted with use of the following

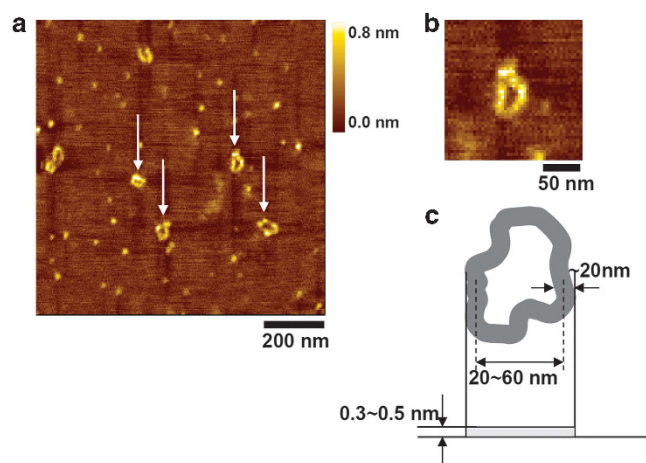


Figure 1 Atomic force microscopy (AFM) images of (a) cyclic poly(sodium styrenesulfonate) (c-PSS) on a mica substrate, in which arrows indicate isolated macromolecules, and (b) an enlarged image of (a). (c) A schematic representation of a cyclic molecule on a two dimensional plane.

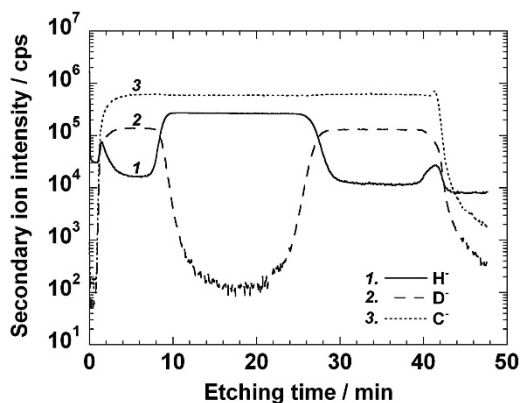


Figure 2 A typical dynamic secondary ion mass spectroscopy (DSIMS) profile of H⁻, D⁻ and C⁻ for a (l-hPS/l-dPS) bilayer film.

reported procedure by Whitlow and Wool.⁶⁷ Assuming that the derivative of secondary D⁻ intensity, I_{D^-} , can be expressed by a Gaussian function, the interfacial thickness was defined as twice the s.d. of the Gaussian function, corresponding to the depth range where I_{D^-} arose from 16–84% of the maximum value.

Figure 3 represents double logarithmic plots of time evolution of the interfacial thicknesses at the C-bilayer-1 and L-bilayer-1 interfaces.⁶⁸ Both thicknesses of the C-bilayer-1 and L-bilayer-1 interfaces increased with increasing time, t , and those of the C-bilayer-1 bilayer films were much higher than that of the L-bilayer-1 at any given t . This means that diffusion of c-PS was much faster than that of l-PS. For the L-bilayer-1, interfacial thickness was proportional to $t^{0.22}$ at shorter times, whereas it was proportional to $t^{0.52}$ at longer times. The crossover appeared at approximately $t \sim 5 \times 10^3$ s, which agrees well with the reptation time, τ_d , calculated to be 4.0×10^3 s for l-PS with a M_w of 115k at 120 °C.⁶⁹ Previous studies on interdiffusion revealed that interfacial thickness evolved with $t^{1/4}$ at $t < \tau_d$, whereas it increased with $t^{1/2}$ at $t > \tau_d$.^{67,69} Our result is in good agreement with previous results, and it can be understood by taking into account the two time regimes of diffusion, that is, segmental diffusion at $t < \tau_d$ and conventional Fickian diffusion of the whole chain at $t > \tau_d$. However, for the C-bilayer-1 interface, an increase in interfacial thickness was initially proportional to $t^{0.19}$, whereas it was proportional to $t^{0.48}$ after $t \sim 3 \times 10^3$ s. Although Fickian diffusion clearly occurred at $t > 3 \times 10^3$ s, some sort of diffusion over a fairly long distance was clearly observed at the shorter time. In general, displacement of the center of mass for a linear polymer is an order of chain dimension, R_g (~ 9 nm), at $t < \tau_d$. In this case, however, the interfacial thickness for the C-bilayer-1 interface evolved with $t^{0.19}$ although it reached $2R_g$. This result might imply that some constraints existed for c-PS but that its spatial scale must have been larger than the entanglement network for the corresponding linear chain.

Temperature dependence of mutual diffusion coefficient for cyclic polystyrenes

Depth profiles of normalized D⁻ ion intensity were analyzed by the following equation derived from Fick's second law:^{63,67}

$$C(z) = 0.5 \left[1 - \operatorname{erf} \left(\frac{z}{\sqrt{a^2 + 4Dt}} \right) \right] \quad (1)$$

where z , a , D and t are the distance from the interface, an instrument function (= approximately 10 nm), a diffusion coefficient and time, respectively. D values were extracted from each depth profile by a

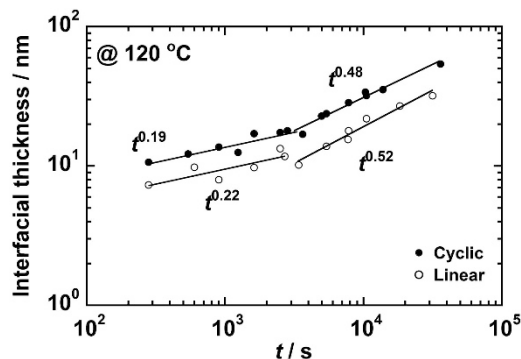


Figure 3 Time evolution of interfacial thicknesses of C-bilayer-1 and L-bilayer-1. (Reprinted with permission from Kawaguchi *et al.*⁶⁸).

fitting analysis using Equation (1). The analytical methods were described in detail in our previous study.⁶⁸

Figure 4 compares the temperature dependence of D values for c-PS and l-PS, D_C and D_L . Open and filled circles denote the D_C and D_L values with M_w values of 113k and 121k, respectively. The broken line is the calculated D_L values reported by Kramer *et al.*⁷⁰ According to their paper, the D_L value can be calculated based on the following empirical equations:

$$\log \frac{D}{T} = A - \frac{B}{T - T_V} \quad (2)$$

$$A = -9.49 - 2 \log \left(\frac{M_w}{255\,000} \right) \quad (3)$$

where T is an absolute temperature, T_V is the Vogel temperature ($=322$ K), B is an activation temperature ($=710$ K) $\log(\text{cm}^2 \text{s}^{-1} \text{K})$, and M_w is the molecular weight of the sample. For the linear case in Figure 4, the M_w value for linear polystyrene was calculated to be 121k from the arithmetic average of the M_w s of the samples. By substituting these values into Equations (2) and (3), the temperature dependence of l-PS of 121k can be described as:

$$D_L = 1.43 \times 10^{-9} \times T \times 10^{\left(\frac{-B}{T - T_V} \right)} \quad (\text{for l-PS with } M_w \text{ of } 121\text{k}) \quad (4)$$

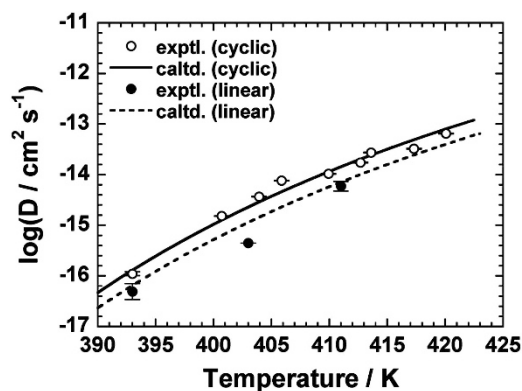


Figure 4 Temperature dependence of mutual diffusion coefficients, D , of C-bilayer-1 and L-bilayer-1. Open and filled circles denote the experimental D values for C-bilayer-1 and L-bilayer-1, respectively. The broken line is the calculated D values of l-PS with a M_w of 121k (Equation 4). The solid line denotes the calculated values for c-PS (Equation 6). (Reprinted with permission from Kawaguchi *et al.*⁷¹).

Our experimental D_L values are shown by the filled circles and are consistent with the calculated ones shown by the broken line. Taking a slight difference in the molecular weights of linear and cyclic molecules into account, the temperature dependence of D_L with a M_w of 113k can be expressed as:

$$D_L = 1.65 \times 10^{-9} \times T \times 10^{\left(\frac{-B}{T - T_V} \right)} \quad (\text{for l-PS with } M_w \text{ of } 113\text{k}) \quad (5)$$

To analyze the data for c-PS, the solid line was obtained by a fitting process using a prefactor as only a fitting parameter and keeping the B and T_V values the same as those used for the l-PSs. In other words, the fitting analysis was conducted by using Equation (5), maintaining the contour shape of the curve and shifting it vertically. The solid line is in good agreement with the experimental values for c-PS shown in open circles and can be expressed by Equation (6).

$$D_C = 3.30 \times 10^{-9} \times T \times 10^{\left(\frac{-B}{T - T_V} \right)} \quad (\text{for c-PS with } M_w \text{ of } 113\text{k}) \quad (6)$$

It is apparent from Equations (5) and (6) that the absolute D_C value was approximately twofold larger than that for the corresponding l-PS at all the temperatures employed. Hence, the mutual diffusion data proved that the segmental friction coefficients of l-PS and c-PS are the same.⁷¹

Molecular weight dependence of diffusion coefficients

Figure 5a shows a double logarithmic plot of D versus M_w at 393 K for C-bilayers and L-bilayers, respectively, where open and filled circles denote the D_C and D_L values, respectively. The error bars are the s.d. of the D values obtained by multiple independent experiments. Here, the slope of the double logarithmic plot is defined as ν . The ν values of the data, separated in two regimes, will be discussed: $M_w \leq M_e$ and $M_w > M_e$, being recognized as 'unentangled ring' and 'entangled ring' regimes, respectively.

The ν values for the L-bilayers were -2.0 for $M_w > M_e$ and -2.6 for $M_w \leq M_e$. The ν value for $M_w > M_e$ strongly suggests that the chains in the L-bilayers moved based on the reptation theory,^{72,73} whereas the ν value for $M_w \leq M_e$ was an unreasonable value of -2.6 , probably due to the decrease in the T_g s at the molecular weight region. However, the ν values for the C-bilayers were -1.9 at $M_w > M_e$ and -2.2 at $M_w \leq M_e$. The D_C values were larger than the D_L ones at $M_w > M_e$ and vice versa at $M_w \leq M_e$, resulting in the crossover of D_C and D_L values at approximately 30k. This behavior is in good agreement with Monte Carlo simulations of cyclic and linear alkanes.⁵²

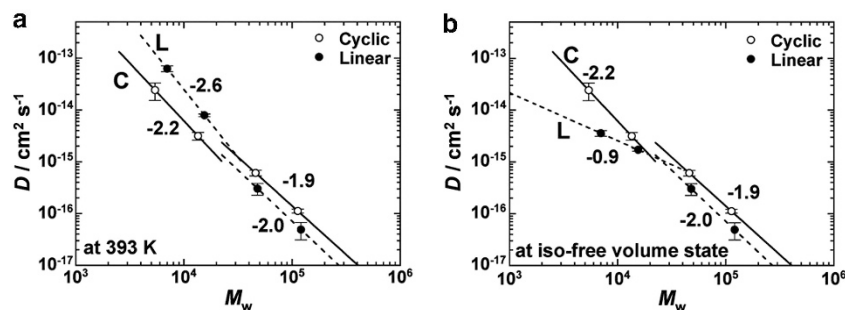


Figure 5 (a) Double-logarithmic plots of D versus M_w of C-bilayers and L-bilayers (a) at 393 K and (b) at an iso-free volume state ($T - T_g = 20$ K). Open and filled circles denote the D values of C-bilayers and L-bilayers, respectively. The solid and broken lines are the best-fit calculated values, and the numbers are the exponent values of the double logarithmic plots. (Reprinted with permission from Kawaguchi *et al.*⁷¹).

To discuss the relation between D and M_w at an iso-free volume condition, the D_L values of L-bilayer-3 and L-bilayer-4 were recalculated. As the temperature dependence of the segmental frictional coefficient for c-PS was the same as that for l-PS, as proved in the former section, the D_L values were estimated using the temperature dependence of D values. As the T_g s of l-hPS-16k and l-dPS-15k were approximately 5 K lower than the other l- and c-PSs with $M_w > M_e$, the D_L value for the L-bilayer-3 at 388 K was estimated taking this T_g difference into account. Similarly, the D_L value for the L-bilayer-4 at 383 K was also estimated. The D_C values were not recalculated because the T_g s of cyclic polystyrenes can be regarded as constant and independent of M_w . Figure 5b shows double logarithmic plots of D_C and D_L values versus M_w at iso-free volume conditions, where $T - T_g =$ approximately 20 K is the same as those of all the C-bilayers and L-bilayers. At the iso-free volume condition, the D_C value was larger than D_L for all the molecular weights. The ν values for D_L were -2.0 at $M_w > M_e$ and -0.9 at $M_w \leq M_e$, which are consistent with the reptation and Rouse models, respectively. Moreover, a previous experimental report on the diffusion of polybutadiene revealed that the ν value was -2.3 for sufficiently large M_w .⁷⁴ In either case, the result of linear polystyrenes was quite reasonable because the critical entanglement molecular weight of l-PS is approximately 30k.

For cyclic polymers at $M_w > M_e$, the theory based on the lattice-animal conformation predicted that D_C was proportional to $N^{-2.0}$.⁴⁹ A recent molecular dynamics simulation of cyclic polyethylenes by Hur *et al.*⁵⁹ revealed that the ν value was -1.9 if the M_w was sufficiently large. They claimed that the ring diffusion coefficients exhibited a broad crossover regime from unentangled to entangled dynamics and that D_C was proportional to $N^{-1.2}$ for small rings and to $N^{-1.9}$ for large rings.⁵⁹ Our result of $\nu = -1.9$ corresponds well to the molecular dynamics simulation⁵⁹ as well as the theory based on the lattice-animal picture.^{37,48,49} This result clearly indicates that entangled cyclic polystyrenes exhibit completely different topological arrangement from their linear counterparts, such as the lattice animal conformation.^{37,48,49}

However, molecular dynamic simulations exhibited $\nu = -1.0$ for $M < M_e$ and $\nu = -1.2$ around the transition from unentangled to the entangled states.⁵⁴ Experimental results of unentangled cyclic poly(oxyethylene)s with M_w ranging from 400 to 1500 showed that D is proportional to $N^{-1.12}$ on the basis of the NMR spin-spin relaxation technique.⁴¹ Both groups concluded that the diffusion of unentangled rings can be explained in terms of the Rouse model. However, our data exhibited $\nu = -2.2$, which is inconsistent with the previous results. The possible reasons for the deviation of our results might be related to the purity, specifically, the difference in T_g s among the samples for the smallest ring. The effect of small amounts of linear contaminants on the diffusion of cyclic molecules might be more significant in the low- M_w regime than in the high- M_w regime because the T_g of the linear molecules is lower than that of the corresponding cyclic molecule in this regime. Hence, the linear contaminants can diffuse much faster than the cyclic molecules at the same annealing temperature. Another effect of linear contaminants may be the surface segregation at the original surface, which is the bilayer interface, owing to the low surface energy of the chain end moiety (diphenyl ethylene). If these two effects occurred, cyclic molecules including a small amount of linear contaminants would diffuse evidently faster than ideal pure cyclic molecules in the low- M_w regime.

CONCLUSIONS

The ring-shaped structure of c-PSS was directly proved by AFM observations. Interdiffusion of c-hPS/c-dPS and l-hPS/l-dPS bilayer

films, being symmetric in terms of both molecular weight and topology, was investigated by DSIMS measurements as functions of temperature and molecular weight. For a M_w of 113k, which is larger than the critical entanglement molecular weight for l-PS, the D_C value was twice as large as the D_L one at all the temperatures employed. The D_C value was larger than the D_L one for all the molecular weights at an iso-free volume condition, whereas a crossover of the D_C and D_L values was observed around M_w of 30k at 393 K because of the T_g reduction of l-PS. The double logarithmic plots of D_C versus M_w exhibited no explicit transition, such as that from unentangled to entangled rings. For cyclic polystyrenes at $M_w > M_e$, the exponent of the plot was -1.9 , corresponding to recent molecular dynamics simulation and the theory based on the lattice-animal picture for entangled rings.

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