Viscoelastic Properties of Dumbbell-Shaped Polystyrenes in Bulk and Solution

Yuya Doi,[*,†,‡] Atsushi Takano,[*,†] Yoshiaki Takahashi,[*,§] and Yushu Matsushita[†,∥]

[†] *Department of Molecular and Macromolecular Chemistry and* [‡] *Department of Materials Physics, Nagoya University, Nagoya, Aichi 464-8603, Japan*

[§] *Institute for Materials Chemistry and Engineering, Kyushu University, Kasuga, Fukuoka 816-8580, Japan*

[∥] *Toyota Physical and Chemical Research Institute, Nagakute, Aichi 480-1192, Japan*

*correspondence authors: ydoi@mp.pse.nagoya-u.ac.jp (YD), atakano@chembio.nagoya-u.ac.jp (AT) and takahashi.yoshiaki.898@m.kyushu-u.ac.jp (YT)

ABSTRACT: This study examined viscoelastic properties of two flexible dumbbell-shaped polystyrene (PS) samples, D-30/120/30 and D-30/240/30, which possess the same ring size ($M_R \sim 30$ kg/mol) and different length of central linear chains ($M_L \sim 120$ and 240 kg/mol) in bulk and in solution. In bulk, both dumbbell PS samples exhibited an extremely long entanglement plateau in dynamic oscillatory measurements, and their terminal relaxation behavior was not observed in our experimental window. In stress relaxation measurements, dumbbell samples in bulk exhibited considerably slower terminal relaxation than high molecular weight linear PS sample ($M \sim 10^6$ g/mol), and a clear difference between two dumbbell PS samples was observed in long time regime, i.e., terminal relaxation of D-30/240/30 is much slower than that of D-30/120/30. These results suggest that (i) the dumbbell polymer forms a characteristic "network" where two rings on both ends in a molecule spontaneously thread the ring part of other dumbbell chains and (ii) this type of interchain interaction resulting in network formation becomes more dominant than usual entanglements similar to linear chains. The network of dumbbell chains starts to relax their stress when the intermolecular threading is released, and this release process tends to occur more frequently for the dumbbell with the shorter central chain, D-30/120/30, than that with the longer one, D-30/240/30. In dioctyl phthalate (DOP) solutions of D-30/240/30, where DOP is known as a θ-solvent for PS at 22 °C, at relatively high concentration regime (i.e., 20-30 wt%), the solutions exhibited an entanglement plateau and higher viscosity than the corresponding linear PS solutions, suggesting that the characteristic entanglement originating from intermolecular threading of dumbbell chains is still dominant in solution. To the contrary, at lower concentration regime (≤ 8 wt%), the D-30/240/30 solutions exhibited similar viscosities to the linear PS ones, wherein the dumbbell molecules behave like unentangled/isolated chains.

INTRODUCTION

Understanding the relationship between polymer chain architecture and polymer dynamics is one of the central subjects in polymer physics. In particular, studies on the dynamics of ring polymers, which possess no chain ends, have been pursued[1-10] for the past decades with the development of purification techniques.[11-12] Recent rheological experiments revealed that pure ring polymer melts exhibits no rubbery plateau even though they have sufficiently higher molecular weight M than the entanglement molecular weight M_e, up to the number of entanglement $M/M_e \sim 15$, and showed much faster terminal relaxation compared with their linear counterparts.[1,7] These experimental facts suggest the molecular motion of ring chains is considerably different from that of linear ones, where the latter is well-described by the reptation model.[13-14] To elucidate the relaxation mechanism of ring polymers, various theoretical concepts[15-23] have been proposed up to date. Nevertheless, the dynamical molecular picture of rings has not been fully understood yet,[9] and it is still being pursued extensively.

Another feature of ring polymer in bulk is that its dynamics is extremely sensitive to the presence of linear chain. Kapnistos et al. systematically examined the influence of linear chain contaminants in ring samples on their rheological response.[1] They revealed that the ring polystyrene (PS) sample (M = 198 kg/mol, $M/M_e \cong 11$) exhibited continuous changes of viscoelastic responses by blending the linear counterpart, i.e., (i) the terminal relaxation is significantly delayed when blending ratio of the linear chain Φ_L is even only 0.07%, (ii) an entanglement plateau appears at $\Phi_L \sim 1\%$, and (iii) slower terminal relaxation than the simple linear counterpart is seen at $\Phi_L \sim 50\%$. Some other experiments[24-26] and computer simulations[27-29] also showed essentially similar results. These results suggest that linear chains spontaneously thread multiple rings due to the entropic driving force,[30] and hence they form intermolecular ring-linear entanglement.

Relating to the above facts, we recently reported the characteristic viscoelastic properties of tadpole-shaped polymers, where a ring is connected to one end of a linear chain.[31-32] When the linear tail chain of tadpole samples has sufficiently higher M than M_e, they exhibited a clear entanglement plateau with the same plateau modulus G_N with the linear polymers, and much slower terminal relaxation than their component ring and linear chains as well as than the ring/linear blends. These properties can be related to the spontaneous intermolecular ring-linear penetration. Recent simulation study also supports our interpretation of the dynamics of tadpole polymers.[33]

It is interesting to examine the rheological properties of flexible dumbbell-shaped polymers where rings are attached on both ends of a linear chain and having no free chain ends; hereafter, it is simply called dumbbell polymers.   There must be basically two possibilities of the dynamics of dumbbell polymers.   One is that they behave as less entangled systems.   This is simply because they have smaller radii of gyration than the corresponding linear chains having the same molecular weight, though they have a somewhat bulky part at both ends of central linear chains.   This molecular shape resembles pom-pom-shaped polymers where unentangled short branches are attached on both ends of a linear chain.   Since the short branches act like diluents, the pom-pom polymers relax faster than corresponding linear ones.[34]   If the ring part of dumbbells is relatively small and unentangled, it may give a similar effect to pom-poms, and dumbbell polymers are expected to relax faster than the corresponding linear ones.

Another possibility is that dumbbell chains behave as considerably slow relaxation systems due to the spontaneous intermolecular interactions.   In fact, the ring-ring threading is one of the ideas to explain the mechanism of broader and slower terminal relaxation for high molecular weight rings than the model predictions.[35-39]   In the case of ring/linear blends, chain ends of threading linear chains can move freely.   For tadpole polymers, the motion of one chain end of a linear part where a ring is attached is heavily retarded by the treading of the other molecules, while another chain end of the tadpole is still movable.[31-32]   In the case of dumbbell polymers, if the ring part of both chain ends are threaded by the other dumbbell molecules, their motion is heavily constrained, and hence their dynamics could be drastically slow.   As far as we know, there exist no experimental studies on the dynamics of dumbbell-shaped polymers, and hence it must provide us new insights into the relationship between the polymer chain architecture and dynamics.

In this study, we have examined the viscoelastic properties of dumbbell-shaped polystyrene (PS) samples in bulk and in solution.   We previously reported on the synthesis of a dumbbell PS sample by anionic polymerization followed by high-performance liquid chromatography (HPLC) purification.[40]   Following the same manner, we newly prepared two dumbbell PS samples, D-30/120/30 and D-30/240/30, where the ring parts are the same size ($M_R \sim 30$ kg/mol) while the central linear parts have different length ($M_L \sim 120$ and 240 kg/mol).   For the bulk samples, dynamic oscillatory and stress relaxation measurements were conducted, and their viscoelastic properties were compared with those for linear PS with various molecular weights.   For the solution samples, D-

30/240/30 was dissolved in dioctyl phthalate (DOP), which is known as a theta solvent for linear PS at 22 °C,[41] at various concentrations, their dynamic oscillatory measurements were conducted, and the concentration dependence of their zero-shear viscosities and steady-state recoverable compliances was discussed in comparison with linear PS samples.

EXPERIMENTAL SECTION

Two dumbbell-shaped polystyrene (PS) samples, D-30/120/30 and D-30/240/30, were newly prepared in this study in the same manner as reported previously.[40]　Sample preparation procedures are briefly described as follows, and the details are summarized in the Supporting Information (Section S1).　The ring PS sample, R-30 (M_w = 33.7 kg/mol, M_w/M_n = 1.02, purity = 99.9%) previously prepared[40] was used as a ring component of two dumbbell polymers, while two linear PSs, L-120 (M_w = 119 kg/mol, M_w/M_n = 1.06) and L-240 (M_w = 241 kg/mol, M_w/M_n = 1.03), were anionically synthesized from styrene monomer with naphthalene potassium as a bifunctional initiator in THF at −78 °C under high-vacuum (~ 1 × 10^{-3} Pa).　Bifunctional living linear PS solutions thus obtained were gradually added to the THF solution of R-30, and the mixture solutions were kept stirring at −78 °C for 1 day.　The targeted dumbbell samples were selectively isolated from the coupling reaction products by repeated size exclusion chromatography (SEC) and interaction chromatography (IC) fractionations.　The samples finally obtained were precipitated into an excess amount of methanol, followed by the freeze-drying from 1,4-dioxane solution.　Table 1 summarizes the molecular characteristics of two dumbbell PS samples determined by SEC combined with multi-angle light scattering (MALS) and IC measurements.　The details of the characterization methods were reported previously.[40,42]　Both dumbbell PS samples were confirmed to have high purity with a negligible amount of linear contaminants.　The details of the sample characterization are shown in the Supporting Information (Section S1).

Table 1. Molecular characteristics of two dumbbell-shaped polystyrene samples

Samples	$10^{-3}M_w$ [a]	$10^{-3}M_{w,R}$ [a]	$10^{-3}M_{w,L}$ [a]	M_w/M_n [b]	purity [c]
D-30/120/30	180		119	1.01	> 99%
		33.7			
D-30/240/30	314		241	1.01	> 99%

Estimated from (a) SEC-MALS, (b) SEC and (c) IC measurements

For two dumbbell PS samples, rheological measurements were conducted in bulk and in solution with a laboratory rheometer (ARES-G2, TA Instruments) in a cone-plate fixture with the diameter of 8 mm and the gap angle of 0.1 rad, or, a parallel plate fixture with a diameter of 8 mm. From dynamic oscillatory measurements, the linear viscoelastic storage and loss moduli, G' and G'', were obtained at various angular frequencies ω. The strain amplitude was kept small (≤ 0.1) to ensure the linearity of G' and G'' data. For bulk samples, the measurements were made in nitrogen atmosphere at $120 \leq T / \,^{\circ}\mathrm{C} \leq 200$ to prevent the degradation of the samples during measurements. The time-temperature superposition holds for G' and G'' data, and all the data were reduced at the reference temperature, $T_\mathrm{r} = 180\ ^{\circ}\mathrm{C}$.[43] From stress relaxation measurements under small strain ($\leq$ 0.1) at 180 $^{\circ}$C, the linear stress relaxation moduli $G(t)$ were obtained. The measurements for two dumbbell PS samples in bulk were conducted just after their dynamic oscillatory measurements. For comparison, $G(t)$s of two commercially available monodisperse linear PS samples, L-1090 and L-430 (M_w = 1090 and 427 kg/mol, $M_\mathrm{w}/M_\mathrm{n}$ < 1.1; Tosoh Co.) as well as those of the linear components of the dumbbells, L-120 and L-240, were measured. The samples in bulk for the above rheological measurements were prepared by heating in a vacuum oven at 170 $^{\circ}$C for 3 days under vacuum and annealed to room temperature. After all rheological measurements, SEC and IC measurements were conducted to confirm that no chain degradation of the samples occurred, and the details are shown in the Supporting Information (Section S2).

For solution samples, the dynamic oscillatory measurements were conducted under nitrogen atmosphere at $22 \leq T / \,^{\circ}\mathrm{C} \leq 50$, and the master curves of G' and G'' reduced at 22 $^{\circ}$C were composed by horizontally shifting the data at each temperature. As for the sample preparation, a prescribed amount of D-30/240/30 after rheological measurements in bulk and dioctyl phthalate (DOP; Kishida Chemical Co., special grade) was weighed into a vial, and dissolved in a 30-fold excess of co-solvent, cyclohexane (Kishida Chemical Co., special grade), at 40 $^{\circ}$C over a week. Then, the co-solvent was evaporated at 40 $^{\circ}$C for 2-3 days and the residual solvent was completely dried under vacuum at room temperature for one day. First, the solution of D-30/240/30 in DOP at ca. 30 wt% was prepared, and after the measurements the sample was reused by diluting with additional DOP by ca. 20, 12, 8, 6, 3 wt%, in turn. For comparison, solutions of three linear PS, L-240 (M_w = 241 kg/mol), L-430 (M_w = 427 kg/mol) and L-1090 (M_w = 1090 kg/mol), in DOP at the same concentration range were prepared, and their measurements were repeatedly conducted in the same manner.

RESULTS AND DISCUSSION

Viscoelastic Properties of Dumbbell-Shaped PS in Bulk. Figure 1a and 1b show the angular frequency ω dependence of the storage and loss moduli, G' and G'', for the two dumbbell PS samples in bulk. The rheological data for the linear and ring components of the dumbbell samples are shown together in Figure 1. A direct comparison of G', G'' and tan δ between two dumbbell samples is shown in Figure S7 in the Supporting Information. The master curves were composed at the reference temperature T_r = 180 °C by horizontally shifting the data at each T, as reported previously.[7,9,31,32] Ordinal vertical shift by b_T = $\rho(T_r)T_r/\rho(T)T$, where $\rho(T)$ is the density of polystyrene at arbitrary temperature T represented as $\rho(T) = 1.25 - 6.05\times10^{-4}\,T$,[44] was also employed for all data. The temperature dependence of horizontal shift factors a_T for the dumbbell PS samples is shown in Figure 2. From Figure 2, it is clear that the time-temperature superposition equally holds for two dumbbell polymers by using the same a_T with the linear PS samples following the Williams-Landel-Ferry (WLF) equation of log $a_T = -C_1(T - T_r)/(C_2 + T - T_r)$ with C_1 = 6.2 and C_2 = 143 K at T_r = 180 °C.[43] This result indicates that the averaged local friction (in other words, the glass transition temperature) of the dumbbell PS samples is basically the same with that of linear PS.
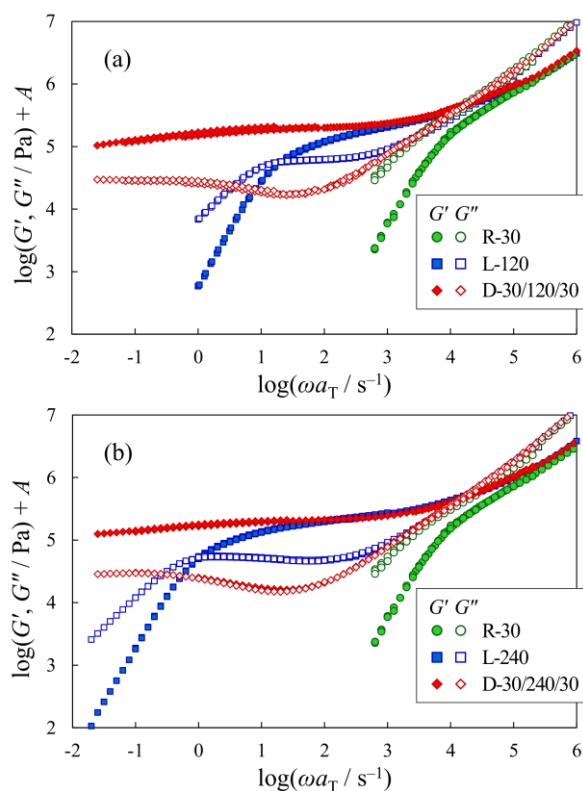

Figure 1. Master curves of G' and G'' vs ω for (a) D-30/120/30 and (b) D-30/240/30 reduced at 180 °C, compared with those for their linear and ring components. The moduli for D-30/120/30 and D-30/240/30 are vertically shifted with a constant A, 0.20 and 0.22, respectively, in a logarithmic scale.
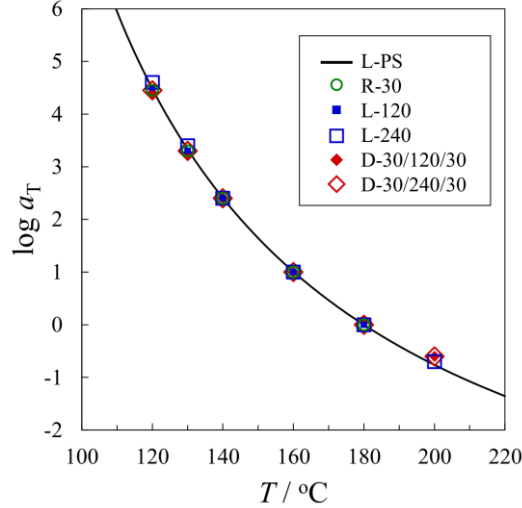
Figure 2. Temperature dependence of horizontal shift factors a_T for dumbbell PS samples and their ring and linear components reduced at $T_r = 180 \; ^oC$. The solid curve indicates the dependence for linear PS samples estimated from the WLF equation expressed as $\log a_T = -6.2(T - T_r)/(143 + T - T_r)$ at $T_r = 180 \; ^oC$.[43]

In Figure 1, an additional vertical shift in a whole T range for the dumbbell samples is employed to compensate considerably lower moduli than those of the other samples even in the glass transition region at high ω ($> 10^4 \; s^{-1}$) as described in Section S3.1 in the Supporting Information. In particular, the G' and G'' data were vertically shifted with constants A of 0.20 and 0.22 for D-30/120/30 and D-30/240/30, respectively, in a logarithmic scale. Note that $\tan \delta$ of the dumbbell polymers at high ω is overlapped well with those of linear PS samples without any vertical shift as shown in Figures S5 and S6. Although the exact reason for their lower moduli is not known, we conceive this is possibly originating from an experimental artifact where the samples did not completely cover/attach the cone-plate geometry during the measurements due to very long relaxation times of the dumbbell polymers as reported in this study. Even if the reason for lower moduli is different from the above, the main conclusion of this study may not be seriously affected.

In Figure 1a, L-120 as the centered linear chain exhibits an entanglement plateau in G' at $\omega = 10^4$–$10^2 \; s^{-1}$ followed by the terminal relaxation, i.e., $G' \sim \omega^2$ and $G'' \sim \omega^1$ at $\omega < 10^1 \; s^{-1}$ since its molecular weight is sufficiently higher than the entanglement molecular weight M_e ($= 18.0 \; kg/mol$ for linear PS).[43] In contrast, the ring R-30 sample exhibits no rubbery plateau and much faster terminal relaxation due to its ring topology as well as its small molecular weight. The dumbbell D-30/120/30 sample exhibits an extremely long rubbery plateau in a wide ω range covering 10^4–$10^{-2} \; s^{-1}$, and its terminal relaxation is not observed in our experimental window. This behavior is similar

to highly-entangled linear polymers having very high molecular weight and/or cross-linked polymers. In Figure 1b, the dumbbell sample with a longer central linear chain, D-30/240/30, exhibits a quite similar viscoelastic response to D-30/120/30, i.e., a remarkably long plateau at $\omega = 10^4$–10^{-2} s^{-1} and no terminal relaxation is observed. In fact, as shown in Figure S7 of the Supporting Information, the viscoelastic spectra of D-30/120/30 and D-30/240/30 are overlapped well in the ω range employed.

Here, we focus on the plateau modulus G_N of the dumbbell polymers in Figure 1. The G_N of dumbbell PS samples agrees well with those of linear PS samples ($\cong 2.0 \times 10^5$ Pa)[7,43] after vertically shifting the data using the factor A, suggesting that the dumbbell polymers examined in this study have essentially the same entanglement density with linear polymers in bulk. If the ring part of dumbbell chains is not incorporated into the entanglement network and just behaves as diluents, their G_N values should decrease compared with the simple linear chains. In fact, some pom-pom-shaped polymers exhibited lower G_N values than the corresponding linear ones because their branch chains relaxed very fast and acted as diluent.[34] Thus, we have to admit that the ring parts as well as the linear one of the dumbbell polymers contributes to the formation of entanglement network by the intermolecular interactions.

Considering the above discussion, we can depict a schematic illustration of entangled dumbbell chains, which can be classified into a novel pseudo-crosslinked physical network, as shown in Figure 3a, where one chain is highlighted in red. Dumbbell polymers are thought to form intermolecular ring-ring penetration, i.e., one dumbbell chain threads the ring part of other molecules, resulted in forming "pseudo-crosslinked" network, in addition to the normal entanglement generated in long linear parts. Hereafter, we call this phenomenon as "intermolecular threading of dumbbell polymers". This characteristic entanglement of dumbbell chains preserves the long relaxation time of conventional entanglements to exhibit almost the same G_N value with the simple linear polymers.

We conceive that the chain conformation of dumbbell chains shown in Figure 3a is thermodynamically stable for the following reason. The ring chains having higher molecular weight than M_e are known to have compact dimensions in bulk compared with the Gaussian rings due to their topological constraints, i.e., the non-crossability of intra/inter-chains, as confirmed by experimental and simulation studies.[45-46] When ring samples in bulk contain some linear contaminants, the rings spontaneously expand by incorporating linear chains to release the topological constraints of rings.[30,47] The centered linear chains in the present dumbbell polymers

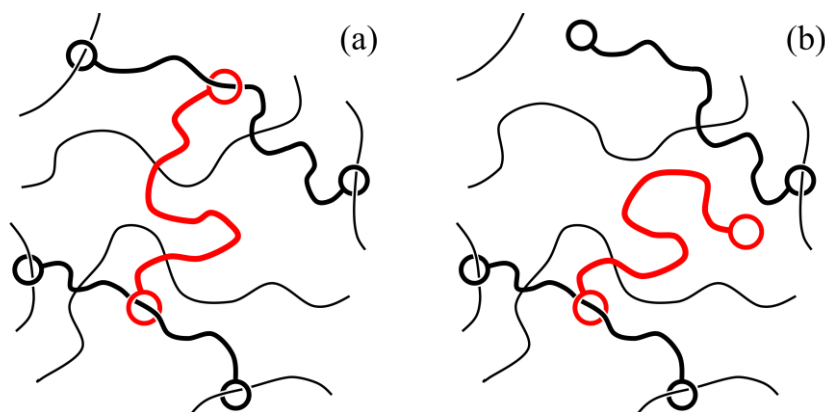may affect conformations of ring parts due to this intermolecular threading.

Figure 3. Schematic illustration of entangled dumbbell polymer chain network: (a) Pseudo-network formation due to intermolecular threading and (b) a part of chain relaxation owing to a partial release from threading.

The extremely slower terminal relaxation of the dumbbell polymers can be also related to the featured entanglement of dumbbell chains as illustrated in Figure 3a. Blends of ring and linear polymers are known to exhibit slower terminal relaxation than the simple linear ones under certain conditions, i.e., specific molecular weight and blending ratio, due to the spontaneous intermolecular ring-linear penetration.[1,24-26] Moreover, tadpole polymers exhibit much slower terminal relaxation than their component ring/linear polymer blends due to the unique molecular architecture where one end of a linear chain is attached on a ring.[31] Based on the above experimental facts, it seems to be reasonable for dumbbell polymers to exhibit significantly slower terminal relaxation if both rings attached on chain ends of a central linear chain are threaded by other dumbbell molecules.

To examine the viscoelastic properties of the dumbbell polymers in a long-time range, stress relaxation measurements were conducted at 180 °C just after the dynamic viscoelastic measurements. Figure 4 shows the relaxation moduli $G(t)$ against time t of two dumbbell PS samples, D-30/120/30 and D-30/240/30, compared with those for a linear PS with M_w = 1090 kg/mol, L-1090 and a four-arm star PS samples with the molecular weight of one arm, M_a = 260 kg/mol, denoted as 4S-260, where the latter was originally reported by Graessley and Roovers,[48] and the authors converted their G' and G'' data into $G(t)$ by the iteration method reported in the literature.[49] Figure S8 in the Supporting Information shows the $G(t)$ data of two dumbbells compared with those of linear PS samples with various molecular weights. Note that the moduli for two dumbbell PS were vertically shifted with the same extent (A was estimated to be 0.20 and 0.22 in a logarithmic scale for D-

30/120/30 and D-30/240/30, respectively) with the dynamic viscoelastic measurements (*cf.* Figure 1). In Figure S9 in the Supporting Information, we confirmed that G' and G'' obtained in dynamic oscillatory measurements were overlapped with those transformed from $G(t)$ in stress relaxation measurements for the dumbbell and linear PS samples in the same ω range. The details are summarized in the Supporting Information (Section S3.2).
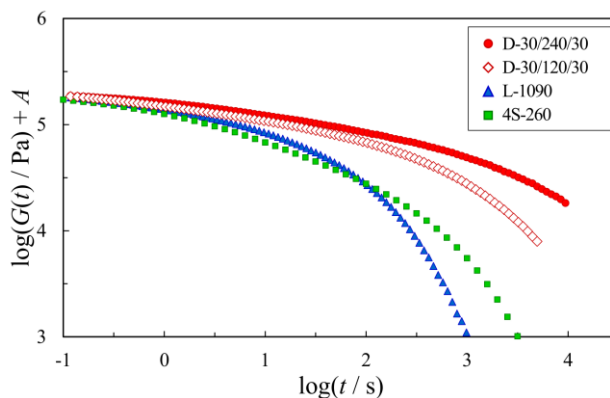

Figure 4. Relaxation moduli $G(t)$ of D-30/120/30 and D-30/240/30, compared with L-1090 and 4S-260[48] at 180 ℃. The moduli of D-30/120/30 and D-30/240/30 were vertically shifted with $A = 0.20$ and 0.22, respectively, in a logarithmic scale.

In Figure 4, both dumbbell PS samples exhibit considerably slower terminal relaxation than the high molecular weight linear PS, L-1090 ($M \sim 10^6$ g/mol). Moreover, a clear difference between D-30/120/30 and D-30/240/30 is observed in long t (≥ 10 s) regime, i.e., D-30/120/30 exhibits faster $G(t)$ decay than D-30/240/30. This difference was hardly observed in the dynamic measurements (*cf.* Figure 1) due to the limitation of the observation time range. Although we measured up to 5×10^3 s for D-30/120/30 and 1×10^4 s for D-30/240/30 at 180 ℃, the full terminal relaxation was not observed for both samples even in the stress relaxation measurements.

Well-entangled star polymers are known to exhibit slower and much broader terminal relaxation than the corresponding linear ones.[48] In fact, the chain motion of star polymers is known as a "retraction" process[50-52] where each arm chain retracts, i.e., contour fluctuation, toward the branch point to escape from their confinement space. In Figure 4, the data for the star polymer, 4S-260, which possesses M_a similar to the central linear chain for D-30/240/30 are added and compared. From this figure, it is evident that D-30/120/30 as well as that for D-30/240/30 exhibit apparently slower terminal relaxation than 4S-260. From these results, we can safely conclude that the relaxation mechanism of entangled dumbbell polymers is different from that of star polymers.

The relaxation mechanism of dumbbell chains in bulk is discussed although it is qualitative. As described above, at short t regime at 180 °C, the global motion of each dumbbell chain is hindered due to the network structure originating from intermolecular dumbbell chain threading which traps ordinal entanglement dynamics, as depicted in Figure 3a. In fact, the modulus in a plateau region is slowly/smoothly decreased without any step changes, suggesting that the dumbbell molecules form a homogeneous entanglement network. To the contrary, the modulus starts to decrease at longer time in stress relaxation measurements in Figure 4, suggesting that a part of the intermolecular threading begins to be released. In this situation, as schematically illustrated in Figure 3b, a dumbbell chain whose at least one ring is released from the threading can move and relax its stress, although the chain still has a bulky ring group on its chain end. Note that the states of the network illustrated in Figures 3a and 3b should be always in equilibrium. From the above, we conceive that the terminal relaxation of dumbbell chains in bulk is related to the probability of the threading-release process. In fact, the density of the intermolecular threading for D-30/120/30 is higher than that for D-30/240/30, because of the difference in the fraction of ring units in the molecules. Hence, it is probably reasonable to consider that the release of intermolecular threading tends to occur more frequently for D-30/120/30 than D-30/240/30.

Moreover, we should make a comment on the characteristics of this dumbbell chain network. As described in the Experimental Section, we conducted SEC measurements of the dumbbell PS samples after rheological measurements, and confirmed that the samples were neither thermally degraded nor chemically-crosslinked (*cf.* Figure S4 in the Supporting Information). In addition, we focus on the experimental fact that the sample was easily and completely dissolved in an eluent THF. This fact also supports intermolecular penetration in the present molecules is a reversible phenomenon depending on polymer concentration. This issue will be discussed in detail in the following sub-section.

Viscoelastic Properties of Dumbbell-Shaped PS in Solution. As shown in the above sub-section, two dumbbell-shaped PS samples, D-30/120/30 and D-30/240/30, in bulk exhibited an extremely long rubbery plateau, which suggests that the dumbbell polymer chains form featured entanglement network originating from intermolecular threading coupled with normal entanglements. In this sub-section, we investigated the viscoelastic/entanglement behavior changes of the D-30/240/30 sample

diluted with a low molecular weight solvent at various concentrations. Here, dioctyl phthalate (DOP) was used as a dilutant, which is known as a θ-solvent for linear PS at 22 °C.[41]

Figure 5a, 5b and 5c show the master curves of G' and G'' vs ω for D-30/240/30 solutions dissolved in DOP reduced at 22 °C at concentrations of ca. 30, 20 and 12 wt%, respectively. For comparison, the data for L-430 and L-240 solutions at the same concentrations are shown together in Figure 5. The data of the solutions at further low concentrations, i.e., ca. 8, 6 and 3 wt%, are shown in Figure S10, while the data of L-1090 solutions at various concentrations are shown in Figure S11. The overlap threshold concentration c^* of D-30/240/30 and linear PS solutions is, ca. 2–4 g/mL which is comparable to the lowest concentration, 3 wt%, treated in this study. The details of c^* for the solutions used in this study are summarized in the Supporting Information. The information on the solutions, i.e., the concentration c in the unit of g/mL and the zero-shear viscosity, is also summarized in Table S1.
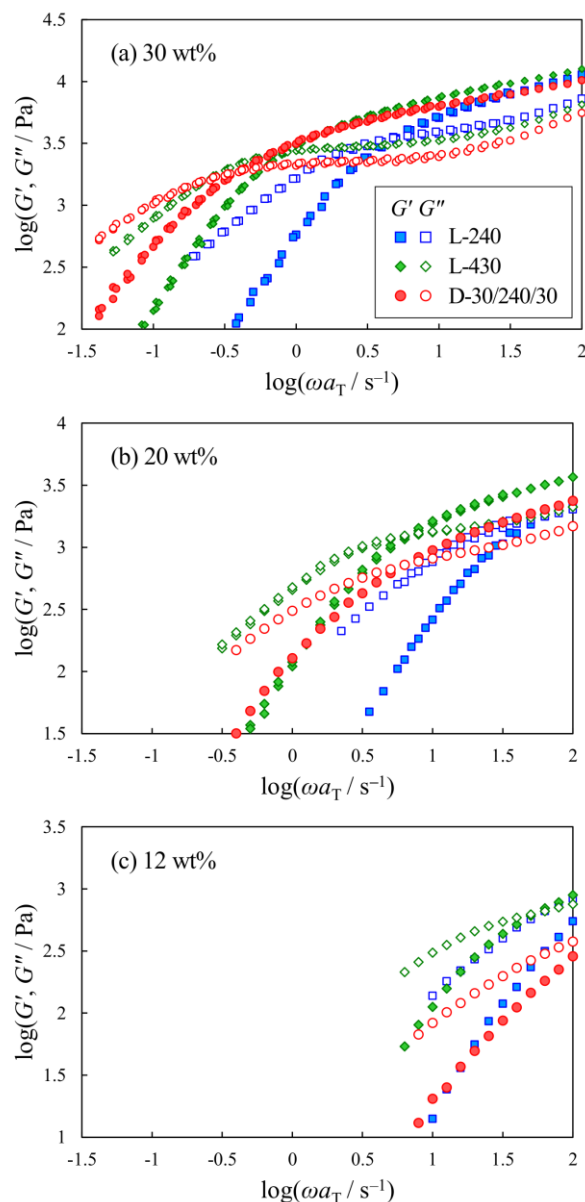
Figure 5. Master curves of G' and G'' vs ω for D-30/240/30 solutions in DOP at (a) 30, (b) 20 and (c) 12 wt %, reduced at 22 °C, comparing with those for L-240 and L-430.

In Figure 5, D-30/240/30 and two linear PS solutions exhibit an entanglement rubbery plateau at 30 and 20 wt%, while a plateau is not observed at 12 wt%. D-30/240/30 solutions at all three concentrations in Figure 5 exhibit a clear terminal relaxation, in clear contrast to the non-terminal-relaxation behavior in the corresponding bulk system in Figure 1. It is noteworthy that at a glance the D-30/240/30 solution at 30 wt% exhibits a slower terminal relaxation than L-240 and L-430, while the relaxation time of D-30/240/30 solutions becomes close to that of L-430 and L-240 as decreasing the polymer concentration. These results suggest that (i) the D-30/240/30 solutions at concentrated regime, i.e., 30-20 wt%, still remain the featured entanglement effect originating from intermolecular threading of dumbbell molecules as was seen in the bulk system (*cf.* Figure 3a) and (ii) the solutions

13

at dilute regime, i.e., 12 wt% or less, behave like simple linear polymer solutions with the similar molecular weight due to their less threading/entanglement effect. Then, this behavior is discussed quantitatively in terms of the zero-shear viscosity η_0 and the steady-state recoverable compliance J_e of the solutions.

From the master curves of G'' in Figure 5 and Figure S8, η_0s for D-30/240/30 solutions at various concentrations c were estimated from the relationship of $\eta_0 = \lim_{\omega \to 0}\{G''(\omega)/\omega\}$, and the η_0 values obtained were summarized in Table S2 in the Supporting Information. In Figure 6, the c dependence of η_0 for D-30/240/30 solutions in DOP is shown, referring to the data for linear PS with different molecular weights, where the viscosity of the solvent DOP ($\eta_S = 71.2$ mPa·s at 22 °C)[53] is subtracted from η_0 in Figure 6. In Figure 6a, all three linear PS solutions exhibit a power-law dependence of $\eta_0 \sim c^{6.0\pm0.4}$ at the concentrated regime, which agrees well with the theoretical prediction[13,54] as well as previous experimental results[55-57] within a range of error. In contrast, the dumbbell polymer solutions exhibit a considerably stronger c dependence of η_0 than the linear polymer ones. Note that the deviation of the viscosity at lower c side for both linear and dumbbell samples originates from the disappearance of entanglement effects.[54-57] Thus, Figure 6a suggests that the characteristic entanglement effect of dumbbell chains is eliminated with decreasing polymer concentration, i.e., with increasing solvent fraction. In fact, as described above, we experimentally confirmed that ring polymers prefer low molecular weight solvents rather than linear chains to incorporate.[47]
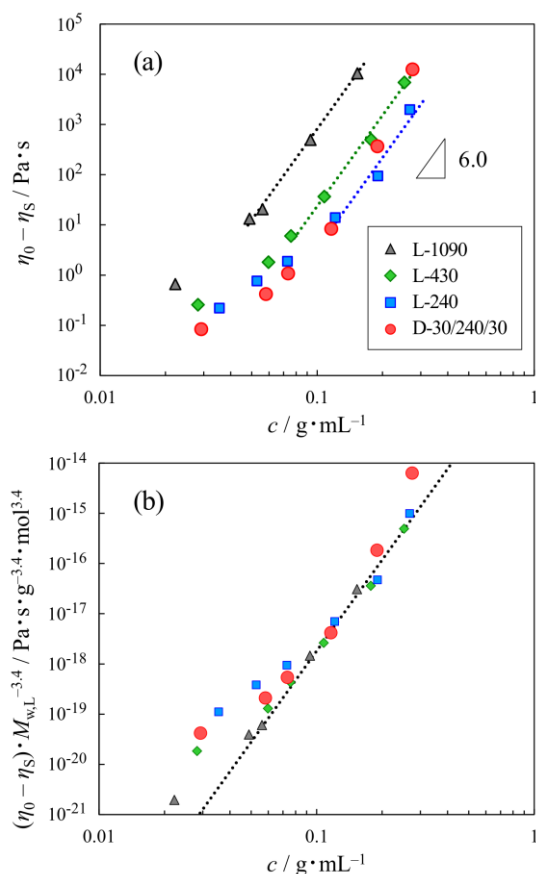
Figure 6. Concentration dependence of (a) the viscosity $\eta_0 - \eta_S$ and (b) $(\eta_0 - \eta_S)/M_{w,L}^{3.4}$ for D-30/240/30 solutions in DOP at 22 °C, compared with those for linear PS solutions. Dotted lines indicate the approximate straight lines for linear PS solutions with a slope of 6.0 at high c regime.

Figure 6b shows the viscosity data normalized by the molecular weight to the power of 3.4, i.e., $M_w^{3.4}$. Note that for D-30/240/30 solutions, the molecular weight of the central linear part, $M_{w,L}$ (= 241 kg/mol), was used instead of the total molecular weight $M_{w,total}$ (= 314 kg/mol) to make the plot in Figure 6b. The difference using $M_{w,L}$ and $M_{w,total}$ for D-30/240/30 solutions is shown in Figure S12 of the Supporting Information. The data of three linear PS solutions with different molecular weights are unified into a straight line with a slope of 6.0 at the concentrated regime. The dumbbell D-30/240/30 solutions exhibit higher $(\eta_0 - \eta_S)/M_{w,L}^{3.4}$ values at higher c (ca. 20 and 30 wt%). This result strongly suggests the characteristic entanglement effect of dumbbell chains still exists in concentrated solutions. This c dependence of the viscosity for the dumbbell solutions at high c seems exponential rather than a power-law. In fact, it is known that entangled star or branched polymers exhibit the exponential dependence on concentration for their viscosities.[58]

The viscosity data of the D-30/240/30 solution at 12 wt% lies on the line of $\eta \sim c^{6.0}$ for linear PS ones, and at the lower c ($\leq$ 8 wt%) the data of D-30/240/30 are deviated from the line of $\eta \sim c^{6.0}$ in

the same trend as linear PS solutions. These results suggest the characteristic entanglement of dumbbell chains as well as normal entanglement disappeared in this c region. In other words, at lower c ($\leq$ 8 wt%), the dumbbell polymers behave like unentangled/isolated chains in the same manner as for the linear polymers. It is probably reasonable that at this low concentration region, the viscosity data for D-30/240/30 is located between that for L-240 and L-430, since the total molecular weight, 314 kg/mol, and therefore the chain size of isolated D-30/240/30 is in between those for L-240 and L-430.

Next, to discuss the broadness of the terminal relaxation of D-30/240/30 solutions in DOP, the steady-state recoverable compliance J_e was estimated from the terminal relaxation region by the following relationship, $J_e = (1/\eta_0^2)\lim_{\omega \to 0}\{G'(\omega)/\omega^2\}$, and the J_e values obtained were summarized in Table S3 in the Supporting Information. Figures 7a and 7b exhibit the concentration dependence of the compliances divided by the molecular weight J_e/M_w and the reduced compliances J_{eR}, reported for linear and star polymers by Raju et al.,[59] respectively. The latter is defined as[59]

$$J_{e,R} = \frac{J_e c R T}{g_2 M_w}\left\{\frac{\eta_0}{\eta_0 - \eta_S}\right\}^2 \qquad (1)$$

where R is the gas constant, T is the temperature in Kelvin unit. g_2 is a factor reflecting the structures of star and other branching polymers, but here g_2 for D-30/240/30 was regarded as unity. The simple concentration dependence of J_e is shown in Figure S13 in the Supporting Information.

In Figure 7a, the J_e/M_w data for linear PS solutions exhibit c^{-1} dependence, which reflects the behavior of less-entanglement ($M/M_e < 10$) systems,[59] though the data are not completely merged. In contrast, for D-30/240/30 solutions, their J_e/M_w data exhibit a clearly different c-dependence from that for linear PS ones. In particular, in the intermediate c regime (i.e., 12 and 20 wt%), their J_e/M_w values are considerably higher than those for linear PS solutions. This result suggests that in this c regime, the dumbbell polymers behave like linear or branched molecules having extremely higher molecular weights via intermolecular penetration. In contrast, in the low c regime ($\leq$ 8 wt%), the J_e/M_w values for D-30/240/30 solutions get closer to those for linear PS ones, which means that the intermolecular penetration of the dumbbell chains disappears and the polymers behave like unentangled/isolated linear chains.

The reduced compliance J_{eR} is basically proportional to $J_e c/M_w$ since $(\eta_0 - \eta_S)/\eta_0$ in eq. 1 is almost constant in our present c range. In Figure 7b, $J_{e,R}$ for linear PS solutions are almost independent to

c, while the dumbbell PS solutions exhibit an overshoot phenomenon of $J_{e,R}$, which is consistent with the results in Figure 7a.
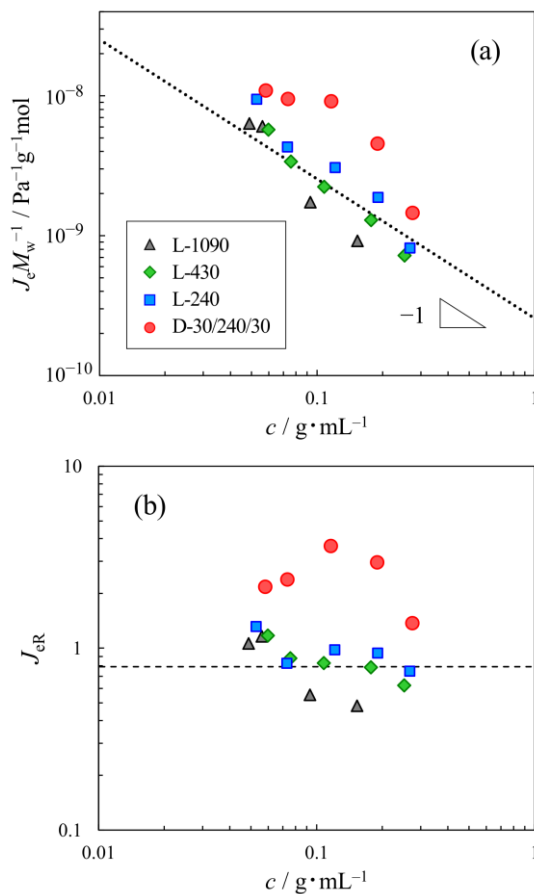

Figure 7. Concentration dependence of (a) J_e/M_w and (b) reduced compliances, J_{eR},[59] for D-30/240/30 solutions in DOP at 22 °C, compared with those for linear PS solutions.   Dotted and dashed lines indicate the approximate straight lines for linear PS solutions with a slope of -1 and 0, in panel (a) and (b), respectively.

From the viscosity and compliance data in solution systems shown above, we confirmed that (i) the D-30/240/30 solutions at relatively high c regime (i.e., 30 and 20 wt%) still exhibit the characteristic entanglement effect originating from intermolecular penetration of dumbbell molecules, (ii) this effect becomes weaker as the concentration of the solution is getting lower, and (iii) finally at lower c regime ($\leq$ 8 wt%) the dumbbell polymers behave like unentangled/isolated chains in the same manner as that in linear polymer systems.

CONCLUSION

We have examined the viscoelastic properties of two dumbbell PS samples, D-30/120/30 and D-30/240/30, in bulk and in solutions. In dynamic viscoelastic measurements, two dumbbell samples in bulk exhibited an extremely long rubbery plateau having the equivalent G_N to that for linear PS, and their terminal relaxation was not observed in our experimental window. These results indicate that the dumbbell chains form a characteristic "network" originating from intermolecular threading in addition to the conventional entanglement. In stress relaxation measurements, two dumbbell samples exhibited considerably slower terminal relaxation than high molecular weight linear PS ($M \sim 10^6$ g/mol) in bulk, and a clear difference between two dumbbell samples was observed at long t regime, i.e., D-30/120/30 relaxes faster than D-30/240/30. These results suggest that the relaxation of the stress for dumbbell chains begins when the intermolecular threading of dumbbells is released, and the probability of the threading release for D-30/120/30 should be higher than that for D-30/240/30 due to the difference in the centered linear chain length.

Furthermore, the viscoelastic properties of D-30/240/30 solutions dissolved in DOP at different six concentrations were examined. At higher c (i.e., 30 and 20 wt%), the solutions exhibited an entanglement plateau in G' and higher viscosity than the corresponding linear PS ones. In addition, at 20 and 12 wt%, D-30/240-30 solutions exhibited considerably higher compliance values than the linear ones. These results suggest that the characteristic entanglement due to the intermolecular threading is still alive at this c regime. In contrast, at lower c regime ($\leq$ 8 wt%), the D-30/240/30 solutions exhibited viscosities and compliances similar to the linear PS ones. This result suggests that the dumbbell chains behave like an unentangled/isolated chain at dilute regime, which is consistent with our previous experimental results on the simple trivial rings; the rings prefer to incorporate low molecular weight solvents rather than linear polymer chains. From the above, we have comprehensively elucidated the characteristics of concentration-dependent viscoelastic properties of dumbbell-shaped polymers in bulk and in solution in relation to the featured entanglement generated in the present molecular system.

ASSOCIATED CONTENT

Supporting Information: Figure S1-S13 and Table S1-S3, Sample preparation, characterization and rheological data of dumbbell-shaped polystyrene samples in bulk and solution (PDF)

ACKNOWLEDGEMENTS

REFERENCES

1. Kapnistos, M.; Lang, M.; Vlassopoulos, D.; Pyckhout-Hintzen, W.; Richter, D.; Cho, D.; Chang, T.; Rubinstein, M. Unexpected Power-Law Stress Relaxation of Entangled Ring Polymers. *Nat. Mater.* **2008**, *7*, 997-1002.

2. Bras, A. R.; Pasquino, R.; Koukoulas, T.; Tsolou, G.; Holderer, O.; Radulescu, A.; Allgaier, J.; Mavrantzas, V. G.; Pyckhout-Hintzen, W.; Wischnewski, A.; Vlassopoulos, D.; Richter D. Structure and Dynamics of Polymer Rings by Neutron Scattering: Breakdown of the Rouse Model. *Soft Matter*, **2011**, *7*, 11169-11176.

3. Kawaguchi, D.; Ohta, Y.; Takano, A.; Matsushita, Y. Temperature and Molecular Weight Dependence of Mutual Diffusion Coefficient of Cyclic Polystyrene/Cyclic Deuterated Polystyrene Bilayer Films. *Macromolecules* **2012**, *45*, 6748-6752.

4. Pasquino, R.; Vasilakopoulos, T. C.; Jeong, Y. C.; Lee, H.; Rogers, S.; Sakellariou, G.; Allgaier, J.; Takano, A.; Bras, A. R.; Chang, T.; Gooβen, S.; Pyckhout-Hintzen, W.; Wischnewski, A.; Hadjichristidis, N.; Richter, D; Rubinstein, M.; Vlassopoulos, D. Viscosity of Ring Polymer Melts. *ACS Macro Lett.* **2013**, *2*, 874-878.

5. Bras, A. R.; Gooβen, S.; Krutyeva, M.; Radulescu, A.; Farago, B.; Allgaier, J.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D. Compact Structure and Non-Gaussian Dynamics of Ring Polymer Melts. *Soft Matter* **2014**, *10*, 3649-3655.

6. Gooβen, S.; Bras, A. R.; Krutyeva, M.; Sharp, M.; Falus, P.; Feoktysov, A.; Gasser, U.; Pyckhout-Hintzen, W.; Wischnewski, A.; Richter, D. Molecular Scale Dynamics of Large Ring Polymers. *Phys. Rev. Lett.* **2014**, *113*, 168302.

7. Doi, Y.; Matsubara, K.; Ohta, Y.; Nakano, T.; Kawaguchi, D.; Takahashi, Y.; Takano, A.; Matsushita, Y. Melt Rheology of Ring Polystyrenes with Ultrahigh Purity. *Macromolecules* **2015**, *48*, 3140-3147.

8. Yan, Z. C.; Costanzo, S.; Jeong, Y.; Chang, T.; Vlassopoulos, D. Linear and Nonlinear Shear Rheology of a Marginally Entangled Ring Polymer. *Macromolecules* **2016**, *49*, 1444-1453.

9. Doi, Y.; Matsumoto, A.; Inoue, T.; Iwamoto, T.; Takano, A.; Matsushita, Y.; Takahashi, Y.; Watanabe, H. Re-Examination of Terminal Relaxation Behavior for High Molecular Weight Ring Polystyrene Melts. *Rheol. Acta* **2017**, *56*, 567-581.

10. Huang, Q.; Ahn, J.; Parisi, D.; Chang, T.; Hassager, O.; Panyukov, S.; Rubinstein, M.; Vlassopoulos, D. Unexpected Stretching of Entangled Ring Macromolecules. *Phys. Rev. Lett.* **2019**, *122*, 208001.

11. Pasch, H. Trathnigg, B. *HPLC of Polymers*; Springer: Berlin, 1998.

12. Lee, H. C.; Lee, H.; Lee, W.; Chang, T.; Roovers, J. Fractionation of Cyclic Polystyrene from Linear Precursor by HPLC at the Chromatographic Critical Condition. *Macromolecules* **2000**, *33*, 8119-8121.

13. de Gennes, P. G. *Scaling Concept in Polymer Physics*; Cornell University: New York, 1979.

14. Doi, M.; Edwards, S. E. The *Theory of Polymer Dynamics*; Clarendon: Oxford, UK, 1986.

15. Wedgewood, L. E.; Ostrov, D. N.; Bird, R. B. A Finitely Extensible Bead-Spring Chain Model for Dilute Polymer Solutions. *J. Non-Newtonian Fluid Mech.* **1991**, *40*, 119-139.

16. Watanabe, H.; Inoue, T.; Matsumiya, Y. Transient Conformational Change of Bead-Spring Ring Chain during Creep Process. *Macromolecules* **2006**, *39*, 5419-5426.

17. Tsolou, G.; Statikis, N.; Baig, G.; Stephanou, P. S.; Mavrantzas, V. G. Melt structure and Dynamics of Unentangled Polyethylene Rings: Rouse Theory, Atomistic Molecular Dynamics Simulation, and Comparison with the Linear Analogues. *Macromolecules* **2010**, *43*, 10692-10713.

18. Khokhlov, A. R.; Nechaev, S. K. Polymer Chain in an Array of Obstacles. *Phys. Lett.* **1985**, 112A, 156-160.

19. Rubinstein, M. Dynamics of Ring Polymers in the Presence of Fixed Obstacles. *Phys. Rev. Lett.* **1986**, *57*, 3023-3026.

20. Obukhov, S. P.; Rubinstein, M. Duke, T. Dynamics of a Ring Polymer in a Gel. *Phys. Rev. Lett.* **1994**, *73*, 1263-1266.

21. Milner, S. T.; Newhall, J. D. Stress Relaxation in Entangled Melts of Unlinked Ring Polymers. *Phys. Rev. Lett.* **2010**, *105*, 208302.

22. Smrek, J.; Grosberg, A. Y. Understanding the Dynamics of Rings in the Melt in Terms of the Annealed Tree Model. *J. Phys.: Condens. Matter* **2015**, *27*, 064117.

23. Ge, T.; Panyukov, S.; Rubinstein, M. Self-Similar Conformations and Dynamics in Entangled Melts and Solutions of Nonconcatenated Ring Polymers. *Macromolecules* **2016**, *49*, 708-722.

24. Nam, S.; Leisen, J.; Breedveld, V.; Beckham, W. Melt Dynamics of Blended Poly(oxyethylene) Chains and Rings. *Macromolecules* **2009**, *42*, 3121-3128.

25. Krutyeva, M.; Allgaier, J.; Richter, D. Direct Observation of Two Distinct Diffusive Modes for Polymer Rings in Linear Polymer Matrices by Pulsed Field Gradient (PFG) NMR. *Macromolecules* **2017**, *50*, 9482-9493.

26. Parisi, D.; Ahn, J.; Chang, T.; Vlassopoulos, D.; Rubinstein, M. Stress Relaxation in Symmetric Ring-Linear Polymer Blends at Low Ring Fractions. *Macromolecules* **2020**, *53*, 1685-1693.

27. Subramanian, G.; Shanbhag, S. Self-Diffusion in Binary Blends of Cyclic and Linear Polymers. *Macromolecules* **2008**, *41*, 7239-7242.

28. Halverson, J. D.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. Rheology of Ring Polymer Melts: From Linear Contaminations to Ring-Linear Blends. *Phys. Rev. Lett.* **2012**, *108*, 038301.

29. Tsalikis, D. G.; Mavrantzas, V. G. Size and Diffusivity of Polymer Rings in Linear Polymer Matrices: The Key Role of Threading Events. *Macromolecules* **2020**, *53*, 803-820.
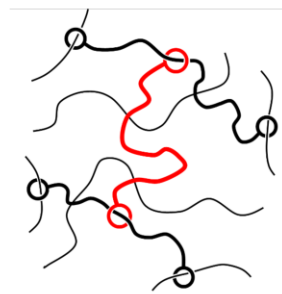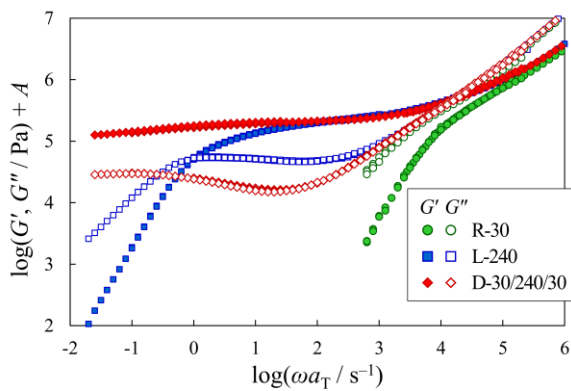
30. Subramanian, G.; Shanbhag, S. Conformational Free Energy of Melts of Ring-Linear Polymer Blends. *Phys. Rev. E* **2009**, *80*, 041806.

31. Doi, Y.; Takano, A.; Takahashi, Y.; Matsushita, Y. Melt Rheology of Tadpole-Shaped Polystyrenes. *Macromolecules* **2015**, *48*, 8667-8674.

32. Doi, Y.; Takano, A.; Takahashi, Y.; Matsushita, Y. Melt Rheology of Tadpole-Shaped Polystyrenes with Different Ring Sizes. *Soft Matter* **2020**, *16*, 8720-8724.

33. Rosa, A.; Smrek, J.; Turner, M. S.; Michieletto, D. Threading-Induced Dynamical Transition in Tadpole-Shaped Polymers. *ACS Macro Lett.* **2020**, *9*, 743-748.

34. van Ruymbeke, E.; Kapnistos, M.; Vlassopoulos, D.; Huang, T.; Knauss, D. M. Linear Melt Rheology of Pom-Pom Polystyrenes with Unentangled Branches. *Macromolecules* **2007**, *40*, 1713-1719.

35. Michieletto, D.; Marenduzzo, D.; Orlandini, E.; Alexander, G. P.; Turner, M. S. Threading Dynamics of Ring Polymers in a Gel. *ACS Macro Lett.* **2014**, *3*, 255-259.

36. Lee, E.; Kim, S.; Jung, Y. Slowing Down of Ring Polymer Diffusion Caused by Inter-Ring Threading. *Macromol. Rapid Commun.* **2015**, *36*, 1115-1121.

37. Smrek, J.; Grosberg, A. Y. Minimal Surfaces on Unconcatenated Polymer Rings in Melt. *ACS Macro Lett.* **2016**, *5*, 750-754.

38. Tsalikis, D. G.; Mavrantzas, V. G.; Vlassopoulos, D. Analysis of Slow Modes in Ring Polymers: Threading of Rings Controls Long-Time Relaxation. *ACS Macro Lett.* **2016**, *5*, 755-760.

39. Smrek, J.; Kremer, K.; Rosa, A. Threading of Unconcatenated Ring Polymers at High Concentrations: Double-Folded vs Time-Equilibrated Structures. *ACS Macro Lett.* **2019**, *8*, 155-160.

40. Doi, Y.; Takano, A.; Matsushita, Y. Synthesis and Characterization of Dumbbell-Shaped Polystyrene. *Polymer* **2016**, *106*, 8-13.

41. Berry, G. C. Thermodynamic and Conformational Properties of polystyrene. II. Intrinsic Viscosity Studies on Dilute Solutions of Linear polystyrenes. *J. Chem. Phys.* **1967**, *46*, 1338-1352.

42. Doi, Y.; Ohta, Y.; Nakamura, M.; Takano, A.; Takahashi, Y.; Matsushita, Y. Precise Synthesis and Characterization of Tadpole-Shaped Polystyrenes with High Purity. *Macromolecules* **2013**, *46*, 1075-1081.

43. Ferry, J. D. *Viscoelastic Properties of Polymers*, 3rd ed.; Wiley, New York, 1980.

44. Zoller, P.; Walsh, D.; eds.; *Standard Pressure-Volume-Temperature Data for Polymers*; Technomic Publishing Co.: New York, 1995.

45. Halverson, J. D.; Lee, W. B.; Grest, G. S.; Grosberg, A. Y.; Kremer, K. Molecular Dynamics Simulation Study of Nonconcatenated Ring Polymers in a Melt. I. Statics. *J. Chem. Phys.* **2011**, *134*, 204904.

46. Iwamoto, T.; Doi, Y.; Kinoshita, K.; Ohta, Y.; Takano, A.; Takahashi, Y.; Nagao, M.; Matsushita, Y. Conformations of Ring Polystyrenes in Bulk Studied by SANS. *Macromolecules* **2018**, *51*, 1539-1548.

47. Iwamoto, T.; Doi, Y.; Kinoshita, K.; Takano, A.; Takahashi, Y.; Kim, E.; Kim, T. H.; Takata, S.; Nagao, M.; Matsushita, Y. Conformations of Ring Polystyrenes in Semidilute Solutions and in Linear Polymer Matrices Studied by SANS. *Macromolecules* **2018**, *51*, 6836-6847.

48. Graessley, W. W.; Roovers, J. Melt Rheology of Four-Arm and Six-Arm Polystyrenes. *Macromolecules* **1979**, *12*, 959-965.

49. Watanabe, H.; Matsumiya, Y.; Inoue, T. Dielectric and Viscoelastic Relaxation of Highly Entangled Star Polyisoprenes: Quantitative Test of Tube Dilation Model. *Macromolecules* **2002**, *35*, 2339-2357.

50. de Gennes, P. G. Reptation of Stars. *J. Phys. (Paris)* **1975**, *36*, 1199-1203.

51. Doi, M.; Kuzuu, N. Rheology of Star Polymers in Concentrated Solutions and Melts. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 775-780.

52. Pearson, D. S.; Helfand, E. Viscoelastic Properties of Star-Shaped Polymers. *Macromolecules* **1984**, *17*, 888-895.

53. Viswanath, D. S.; Natavajan, G. *Data Book on the Viscosity of Liquids*, Hemisphere, New York, 1989.

54. Colby, R. H. Structure and Linear Viscoelasticity of Flexible Polymer Solutions: Comparison of Polyelectrolyte and Neutral Polymer Solutions. *Rheol. Acta* **2010**, *49*, 425-442.

55. Takahashi, Y.; Isono, Y.; Noda, I.; Nagasawa, M. Zero-Shear Viscosity of Linear Polymer Solutions over a Wide Range of Concentration. *Macromolecules* **1985**, *18*, 1002-1008.

56. Takahashi, Y.; Noda, I.; Nagasawa, M. Steady-State Compliance of Linear Polymer Solutions over a Wide Range of Concentration. *Macromolecules* **1985**, *18*, 2220-2225.

57. Takahashi, Y.; Umeda, M.; Noda, I. Relaxation Times of Polymer Solutions in the Semidilute Region for Zero-Shear Viscosity. *Macromolecules* **1988**, *21*, 2257-2262.

58. Graessley, W. W.; Masuda, T.; Roovers, J. E. L.; Hadjichristidis, N. Rheological Properties of Linear and Branched Polyisoprene. *Macromolecules* **1976**, *9*, 127-141.

59. Raju, V. R.; Menezes, E. V.; Marin, G.; Graessley, W. W.; Fetters, L. J. Concentration and Molecular Weight Dependence of Viscoelastic Properties in Linear and Star Polymers. *Macromolecules* **1981**, *14*, 1668-1674.

Viscoelastic Properties of Dumbbell-Shaped Polystyrenes in Bulk and Solution

Yuya Doi,[*,†,‡] Atsushi Takano,[*,†] Yoshiaki Takahashi,[*,§] and Yushu Matsushita[†,∥]