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Melt Rheology of Tadpole-Shaped Polystyrenes with Different Ring Sizes

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ABSTRACT

In this study, linear melt rheology of a single-tail tadpole-shaped polystyrene, ST-30/80, having ring and linear sizes of M_R ~ 30 kg/mol and M_L ~ 80 kg/mol, respectively, was examined, and the effect of the ring size on the rheological properties of tadpole polymers was discussed by comparing with the data of the tadpole samples having M_R ~ 60 kg/mol previously reported. ST-30/80 exhibits an entanglement plateau and shows clearly slower terminal relaxation than its component ring and linear polymers. When the zero-shear viscosity η_0 for ST-30/80 is plotted against the molecular weight of a linear tail chain, the data point lies on the single curve of η_0 for 4- and 6-arm star polymers and the single-tail tadpoles with M_R ~ 60 kg/mol. These results suggest that the tadpole molecule in this study spontaneously forms characteristic entanglement network, i.e., the intermolecular ring-linear threading, in the same manner as the previous tadpole samples, even though the size of ring part is just slightly larger than the entanglement molecular weight (i.e., M_R ~ 1.8 M_e).

KEYWORDS: tadpole-shaped polymer, ring polymer, melt rheology, ring-linear threading, retraction model

1. INTRODUCTION

Polymer chain topology greatly affects physical properties of polymers. Ring polymers are one class of the model polymers having no chain ends to understand the relationship between the structure and dynamics of polymers. Thanks to the development of synthesis and purification techniques for ring polymers, the properties of pure ring polymers have been gradually revealed in the past 20 years.[1-8]

Understanding the relationship between molecular architecture and rheological properties is the one of the central subjects in polymer physics. For linear polymer melts, their relaxation dynamics is well-understood by the Rouse and reptation models at short and long time scales, respectively.[9-12] When polymer chains have some branches, their dynamics should be different from that for linear polymers. In particular, branched polymers exhibit hierarchical relaxations depending on the hierarchy of polymer chain architectures.[13] Compared with linear and branched polymers, rheological properties of ring polymers have not been understood until recently, mainly due to the difficulty in preparing pure ring polymers. From recent findings, the dynamics of rings can be described by the Rouse-ring model when their molecular weight is relatively low,[3] while the rings exhibit considerably slower terminal relaxation when their molecular weight is sufficiently high.[3,5] To describe this slow dynamics of large ring polymers, several theoretical and simulation studies were conducted,[14-17] but their relaxation mechanism has not been fully elucidated yet. In addition, the properties of ring polymers are strongly influenced by a small amount of linear contaminants, and hence the purity of ring samples is an essentially important parameter to discuss their properties.[3,7]

Tadpole-shaped polymers, where each one linear chain is connected at a certain point on each ring chain, are the simplest model polymers having both ring and linear units in their molecules. Therefore, they must be intriguing especially from the viewpoint of polymer dynamics. Recently, we prepared a series of well-characterized tadpole-shaped polystyrene (PS) samples with different linear tail lengths and investigated their melt rheological properties.[18,19] In those studies, tadpole samples exhibited slower terminal relaxation than their component ring and linear polymers. Moreover, they exhibited characteristic molecular weight dependence of the zero-shear viscosity, η_0, that is, their viscosity drastically increases with increasing the length of linear tail chain and its molecular weight M_w dependence is considerably stronger than that of entangled linear polymers known as the relationship of $\eta_0 \sim M_w^{3.4}$.[11,20] These featured rheological properties of tadpoles are originated from the formation of characteristic entangled network, i.e., intermolecular ring-linear penetration. Furthermore, the relaxation mechanism of tadpole chains was confirmed to be similar to that of star polymers known as the arm retraction model.[21-24] However, in those studies, only one series of tadpole samples having the same ring size (M_R ~ 60 kg/mol; ~3.3 times larger than the entanglement molecular weight M_e (= 18.0 kg/mol for linear PS)) was examined, and the effect of the ring size on the viscoelasticity of tadpole polymers is still unknown.

In this study, therefore, linear viscoelasticity of a tadpole PS sample with a smaller ring size than that used in the previous studies, i.e., consisting of a lower molecular weight ring (M_R ~ 30 kg/mol), whose molecular weight is closer to M_e and a longer linear chain (M_L ~ 80 kg/mol), was investigated, and the relaxation mechanism of the tadpole sample was discussed.

2. EXPERIMENTAL

In this study, a single-tail tadpole-shaped polystyrene (PS) having ring and linear sizes of M_R ~ 30 kg/mol and M_L ~ 80 kg/mol is used, and hence this sample is denoted as ST-30/80 hereafter. The synthesis, purification and characterization of ST-30/80 were reported previously.[25] The characteristics of ST-30/80 is as follows: the total molecular weight and its distribution are $M_{w,total}$ = 114 kg/mol and M_w/M_n = 1.01, respectively, and the purity is 99.9%. The component ring and linear samples, R-30 (M_w = 33.7 kg/mol, M_w/M_n = 1.02, purity = 99.9 %) and L-80 (M_w = 84.0 kg/mol, M_w/M_n = 1.06), were also used as references in rheological measurements. Note that the purity of the ring and tadpole samples were carefully determined by interaction chromatography (IC) as reported previously.[18,26]

Dynamic viscoelasticity of ST-30/80 was measured by the ARES-G2 rheometer (TA-Instruments) with 4 mm diameter parallel plates. The measurements were conducted within a temperature range of $120 \leq T$ / °C ≤ 180 under a nitrogen atmosphere with small linear strains ($\leq$ 5%). The samples for viscoelastic measurements were prepared by thermal molding and annealing as reported previously.[19] Master curves of dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were constructed by applying the time-temperature superposition (TTS) principle with the reference temperature T_r of 160 °C in the same manner as reported previously.[19] Note that the vertical shift was also conducted by reflecting the change of temperature T and density ρ as $b_T = \rho(T_r)T_r/\rho(T)T$, as reported previously.[19] The sample was confirmed that no chain degradations occurred under this measurement condition.[19]

3. RESULTS AND DISCUSSION

Fig. 1(a) shows the angular frequency, ω, dependence of dynamic storage and loss moduli, G' and G'', for the single-tail tadpole-shaped PS, ST-30/80, compared with those of its ring and linear components, R-30 and L-80. The data are reduced to the reference temperature T_r of 160 °C. Fig. 1(b) compares the horizontal shift factors, a_T, obtained from the data for the three samples displayed in Fig. 1(a) against the temperature T. It is evident that the T dependence of the factors for the present ring and tadpole molecules mostly agree with that for linear PS samples described by the following WLF equation; $\log a_T = -6.2(T - T_r)/(112 + T - T_r)$.[19,20]

In Fig. 1(a), L-80 exhibits a short but distinct plateau in G' simply because its molecular weight is larger than the critical entanglement molecular weight M_c (= $2M_e$ = 36.0 kg/mol for linear PS), while R-30 exhibits no plateau because of its ring topology coupled with its low molecular weight. To the contrary, the tadpole molecule, ST-30/80, exhibits a clear plateau in G' suggesting the formation of entanglement network, followed by the terminal relaxation of $G' \sim \omega^2$ and $G'' \sim \omega^1$. The terminal relaxation of ST-30/80 is definitely slower than that of the component L-80, which is qualitatively consistent with the previous results on tadpole PSs with a different ring size ($M_R \sim 60$ kg/mol).[19]

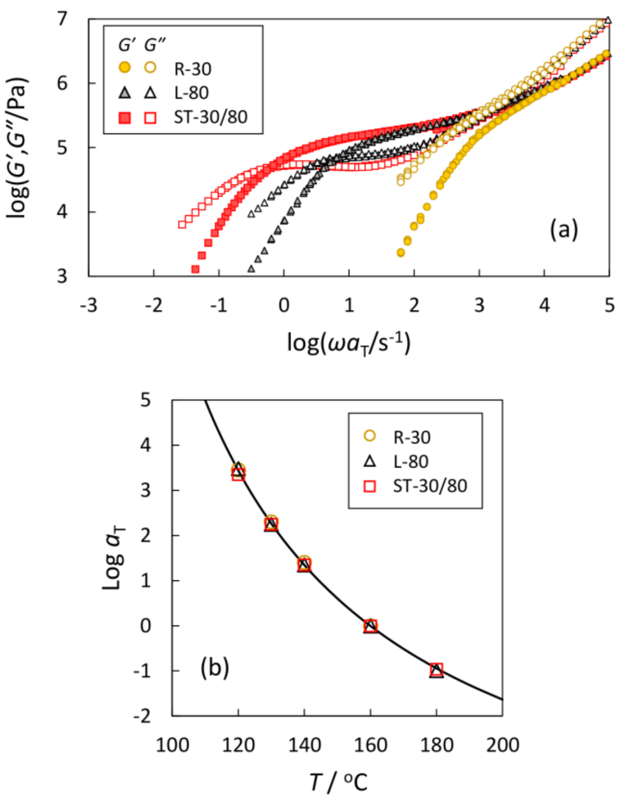

Figure 1 (a) Master curves of G' and G'' against ωa_T for tadpole-shaped PS, ST-30/80, compared with its ring and linear components, R-30 and L-80, reduced at

T_r of 160 °C. (b) Temperature dependence of log a_T for the samples in panel (a). The solid curve indicates the WLF relationship for linear PS samples.[19,20]

From the master curves in Fig. 1(a), two important rheological parameters for ST-30/80 were estimated. First, the plateau modulus G_N for ST-30/80 was determined to be ca. 1.7 × 10^5 Pa from the G' value where tan δ has a minimum. This value is slightly smaller than that for well-entangled linear PSs, ca. 2.0 × 10^5 Pa,[19,20] but they are in the similar level. This result suggests that not only the linear tail but also the ring part of tadpole molecules basically contributes to the formation of entanglement network. In other words, a linear chain in a tadpole certainly penetrates into rings of the other molecules as reported previously, even though the size of ring for the tadpole is just slightly larger than M_e, i.e., $M_R \sim 1.8\, M_e$.

Second, in the terminal relaxation regime, the zero-shear viscosity, η_0, is described by the following relationship:

$$\eta_0 = \lim_{\omega \to 0} \{G''(\omega)/\omega\} \tag{1}$$

The η_0 value for ST-30/80 was estimated to be 2.37 × 10^5 Pa s at T_r = 160 °C, which is clearly larger than that for R-30 ($\eta_{0,\text{R-30}}$ = 4.95 × 10^2 Pa s) and L-80 ($\eta_{0,\text{L-80}}$ = 3.08 × 10^4 Pa s). Note that the errors in η_0 values for those samples are within 5 %. The molecular weight dependence of η_0 will be discussed later.

Fig. 2 compares the master curves of (a) G' and (b) G'' for ST-30/80 with those for the previous single-tail tadpoles with a different ring size, ST-60/X, where X represents the molecular weight of a linear tail in the unit of kg/mol.[19] In Fig. 2, the viscoelastic spectra for all tadpole samples are overlapped at the glass transition regime of $\omega \geq 10^4$ s^{-1} in both G' and G'' data. As increasing the length of a linear chain tail for tadpole molecules, their entanglement plateau becomes more prominent and the terminal relaxation becomes slower. It is noteworthy that the terminal relaxation of ST-30/80 is slower than that of ST-60/70, even though the former has a smaller total molecular weight than the latter.

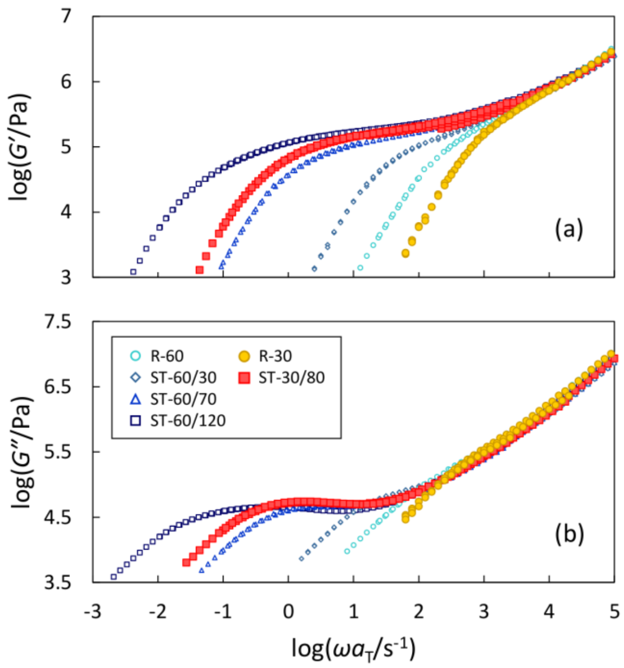

Figure 2 Master curves of (a) G' and (b) G'' for ST-30/80 and R-30, compared with the single-tail tadpole PSs with a different ring size, ST-60/X,[19] and their component ring R-60 reduced at T_r of 160 °C.

To understand the relaxation mechanism of ST-30/80, the molecular weight dependence of η_0 is discussed. Fig. 3(a) shows η_0 for ST-30/80 and ST-60/X samples plotted against their total molecular weight $M_{w,total}$ in a double-logarithmic scale. The η_0 data for linear and ring PSs were obtained from previous studies,[5,7] which includes those reported by several groups, while the data for four- and six-arm star PSs are used in the report by Graessley and Roovers.[26] Note that the η_0 data for the ring PS with the highest M_w (~ 240 kg/mol; R-240) was replaced with the new one,[7] which was supposed to contain ideally no linear contaminants, since the previous data for R-240 was sufficiently affected by non-negligible amount of linear contaminants.[5,7] The zero-shear viscosity of ST-30/80 is clearly higher than that of the corresponding linear PS with the same molecular weight, suggesting that the characteristic entanglement network of tadpole chains was formed, i.e., the spontaneous intermolecular ring-linear threading was taken place in the same manner as reported previously.[19] However, the quantitative discussion is difficult if we deal with the data using the molecular weight for whole molecules, and hence we focus on the length of tails.

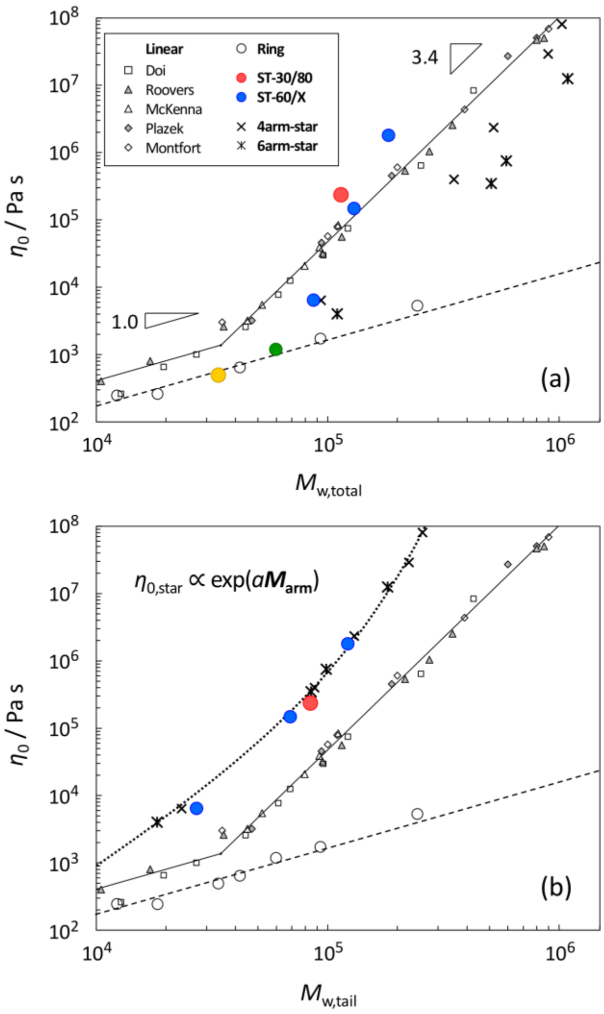

Figure 3 Double-logarithmic plots of η_0 vs (a) $M_{\mathrm{w,total}}$ and (b) $M_{\mathrm{w,tail}}$ of ST-30/80 at T_{r} = 160 °C. The data are compared with linear, ring, 4-arm and 6-arm star and ST-60/X tadpole PSs.[5,7,18,25] The yellow and green circles in panel (a) indicate the date of R-30 and R-60, respectively (i.e., the component rings for tadpoles). The solid and dashed lines indicate the η_0-M_{w} relationship for linear and ring PSs, respectively. The dotted curve in panel (b) indicates an exponential curve for star PSs.

Fig. 3(b) shows η_0 of ST-30/80 and ST-60/X plotted against the molecular weight of a linear tail chain, $M_{\mathrm{w,tail}}$. For comparison, η_0 of 4- and 6-arm star PSs[26] are plotted against the molecular weight of a linear arm chain, $M_{\mathrm{w,arm}}$. The viscosity of star polymers in melt covering the arm number from 4 to 33 is known to be independent of the number of arms, but it depends on the molecular weight of one arm of stars expressed by an exponential function.[27] In addition, the viscosity data for tadpole samples of the previous ST-60/X series stayed on a single exponential curve for star polymers when the data were reduced with $M_{\mathrm{w,arm}}$ and $M_{\mathrm{w,tail}}$

for stars and tadpoles, respectively.[19] These facts indicated that the molecular motion of tadpole molecules can be described by adopting the similar concept for star polymers known as the arm retraction model.[21-24]

As is clearly shown in Fig. 3(b), the data point for ST-30/80 lies on the exponential curve for stars and the ST-60/X series tadpoles. This result suggests that the dynamics of the present tadpole molecule having a smaller ring (M_R ~ 30 kg/mol) but a relatively longer linear tail (M_L ~ 80 kg/mol) can be understood by referring to the same concept for star polymers; explicitly the importance consists in the fact that having (i) a certain ring size, i.e., M_R ~ 1.8 M_e in this study, and (ii) a long linear tail with its molecular weight higher than M_e.

It is known that the retraction model can be applied to describe the motion of the linear chain where one chain end is fixed on a branch point,[21-24] but this model is not covered to explain the dynamics of the ring part for tadpole molecules. In fact, the ring part would hierarchically begin to relax immediately after the threading is released. However, the characteristic relaxation time for the ring R-30 in this study is much shorter than that for the linear L-80 tail and the tadpole ST-30/80 by 2-3 orders of magnitude (*cf.* Fig. 1), and hence the relaxation of the ring part for ST-30/80 is almost negligible.

Finally, we discuss the reason why tadpole molecules spontaneously form intermolecular ring-linear threading. We recently confirmed by small-angle neutron scattering measurements that ring PS chains having the molecular weight larger than M_e (= 18.0 kg/mol for linear PS) have crumpled conformations compared with the Gaussian rings in bulk due to the topological constraints, i.e., non-crossability of intra/inter-chains.[28] In fact, this experimental fact was in good agreement with the simulation results by other groups.[29,30] From these findings, we can safely say that our ring sample R-30 used in this study also possesses the crumpled conformation in bulk. In addition, we experimentally confirmed that rings with higher molecular weight than M_e in linear polymer matrices spontaneously incorporate the surrounding linear chains, and the rings swell naturally to some extent,[31] which is again consistent with the simulation report.[32] For those reasons, the ring part of ST-30/80 spontaneously incorporates the linear part of the other molecules to achieve the thermodynamically stable conformational state by releasing their constraints.

Some previous experimental[33,34] and simulation[35,36] studies reported the structure and dynamics of ring/linear polymer blends where the size of ring is nearly equal to M_e. Those studies reported that threading occurs even for the small rings, and their dynamics becomes slow, although the driving force of the threading is not clearly explained. These results may support our interpretation that the ring-linear threading occurs for the present tadpole sample. In addition, these articles also provide the possibility that the threading may occur even for the tadpole samples with much smaller ring size. The effect of ring-linear threadings has been also studied intensively in ring/linear polymer blends even now,[37,38] and further studies are necessary. In addition, Michieletto et al. very recently reported in their simulation that tadpole polymers exhibited a remarkable slowing down due to the intermolecular threading.[39] Quantitative comparison between our experiments and their simulations would be also interesting.

4. CONCLUSIONS

In this study, we investigated the linear viscoelasticity of a single-tail tadpole PS, ST-30/80, which possesses a smaller ring size (M_R ~ 30 kg/mol ~ 1.8 M_e) than our previous report on ST-60/X series. ST-30/80 exhibited an entanglement plateau and showed slower terminal relaxation than its ring and linear components. In the molecular weight dependence of η_0, ST-30/80 exhibited higher η_0 than the corresponding linear PS having the same molecular weight, which suggests the formation of characteristic entanglement network, i.e., the intermolecular ring-linear threading. When plotting η_0 of ST-30/80 using the molecular weight of a linear tail, $M_{w,tail}$, the data point lies on the single curve of η_0 for stars and ST-60/X tadpoles. These results indicate that the tadpole molecule in this study obeys the similar molecular motion for star polymers known as the retraction model, which is consistent with our previous report on ST-60/X series. Thus, we confirmed that tadpole molecules form intermolecular ring-linear threading when the ring size M_R is ~ 1.8 M_e and having a long tail with its molecular weight of much higher than M_e.

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