Ring polymers are one of the model polymers to understand the relationship between molecular architecture and the dynamics of polymers. This review summarizes the recent rheological studies on pure ring polymers, ring/linear polymer blends, and ring polymer derivatives. Pure ring polymers exhibit different linear and nonlinear rheological properties from linear polymers owing to the absence of chain ends. The presence of linear chains in ring polymers sensitively influences the rheological properties due to the occurrence of spontaneous intermolecular ring/linear threading. This effect becomes significant when a ring and linear chains are connected in a molecule for tadpole-shaped and dumbbell-shaped polymers.

Key Words: Ring polymer / Ring/linear polymer blend / Rheology

INTRODUCTION

Polymer chain architectures strongly affect the rheological properties of polymers. Ring polymers are one of the essential model polymers for studying molecular dynamics owing to the absence of chain ends. The dynamics of linear polymers in melts and concentrated solutions has been investigated\(^1\). When the molecular weight \(M\) of linear polymers is low, their dynamics are explained using the Rouse model\(^2\). As the molecular weight increases, intermolecular entanglement effects, such as a clear plateau region in the modulus and terminal relaxation times following the \(M^{1.4}\) dependence, become obvious\(^3\). These properties are well-explained using the tube model proposed by de Gennes\(^3\) and Doi-Edwards\(^4\). The tube model can be also used to explain the dynamics of entangled branched polymers by considering the effect of branch points in the molecules\(^3,5\). In contrast to linear and branched polymers, the tube model cannot be simply applied to the dynamics of ring polymers. The reason is that the model designates chain ends of polymers as the starting point of the motion, but rings have no chain ends.

In the 1980s, there were several pioneering experimental studies on rheological properties of ring polymer melts by Roovers\(^6,7\) and McKenna et al.\(^8,9\). In these studies, ring polymers exhibit considerably different rheological responses from the corresponding linear ones, but the comprehensive results were not obtained. One of the major causes is the inaccuracy of the sample characterization, especially of the quantitative “purity” estimation of ring samples, mainly due to the limitation of analysis/purification techniques. In 2000, Lee et al.\(^10\) successfully isolated ring polymers from linear ones using liquid chromatography techniques called liquid chromatography at the critical condition (LCCC) and interaction chromatography (IC)\(^11\). These techniques can be used to estimate the purity of ring polymer samples accurately. With the advent of the above purification techniques, rheological studies on ring polymers have been significantly developed in the last 20 years.

This review introduces the recent results on the rheological properties of (i) ring polymers, (ii) ring/linear polymer blends, and (iii) ring polymer derivatives. Not only the linear viscoelasticity (LVE) but also the nonlinear viscoelastic (NLVE) properties of ring polymers have been extensively studied. In parallel efforts to the experiments, theoretical and simulation studies on the dynamics of ring polymers have been significantly progressed, but this review mainly focuses on the experimental studies.

RHEOLOGICAL PROPERTIES OF RING POLYMERS

Kapnistos et al.\(^12\) first reported the LVE properties of ring polystyrene (PS) samples (\(M = 161\) and 198 kg/mol) purified using LCCC. The molecular weights of the samples are sufficiently higher than the entanglement molecular weight \(M_e\) (18.0 kg/mol) for linear PS\(^11\). The ring samples exhibit a
power-law type relaxation modulus without a clear entanglement plateau region. The power-law type relaxation of rings qualitatively agrees with the predictions based on the self-similar dynamics of ring chains in the double-folded lattice-animal (DFLA) model and also the developed fractal loopy globule (FLG) model\textsuperscript{13, 14}. Subsequently, Pasquino et al.\textsuperscript{15} summarized the zero-shear viscosity $\eta_0$ data for purified PS, polyisoprene (PI), and poly(ethylene oxide) (PEO) rings with a wide molecular weight range. They discovered that when the molecular weight is higher than $2M_e$, the rings exhibit $\eta_{0,\text{ring}} \propto M^{2.2 \pm 0.3}$, which is a weaker $M$-dependence than entangled linear polymers, $\eta_{0,\text{linear}} \propto M^{3.4}$.

Doi et al.\textsuperscript{16} prepared purified ring PS samples covering a wide range of molecular weights (i.e., $M = 12.3$–244 kg/mol), and investigated the dynamic linear viscoelasticity. They revealed that when the molecular weight of rings is lower than 90 kg/mol ($\lesssim 5M_e$) the dynamic modulus is described using the Rouse-ring prediction, whereas when the molecular weight is higher than $5M_e$ the modulus exhibits a considerably slower terminal relaxation than the model, as shown in Fig. 1. These results suggest that some intermolecular interactions exist in the ring samples with relatively high molecular weights. Moreover, Doi et al.\textsuperscript{17} examined the terminal relaxation behavior of the ring PS with $M = 244$ kg/mol (R-240) by systematically blending the linear counterpart (L-240) at the fraction $w_L$, ranging from 0.7 % to 4.9 % combined with LCCC/IC measurements. They estimated the relaxation modulus of ideally pure R-240 by extrapolating the modulus data to $w_L = 0$. They confirmed that this pure ring exhibits a broader terminal relaxation than the FLG model. The molecular origin of this discrepancy is not fully understood yet.

In the past 20 years, the LVE properties of pure rings have gradually dawned on us, but the understanding is still incomplete. In particular, there are few reports on ring polymers with sufficiently high molecular weights (i.e., $M/ M_e > 30$). Further studies combined with the theory/simulation as well as other experimental techniques such as diffusion\textsuperscript{18} and spin-echo\textsuperscript{19} measurements, are necessary.

Compared with LVE, there are still a few attempts for the NLVE measurements of pure ring polymers. Yang et al.\textsuperscript{20} presented the nonlinear shear rheological properties of ring PS with $M = 84$ kg/mol. They discovered that under start-up shear flow the ring PS exhibits weaker shear thinning with less stress overshoot than the corresponding linear PS. Parisi et al.\textsuperscript{21, 22} recently reported the same trend even for a ring PS with higher $M (= 185$ kg/mol) (Fig. 2). They further discussed their experimental results by comparing the nonequilibrium molecular dynamics simulations and the shear slit model for ring polymers introducing two different length scales.

Huang et al.\textsuperscript{23} reported the uniaxial elongational rheology of the ring PS with $M = 185$ kg/mol. They found out that the ring exhibits a unique response, that is, a stronger strain-hardening than the corresponding linear sample, even at a relatively low elongational rate $\dot{\varepsilon}$ (Fig. 3(a)). Furthermore, as shown in Fig. 3(b), the ring exhibits a different $\dot{\varepsilon}$ dependence from the linear one. It means that the steady-state

Fig. 1 Dynamic modulus of ring polystyrenes with different molecular weights. The symbols indicate the experimental data, while the curves indicate the Rouse-ring prediction. Reproduced from ref. 16 with permission from the American Chemistry Society.

Fig. 2 Normalized steady-state viscosity against the Weissenberg number and the absolute value of complex viscosity against the Deborah number for linear and ring PS samples. Reproduced from ref. 21 with permission from the American Chemistry Society.
viscosity of the linear PS decreases as a function of $\dot{\varepsilon}^{-1/2}$ at higher $\dot{\varepsilon}$ than the inverse of the reptation time $\tau_d^{-1}$, while for the viscosity of the ring, it first increases and then decreases as $\dot{\varepsilon}^{-1/2}$ with increasing $\dot{\varepsilon}$. The molecular origin of these unique elongational properties has not been fully elucidated. However, it could originate from the compact and crumpled conformations of rings in bulk$^{24,25}$, and the resulting intermolecular interactions as confirmed in LVE of ring polymers$^{12,16}$.

**RHEOLOGICAL PROPERTIES OF RING/LINEAR POLYMER BLENDS**

Rheological properties of ring polymers are sensitive to the presence of linear polymers. Several studies have been conducted to clarify the influence of a small amount of linear contaminant in ring polymers on LVE by Kapnistos et al.$^{12}$ and Doi et al.$^{17}$ Recently, Parisi et al.$^{26}$ conducted the stress relaxation measurements of symmetric ring/linear blends ($M_R = M_L = 185$ kg/mol) at low ring fractions ($\Phi_R = 0.05-0.3$). They examined the contribution of the constraint release (CR) due to the ring/linear threading on the relaxation modulus. Several studies using pulsed-field gradient (PFG)-NMR$^{27,28}$ and neutron spin-echo (NSE)$^{19,29}$ methods have been conducted to selectively observe the motion of ring (or linear) molecules in ring/linear blends. It has been known that linear polymer chains spontaneously thread into rings to release the topological constraints in the conformation of rings$^{30,31}$. To understand the entire picture of the rheology of ring/linear polymer blends, further systematic studies are necessary.

Regarding the NLVE of ring/linear polymer blends, Parisi et al.$^{22}$ examined the nonlinear shear rheology of symmetric and asymmetric ring/linear polystyrene blends ($M_R = 185$ kg/mol and $M_L = 185$ kg/mol or 130 kg/mol) at relatively low ring fractions ($\Phi_R = 0.05-0.3$). They found out that the Weissenberg number dependence of some rheological parameters such as the steady-state viscosity and magnitude of viscosity overshoot is similar to that of the corresponding linear samples. In contrast to the shear rheology, a unique property of ring/linear blends is reported in elongational rheology. Borger et al.$^{32}$ performed uniaxial elongation measurements of a ring/linear blend with $M_R = M_L = 185$ kg/mol at $\Phi_R = 0.3$. They revealed that the blend exhibits an overshoot in the stress growth coefficient, which is essentially different from the pure ring and linear components (Fig. 4(a)). The result suggests that linear chains spontaneously thread into rings at the equilibrium state, but unthreading is induced under elongational flow, as schematically shown in Fig. 4(b).

**RHEOLOGICAL PROPERTIES OF RING POLYMER DERIVATIVES**

This section introduces rheological properties of ring polymer derivatives where ring and linear chains are connected through covalent bonding in a molecule. In particular, this review focuses on “tadpole-shaped polymer”, where a ring is attached on one chain end of a linear chain, and “dumbbell-shaped polymer”, where rings are attached on both ends of a linear chain.

Doi et al.$^{33,34}$ examined the linear rheological properties of tadpole-shaped PS samples where the molecular weights of ring and linear units (i.e., $M_{wR}$ and $M_{wL}$, respectively) are systematically changed. They confirmed that samples with $M_{wR} = 60$ kg/mol and $M_{wL} = 30, 70$ and 120 kg/mol exhibit a clear entanglement plateau and slow terminal relaxation compared to the corresponding linear tail samples and ring/linear blends$^{35}$. Figure 5(a) shows the molecular weight

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Fig. 3 (a) Stress growth coefficient of linear and ring PSs ($M = 185$ kg/mol) at different extensional rates. (b) Steady-state uniaxial elongational viscosity of the linear and ring PSs against the elongational rate. Reproduced from ref. 23 with permission from the American Physical Society.
dependence of \( \eta_0 \) of the tadpoles, and they exhibit a higher exponent than the linear samples of \( M_w \). Moreover, when \( \eta_0 \) of the tadpoles is plotted against the molecular weight of a tail \( M_w,\text{tail} \) instead of \( M_w,\text{total} \) in Fig. 5(b), their dependence is consistent with that for star polymers, which is expressed as an exponential function. These results suggest that the relaxation dynamics of the entangled tadpole-shaped polymers is explained by a concept similar to the retraction motion of star polymers. Doi et al.\(^{34}\) also confirmed a similar behavior of \( \eta_0 \) in a tadpole sample with a smaller ring (\( M_w,\text{R} = 30 \text{ kg/mol} \)). The recent simulation study also reported such a viscosity enhancement of the tadpoles due to the intermolecular ring/linear threading\(^{35}\).

Furthermore, Doi et al.\(^{36}\) reported the viscoelastic properties of dumbbell-shaped PS samples in bulk and solution. They observed that the dumbbell PS, D-30/240/30, where rings with \( M_w,\text{R} = 30 \text{ kg/mol} \) are attached on a linear PS with \( M_w,\text{L} = 240 \text{ kg/mol} \), exhibits an entanglement plateau in a wider frequency range than the corresponding linear PS, L-240, as shown in Fig. 6(a). In addition, they discovered that the dumbbell PS exhibits considerably slower and
broader terminal relaxation than the linear PS in the stress relaxation measurements. This molecular origin is expected that the dumbbell polymers spontaneously form a novel intermolecular entanglement network where a ring part of one dumbbell is threaded by the other molecule, as shown in Fig. 6(b). It is thought that the rearrangement of the intermolecular threading between the dumbbells occurs in a slower time scale than that of the entanglement of simple linear chains.

CONCLUSIONS

In this review, the rheological properties of pure rings, ring/linear polymer blends, and ring polymer derivatives are introduced. It has been found that pure ring polymers exhibit a power-low type stress relaxation, which differs from entangled linear polymers. The characteristic intermolecular interactions of ring polymers also affect the nonlinear rheological properties. The presence of linear chains in ring polymers sensitively influences the linear and nonlinear rheological properties because of the spontaneous intermolecular ring/linear threading. This threading effect significantly works for tadpole-shaped and dumbbell-shaped polymers.

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