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Dynamic Viscoelastic Properties of Multi-Arm Star Polystyrenes in the Molten State

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Multi-arm star polystyrenes with various lengths and number of arms were synthesized, and their dynamic viscoelastic properties were investigated in the molten state. The master curves of the storage modulus for the multi-arm stars showed a shoulder at low frequencies, suggesting that a new mechanical relaxation exists at the long time scales after completion of entanglement relaxation. The enhancement of the zero-shear viscosity compared with the regular star polymers was also observed for the multi-arm star polymers.

Key words: Multi-arm star / Dynamic viscoelasticity / Long-time relaxation / Viscosity enhancement

1. INTRODUCTION

A regular star polymer, a star-shaped polymer with relatively small number of arms, is typical of branched polymers. Rheological properties of the regular star polymers have been studied by experiment¹⁻³⁾ as well as theoretical approach.⁴⁾ It is well known that the entanglement relaxation of the regular star polymers is not affected by the number of arms but is strongly affected by the molecular weight of the arm.

In contrast, multi-arm star polymers consist of many arms, typically more than ten arms. These polymers are considered to have a kind of core-shell structure, due to high chain density at the center of the molecule. Previously, we have studied the rheological properties of multi-arm star polystyrenes in the molten state.⁵⁻⁶⁾ However, the information on the long-time relaxation behavior obtained was not so enough and accurate, primarily because the performance of the rheometer used was not so high comparing with up-to-date rheometers now available.

Multi-arm star polymers have been classified as an ultra-soft colloid system, and their unique dynamics has been reported.⁷⁾ The structure and properties of the multi-arm star polymers were studied by scattering methods⁷⁻¹¹⁾ and computer simulation.^{10,11)} These studies revealed that the polymer systems show a liquid-like ordering. In addition, the systems showed a new mechanical relaxation in the long time region.⁹⁻¹¹⁾ This relaxation is believed to be due to the diffusional motion of the star cores back to the equilibrium state after deformation.

However details of the mechanical relaxation are still unclear at present. To investigate the new mechanical relaxation, the difference in viscoelasticity between the regular and multi-arm stars must be again examined more clearly.

In this study, we synthesized multi-arm star polystyrenes with various lengths and number of arms, and examined the dynamic viscoelasticity of the melts of these multi-arm star polystyrenes.

2. EXPERIMENTAL

Four-types of multi-arm star polystyrenes differing in length and/or number of arms were synthesized by a two-step preparation method. The sample code is listed in Table I. First, linear polystyrene (PS) was prepared by an anionic polymerization method in the mixture of benzene and diethylether using *sec*-butyllithium as an initiator at 0°C for 24hr. Then, a small amount of divinylbenzene (DVB) was added into the solution to couple the active ends. Before the coupling reaction, a small amount of polystyryl anion was recovered and terminated to determine the molecular weights of the arm (precursor). The coupling reaction was continued with stirring the solution for *ca.* 10 days at room temperature. Finally, the product was terminated and purified with methanol. To remove a small amount of lower and higher molecular weight fractions, the product was fractionated from benzene/methanol mixtures. Gel permeation chromatogram (GPC) of the samples was obtained with a Tosoh CCP and

Table I Molecular characteristics and zero-shear viscosity η_0 of star polystyrenes.

	arm			star		P^*	η_0 / 10^5Pas
	$M_w / 10^4$	$M_n / 10^4$	M_w / M_n	$M_w / 10^5$	$M_n / 10^5$	M_w / M_n	
LM23	5.68	5.33	1.07	9.77	9.23	1.06	10.5
LM24	4.50	4.45	1.01	7.54	6.96	1.08	4.67
LM26	2.57	2.37	1.09	10.4	8.76	1.18	0.96
LM27	2.64	2.45	1.08	6.50	5.51	1.18	0.28

*Number of arms defined as a ratio of M_n of a star to that of an arm.

8020 series with a low-angle laser light scattering apparatus (LALLS, Tosoh LS-8000) to determine the molecular weights. Elute solvent was tetrahydrofuran (THF).

Dynamic viscoelasticity of the melts of the star samples was measured by using a Rheometric Scientific ARES rheometer with a cone-plate geometry (25mm ϕ , cone angle 0.04rad). Before the measurement, the powder samples were molded into disk-shape specimens, and these disks were dried at 80°C in vacuo to prevent bubbling. Measurements were performed under nitrogen atmosphere to prevent degradation. The frequency dependence curves of the dynamic storage modulus (G') and loss modulus (G'') were obtained at several temperatures. To construct the master curves, the curves measured at each temperature were shifted horizontally as well as vertically. The reference temperature was set to be 160°C.

3. RESULTS AND DISCUSSION

3.1 Molecular Characterization

A typical GPC profile of a multi-arm star polystyrene, LM23, is shown in Fig.1. The solid and dotted curves represent signals from RI and LS detectors, respectively. Both curves show a single peak. The other multi-arm star polymers also showed similar GPC profiles. Table I lists the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polydispersity index (M_w/M_n) calculated from the GPC curves using both RI and LS signals. The values of M_n , M_w and M_w/M_n for the multi-arm star polymers as well as for the precursor arms are listed in Table I. The number of arms (P), defined as a ratio of M_n of a star to that of an arm, is also summarized in the table.

The number of arms changes the core size of a multi-arm star polymer with a core-shell structure. From Table I, the arms of LM23 and LM24 are about twice longer than those of LM26 and LM27. LM23 and LM24 have roughly the same number of arms as LM27. LM26 has almost the same length of arm as LM27, but the number of arms for LM26 is about 1.5 times more than that for LM27.

Fig.1 GPC Profile of LM23. The solid and dotted curves represent the signals of refractive index (RI) and light scattering (LS) detectors, respectively.

Fig.2 The frequency dependence of the dynamic storage modulus (G') and loss modulus (G'') for LM24 reduced at 160°C. Unfilled and filled symbols correspond to G' and G'' , respectively.

3.2 Dynamic Viscoelasticity

The frequency dispersion curves of G' and G'' for the multi-arm stars were well superimposed to give the master curves, implying that the star polymers are thermorheologically simple. The values of the horizontal shift factor a_T were almost the same for all star samples and obeyed the WLF-type

Fig.3 The frequency dependence of the dynamic storage modulus (G') and loss modulus (G'') for LM26 reduced at 160°C. Unfilled and filled symbols correspond to G' and G'' , respectively

Fig.4. The frequency dependence of the dynamic storage modulus (G') and loss modulus (G'') for LM27 reduced at 160°C. Unfilled and filled symbols correspond to G' and G'' , respectively

Fig.5 The plots of the zero-shear viscosity (η_0) vs. span molecular weight (M_s) at 160°C.

equation. The master curves of G' and G'' for LM24 are shown in Fig.2. The master curves for LM23 were very similar to those for LM24, although we do not show the curves here.

In Fig.2, the transition zone, rubbery-plateau zone, and flow zone are seen in the reduced frequency range examined. The G'' curve in the flow zone shows the relation $G'' \propto \omega$ giving the zero-shear viscosity ($\eta_0 = [G''/\omega]_{\omega \rightarrow 0}$).¹²⁾ The value of η_0 for LM24 is listed in Table I.

Figure 2 also demonstrates that a shoulder is observed in the G' curve at low frequencies where the entanglement relaxation is completed. The existence of this shoulder suggests that a new mechanical relaxation occurs in the long time region.

The master curves for LM26 and LM27 are shown in Figs.3 and 4, respectively. Both samples show the flow behavior characterized by the relation $G'' \propto \omega$ at low frequencies. However, a distinct rubbery-plateau region cannot be observed for LM26 and LM27, as different from the behavior of LM24. Whether or not the entanglements actually exist in the system primarily depends on the molecular weight of the arm (M_a), or equivalently, the span molecular weight (M_s ; $M_s = 2M_a$) of the star samples. The values of M_a for LM23 and LM24 are larger than those of LM26 and LM27, as can be seen from Table I. Absence of the plateau region for LM26 and LM27 may indicate that these samples are non-entangled, while LM23 and LM24 are entangled, as long as judging from the G' and G'' curves, although the sensitivity to the existence of entanglements, of course, depends on features of the physical quantity measured. Even for the non-entangled systems, LM26 and LM27, a shoulder is also found in the G' curve at low frequencies. This shoulder must have the same origin of the relaxation as that for LM24. The long-time relaxation of the multi-arm star polystyrenes appears to be independent of whether or not the systems have entanglements.

Figure 5 shows the plots of η_0 against M_s for multi-arm stars investigated in this study. The figure also contains the data for regular stars^{2,3)} reported in literature. The η_0 data for the regular (4- and 6-arm) stars reported by Graessley and Roovers²⁾ fall on a single curve, and these η_0 data increase exponentially with increasing M_s . This is in good agreement with the experimental results reported by Fetters et al.¹⁾ that η_0 is independent of the number of arms. The η_0 data for 6-arm stars obtained from our previous work³⁾ do not fall on the curve obtained from the data of Graessley and Roovers. The reason for this deviation is not clear, although the deviation might originate partly from the difference in a_T .

Figure 5 clearly shows that the viscosity of our multi-arm stars is enhanced compared with the regular stars. A

comparison of η_0 of LM26 and LM27 reveals an interesting result: η_0 appears to increase as the number of arms increases, although LM26 and LM27 have the same M_a . As is well known, the zero-shear viscosity is governed by the relaxation intensity and relaxation time.¹²⁾ On the basis of the relaxation spectra of the samples, the higher value of η_0 for LM26 is considered to be because LM26 has larger relaxation intensity as well as longer relaxation time than LM27, although we do not show them here.

This behavior, not seen for regular stars, must be characteristic of the multi-arm stars. Pakula et al.⁹⁻¹¹⁾ reported that multi-arm stars exhibit long-time relaxation due to rearrangement of the star molecules having a liquid-like order. The long-time relaxation found for our star PS may have the same molecular origin. However, the relaxation mechanism of the long-time relaxation, and the effects of the number and length of arms on the relaxation have not been fully elucidated yet, as stated in Introduction. Further studies are required for the detailed discussion of the long-time relaxation.

4. CONCLUSIONS

The multi-arm star polystyrene samples were synthesized and the dynamic viscoelastic properties of the melts of the samples were investigated. The master curves of storage modulus G' for the multi-arm stars showed a shoulder at lower frequencies, suggesting that a new mechanical relaxation exists in the long time region where the entanglement relaxation is completed. The multi-arm star polymers also showed a viscosity enhancement compared with the regular stars. The effect of the number of arms on viscosity was observed for the multi-arm star polystyrenes.

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