

Elongational Viscosities of Random and Block Copolymer Melts

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ABSTRACT: The influence of random and block copolymerized structures on the uniaxial elongational viscosity was investigated. The investigated random copolymers were poly(ethylene-*random*-ethyl methacrylate) with comb-branched structure and poly(styrene-*random*-acrylonitrile) with linear structure. The studied block copolymers were poly(styrene-*block*-ethylenebutylene-*block*-styrene) with linear structure. The elongational viscosities of random copolymers showed strain-hardening properties. The strain-hardening property was influenced little by comonomer contents and depended on whether copolymers had linear or branched structures. In contrast, the elongational viscosities of block copolymers gave strain-softening properties. The strain-softening property was not affected by strain rates and block comonomer ratios. The causes of strain-hardening and -softening properties are discussed from relaxation spectrum and damping function based on the Bernstein–Kearsley–Zapas model. The damping functions of linear and branched random copolymers agreed with those of linear and branched homopolymers, respectively. On the other hand, linear block copolymers exhibited stronger damping than linear homopolymers. It was concluded that strain-hardening and -softening properties in the elongational viscosity of random and block copolymerized structures are correlated with their damping functions. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1765–1774, 1998

Key words: uniaxial elongational viscosity; strain-hardening; strain-softening; random copolymer; block copolymer; damping function

INTRODUCTION

Elongational flow is dominant under polymer processing such as sheet molding, blow molding, and melt-spinning. Even under injection-molding process, die entrance flow in abrupt convergence is also governed by elongational deformation. To predict polymer processability including elongational flow, uniaxial elongational viscosity tends to be significant together with shear viscosity. Experimental studies on the uniaxial elonga-

tional viscosity at constant strain rates and constant stress values have been reported frequently,^{1–11} after Meissner developed an uniaxial elongational rheometer.¹² We also developed our homemade elongational rheometer in the late 1970s¹ through modifying Meissner-type design.

In the elongational viscosity measurement, the elongational viscosity is increased abruptly at higher constant strain rates under large strain. This has been called the strain-hardening property. Former studies^{1–11} have shown that the strain-hardening property is enhanced by the existence of a very long relaxation time, which comes from wide molecular weight distribution (MWD) and long chain branching. The main advantage of an elongational rheometer over a

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shear rheometer is the sensitive detection of very long-time relaxation through evaluating the strain-hardening property. This view has been demonstrated by both experiments and constitutive analysis for various homopolymer melts.⁵

For many years, various kinds of copolymers have been used for polymer processing. Copolymerized structures are important for viscoelastic properties of polymer melts, together with molecular parameters such as molecular weight (M_w), MWD, and branched structures. The influence of copolymerized structures on shear-flow properties of polymer melts has been reported.^{13,14} Collins and associates have suggested that the presence of hydroxyl, carboxyl, and nitril have influence on low shear viscosity and activation energy.¹³ Kraus and Gruver compared shear melt properties of random and block copolymers.¹⁴ However, the effect of copolymerized structures on elongational viscosity has been little reported before now. We are aiming to establish a systematic view of the relationship between various copolymerized structures and strain-hardening properties. Previously, we reported the influence of graft copolymerized structure on strain-hardening properties,¹⁵ and we studied the effect of ionic interaction on strain-hardening properties using partially ionized random copolymers.^{16,17}

It is important to understand the cause of the strain-hardening property. The strain-hardening property reflects the increase of modulus. The modulus is divided into a time- and a strain-dependent term based on the Bernstein–Kearsley–Zapas (BKZ) model.^{8,18} Thus, it is significant to understand whether the time- or the strain-dependent term governs the strain-hardening property from a rheological point. The BKZ model, known to be an excellent approximation equation for the uniaxial elongational viscosity of homopolymer melts, is used here to discuss the cause of the elongational property, after confirming the separability of the time- and the strain-dependent terms by experiments. The following are the BKZ equations:

$$\sigma(t) = \int_{-\infty}^t \mu(t-t')h(I,II)C^{-1}(t,t')dt' \quad (1)$$

$$\mu(t-t') = \sum_i \frac{G_i}{\tau_i} \exp\left[-\frac{(t-t')}{\tau_i}\right] \quad (2)$$

$$h(I,II) = \frac{\alpha}{(\alpha-3) + \beta I + (1-\beta)II} \quad (3)$$

$$C^{-1}(t,t') = \begin{bmatrix} \exp[2\dot{\epsilon}(t-t')] & 0 & 0 \\ 0 & \exp[-\dot{\epsilon}(t-t')] & 0 \\ 0 & 0 & \exp[-\dot{\epsilon}(t-t')] \end{bmatrix} \quad (4)$$

where $\mu(t-t')$ is the time-dependent memory function; $h(I,II)$ is the strain-dependent function, i.e., the damping function; and $C^{-1}(t,t')$ is the Finger strain tensor for the uniaxial elongational deformation. The time-dependent function is governed by the relaxation spectrum. The BKZ model teaches that the strain-hardening property is affected by the two terms, the relaxation spectrum and the damping function. Here, the strain-hardening properties of random and block copolymer melts are analyzed and discussed from the two terms.

The separability of the two terms is confirmed by step-shear relaxation experiments.¹⁹ The relaxation spectrum is obtained from the oscillatory shear measurement. The damping function, $h(\gamma)$, is estimated from step-shear stress relaxation experiments.¹⁹ The influence of M_w , MWD, and branched (star, comb) structure on the damping function has been extensively studied.^{8,10,19–31} A review of the damping function was reported by Osaki.³² However, the influence of copolymerized structures on the damping function is not known. Studies on the effect of copolymerized structures on the damping functions are also awaited to understand the effect of copolymerized structures on the strain-hardening property.

EXPERIMENTAL

Poly(ethylene-*random*-ethyl acrylate) (EEA) with ethyl acrylate (EA) contents of 9.0, 19, and 25 wt %, and poly(styrene-*random*-acrylonitrile) (AS) with acrylonitrile (AN) content of 30 wt %, were used. These random copolymers have comb-branched and linear structures, respectively. We used poly(styrene-*block*-ethylenebutylene-*block*-styrene) (SEBS) with ethylenebutylene (EB) contents of 60 and 80 wt %. These block copolymers have linear structures. Polystyrene (PS) was utilized as a reference. Samples of EEA were kindly supplied by Mitsui-DuPont Polychemicals Co., Ltd. Samples of SEBS and PS were kindly provided from Asahi Chemical Industry Co., Ltd. A sample of AS was kindly given by Japan Synthetic Rubber Co., Ltd. The weight- and number-

Table I Characteristics of Samples

Sample	M_n	M_w	M_w/M_n
EEA (EA = 9.0 wt %)	40,000	210,000	5.3
EEA (EA = 19 wt %)	38,000	250,000	6.6
EEA (EA = 25 wt %)	39,000	240,000	6.2
AS (AN = 30 wt %)	85,000	160,000	1.9
PS	110,000	240,000	2.2
SEBS (S/EB wt ratio = 20/80)	47,000	61,000	1.3
SEBS (S/EB wt ratio = 40/60)	47,000	61,000	1.3

averaged molecular weight (M_w and M_n) of polymer samples are listed in Table I. For all samples, three kinds of rheological measurements—elongational viscosity, oscillatory shear, and step-shear stress relaxation—were carried out. Samples of AS, PS, and SEBS were pretreated in a vacuum oven at 80°C for a day to eliminate water before measurement. The vacuum pretreatment was also done for EEA at 60°C for a day before measurement.

We measured the uniaxial elongational viscosity at constant strain rates on our Meissner-type elongational rheometer using rodlike samples. A detailed description and the reliability of our Meissner-type elongational rheometer were given in our previous report.¹ Rodlike samples with diameter of 5 mm and length of 250 to 300 mm were made through slow extrusion on a single-screw extruder. Because some rodlike samples shrank slightly in a heated silicon oil, 10 min of equilibration time was allowed before experiments. The homogeneous elongational deformation and the actual strain rates were checked and calculated with a videotape recorder.

Measurement of oscillatory shear and step-shear stress relaxation experiments were conducted on a rotational rheometer (RDAII, Rheometrics). The test fixtures were parallel disks with diameters of 25 and 8 mm for oscillatory and step-shear experiments, respectively. When we measured linear viscoelastic data, sufficiently small strain was applied.

RESULTS AND DISCUSSION

Elongational Viscosity of Random Copolymers

It is important to clarify the basis of the comparison. In this report, the basis of the comparison is using samples having the same molecular parameter in each group (branched random copolymer,

linear random copolymer, and block copolymer). The effect of comonomer on the strain-hardening property is compared in each group. Finally, the characteristics of strain-hardening property are discussed between random and block copolymers.

Before the elongational measurements, dynamic shear properties of three EEA samples were measured to obtain storage modulus (G') and loss modulus (G'') in the frequency range from 0.01 to 100 rads^{-1} at 140°C. G' and G'' are calculated from the relaxation spectrum from the following equations:

$$G'(\omega) = \sum_i G_i \frac{\omega^2 \tau_i^2}{1 + \omega^2 \tau_i^2} \quad (5)$$

$$G''(\omega) = \sum_i G_i \frac{\omega \tau_i}{1 + \omega^2 \tau_i^2} \quad (6)$$

where G_i is the relaxation modulus and τ_i is the relaxation time. G' and G'' of three EEA samples were found to be approximately similar to one another, suggesting that the relaxation spectrum was almost same among the three EEAs.

First, the elongational viscosities of branched random copolymers were studied. Elongational viscosity was measured in constant strain-rate conditions for three EEA samples at 110 and 140°C. Figure 1 shows the elongational viscosities of three EEA samples as a function of time at 110°C. The elongational viscosities of three EEA samples increased with two steps as a function of time. The first step is gradual viscosity increase in the small strain region, called the linear elongational property; the second is rapid viscosity increase in the large strain region, which is called the strain-hardening property. Gradual viscosity increases in different constant strain-rate conditions fell on a curve for the three EEA samples

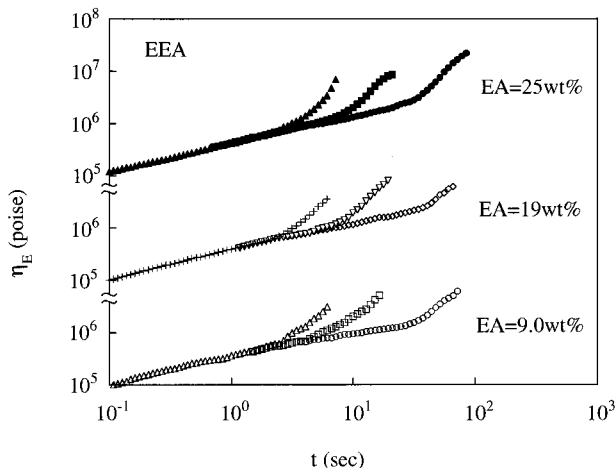


Figure 1 Uniaxial elongational viscosity for EEA melts with EA contents of 9.0, 19, and 25 wt % at 110°C under various constant strain rates (s^{-1}): (Δ) 0.42; (\square) 0.19; (\circ) 0.048; (\times) 0.42; (∇) 0.18; (\diamond) 0.042; (\blacktriangle) 0.39; (\blacksquare) 0.15; (\bullet) 0.042.

and these linear elongational viscosities were almost identical to one another. This result is supported by the fact that dynamic shear properties of the three EEAs were also almost identical to one another.

Next we examined the effect of EA contents on the strain-hardening property of the elongational viscosity. To compare the strain-hardening properties among samples, we used the following strain-hardening parameter (λn), which is the ratio of the nonlinear elongational viscosity ($\eta_{\text{nonlinear}}$) to the linear elongational viscosity (η_{linear}) at the same time^{1,3}:

$$\lambda n = \eta_{\text{nonlinear}} / \eta_{\text{linear}} \quad (7)$$

The strain-hardening parameters of many homopolymers are generally written as

$$\lambda n = \exp(k\gamma^*) \quad (8)$$

where k is a constant showing the intensity of strain-hardening property and γ^* is the effective strain described by

$$\gamma^* = \gamma - \gamma_c \quad \gamma > \gamma_c \quad (9)$$

$$\gamma^* = 0 \quad \gamma < \gamma_c \quad (10)$$

where γ_c is the critical strain at which the strain-hardening property starts to appear. The strain-

hardening parameters were compared at the strain rate of 0.4. Figure 2 shows the strain-hardening parameters of the three EEAs as a function of Hencky strain. The strain-hardening property of EEA does not depend on EA contents from 9.0 to 25 wt %, judging from the slope and the critical strain. In addition, we observed that the strain-hardening parameters of EEAs were hardly affected by strain rates and temperatures. This property is quite similar to low-density polyethylenes (LDPEs).⁵ It is explained by the fact that EEAs have a long chain branched structure, since EEAs, like LDPEs, are polymerized under high pressure conditions. Though EA acts as short branched segments, Figure 2 suggests that the strain-hardening property is governed by long chain branching other than short branched segments. We also confirmed that the strain-hardening properties of poly(ethylene-*random*-vinyl acetate) melts are hardly influenced by vinylacetate contents. These suggest that the strain-hardening property is governed by long chain branching in the case of random copolymer melts.

Second, the elongational viscosities of linear random copolymers were studied. It was difficult to select an AS sample and a PS sample which have the same molecular parameters. To understand the relaxation spectrum difference of the two samples, dynamic shear measurement was carried out for AS at 150°C and for PS at 140°C. G' and G'' curves are slightly different from AS to PS. The longest relaxation time was determined from the point where dynamic shear viscosity was

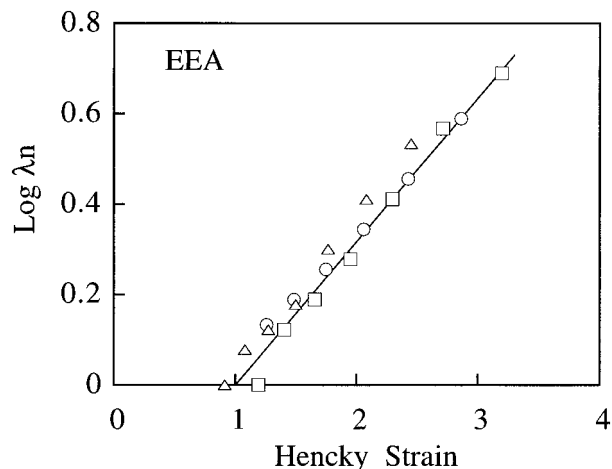


Figure 2 Strain-hardening parameter (λn) as a function of Hencky strain for EEA melts at 110°C around the strain rate of 0.40 (s^{-1}) with various EA contents (wt %): (\circ) 9.0; (\square) 19; (\triangle) 25.

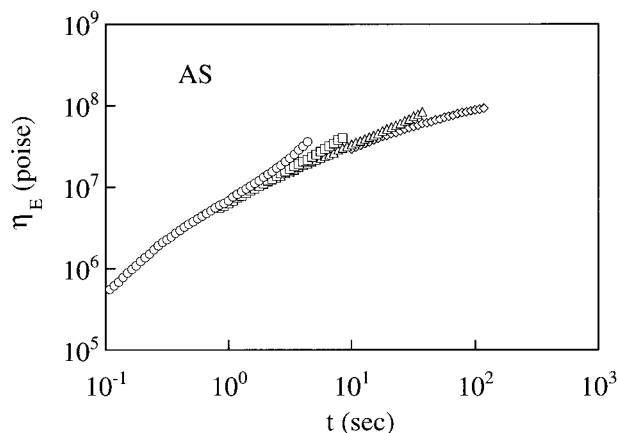


Figure 3 Uniaxial elongational viscosity for AS melt at 150°C under various constant strain rates (s^{-1}): (○) 0.49; (□) 0.18; (△) 0.044; (◇) 0.0037.

decreased from zero shear viscosity. The longest relaxation times of AS at 150°C and PS at 140°C are approximately estimated to be 1,000 and 3,300. The elongational viscosities were measured for AS at 150°C and for PS at 140°C. Figure 3 shows the elongational viscosity of AS, and Figure 4 shows that of PS. Figure 3 suggests that the strain-hardening property of AS was enhanced with larger strain rates, and Figure 4 also suggests that this tendency is observed for PS. These properties are in good agreement with previous studies.^{6,7}

We next compared strain-hardening properties between AS and PS. It is not fair to compare their strain-hardening properties at the same strain rate at the same temperature because AS has a

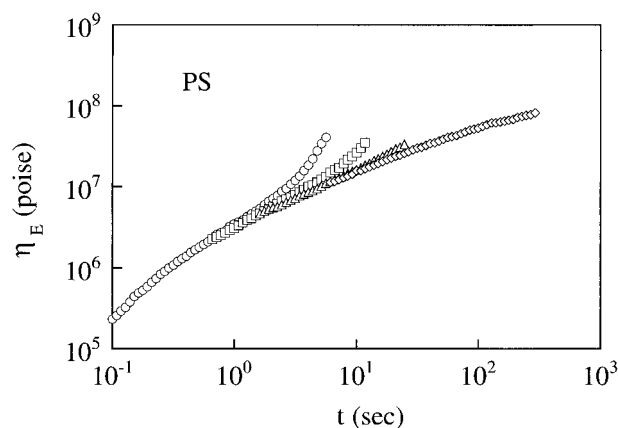


Figure 4 Uniaxial elongational viscosity for PS melt at 140°C under various constant strain rates (s^{-1}): (○) 0.46; (□) 0.16; (△) 0.041; (◇) 0.0043.

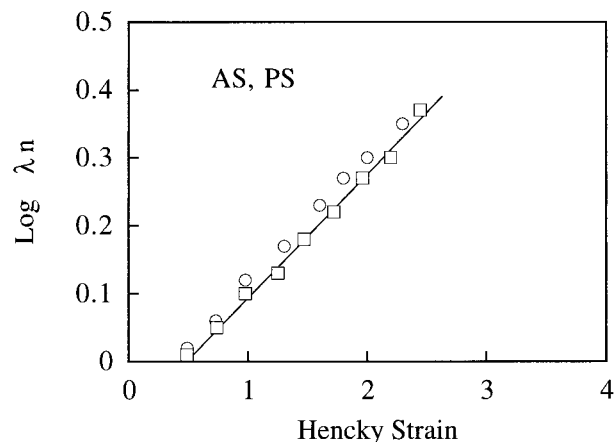


Figure 5 Strain-hardening parameter (λn) as a function of Hencky strain around 500 of the product of a strain rate and the longest relaxation time for (○) PS and (□) AS.

different longest relaxation time than PS. If two polymer samples have different longest relaxation times, the polymer with the longer relaxation time gives a stronger strain-hardening property than the other at the same strain rate. Cancelling the influence of relaxation speed on the strain-hardening property is the basis for studying the influence of comonomer in random copolymers. Takahashi and colleagues proposed that the fair comparison of the strain-hardening property should be carried out at the same value of the product of strain rate and the longest relaxation time to cancel the influence of relaxation speed.¹⁰ According to this method, we compared the strain-hardening property at around 500, which is the product of strain rate and the longest relaxation time. Figure 5 shows the comparison of strain-hardening parameters between AS and PS; it suggests that the strain-hardening property is not changed from AS to PS, if we eliminate the influence of relaxation speed.

Results suggested that strain-hardening properties of random copolymers are hardly influenced by comonomers when we use samples having similar relaxation spectra. Results also showed that the strain-hardening property strongly depends on primary structures (linear or comb-branching). The studied random copolymers have no interaction between polymeric chains, since comonomers are EA and AN. If random copolymers have comonomers, such as methacrylic acid salts, the strain-hardening property is influenced by its contents.^{16,17} Thus, the reason why the strain-hardening property is not

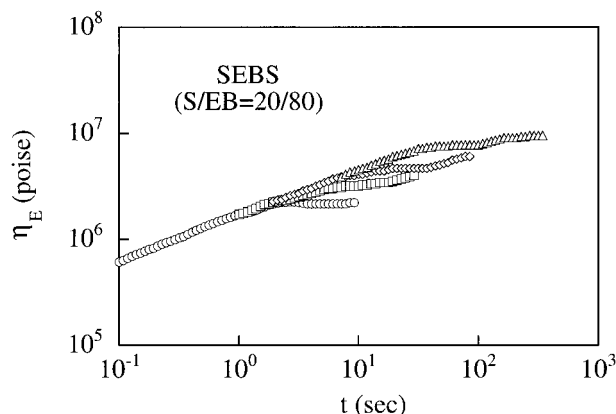


Figure 6 Uniaxial elongational viscosity for SEBS (20/80) at 140°C under various strain rates (s^{-1}): (○) 0.18; (□) 0.040; (◇) 0.013; (△) 0.0030.

influenced by comonomer contents is that comonomers EA and AN have no interaction.

Elongational Viscosity of Block Copolymers

At first we checked the transition temperatures of SEBS block copolymer between one and two phases, as SEBS shows upper critical solution temperature diagram. It is known that the transition temperature is estimated by either rheological or small angle X-ray analysis.³³ Here, the rheological measurement was taken to determine the temperature according to the method of Han and coworkers.³³ We have made two kinds of figures to estimate the transition temperature, dynamic shear viscosity versus frequency, and G'' versus G' . A detailed meaning of G'' as a function G' for block copolymers was described by Han and associates.³³ These figures suggested that transition temperatures of two SEBS samples are above 220°C. Both samples were thermally stable below 220°C by thermogravimetric analysis. All experiments were performed below 220°C, where both samples provided two-phases structures.

Two SEBS samples have identical molecular parameters with different S/EB ratios. The basis of the comparison is using samples having the same molecular parameters. Elongational viscosities of both samples were measured at 140, 160, and 180°C for SEBS (S/EB = 20/80) and at 180, 200, and 220°C for SEBS (40/60). Homogeneous decrease of rod diameter was confirmed for both samples at each condition. As typical examples, Figures 6 and 7 show the elongational viscosity of SEBS (20/80 at 140°C) and that of SEBS (40/60 at 200°C), respectively. Note that both samples ex-

hibit the strain-softening property. This tendency was also observed at other temperatures below 220°C at strain rates from 0.005 to 0.2 s^{-1} . It is remarkable that the block copolymer melts give the strain-softening property. This property is quite opposite to the strain-hardening elongational viscosity of homopolymer melts. The strain-softening parameter seems to be hardly affected by block weight ratio. The block copolymerized structure with two-phase morphology was regarded as the cause of the strain-softening property.

We also evaluated the critical strain. The critical strain for SEBS was around 0.1 for SEBS (20/80) and around 0.2 for SEBS (40/60), which were smaller than those for AS (around 0.5) and EEA (around 1.0). The period, which is from the starting point of the critical strain to the end point, was shorter in SEBS (40/60) than in SEBS (20/80). Data, which came out of constant strain rates just before samples were ruptured, were discarded. The plotted end strain of SEBS (20/80) was around 1.3, while that of SEBS (40/60) was approximately 0.3. The reason for the shorter nonlinear time is that SEBS (40/60) was ruptured in earlier time. This phenomenon was also seen when temperature was raised to 220°C.

Here, the BKZ model^{8,18} is used for further discussion on the influence of random and block copolymerized structures on the strain-hardening and softening property. The BKZ equations [eqs. (1)–(4)] appear in the Introduction section.¹⁶ When we utilized the BKZ model, results of the elongational viscosity confronted us with following questions. In random copolymer samples, the

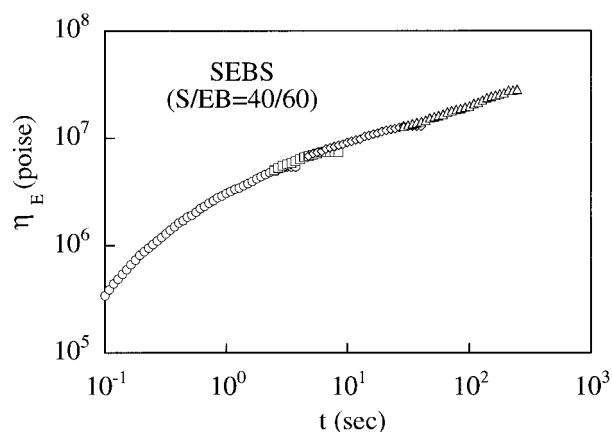


Figure 7 Uniaxial elongational viscosity for SEBS (40/60) at 200°C under various strain rates (s^{-1}): (○) 0.080; (□) 0.034; (◇) 0.013; (△) 0.0029.

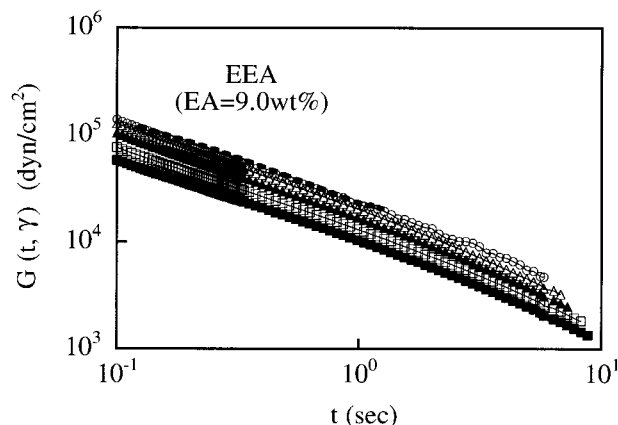


Figure 8 Stress relaxation modulus for EEA with 9.0 wt % of EA at 140°C under different step-shear strains: (○) 0.1; (△) 1.0; (▲) 2.0; (□) 3.5; (■) 5.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

strain-hardening property was hardly affected by comonomer contents. Do comonomer contents have no influence on the damping function? How about the effect of block structure on the damping function? Why does the critical strain differ from random to block copolymers? We have already discussed the relaxation spectrum, which is one of two parameters in the BKZ model, from G' and G'' . The studies on the damping function should give us further information. To answer these questions, we investigated the influence of random and block copolymerized structures on the damping function.

Stress Relaxation Modulus

It is important to check the separability of time and strain terms for random and block copolymers by experiments of step-shear stress relaxation. The separability means that stress relaxation modulus, $G(t, \gamma)$, under various step-strains is simplified by factoring it into the linear stress relaxation modulus, $G^o(t)$, and damping function, $h(\gamma)$.

$$G(t, \gamma) = G^o(t)h(\gamma) \quad (11)$$

This separability has been supported by both the Doi-Edwards theory³⁴ and experiments for homopolymer melts.^{8,10,19-31} Step-shear stress relaxation was measured, since former damping function studies were mainly done under step-shear deformation and it was difficult to apply

step-elongational deformation. The separability was examined for random and block copolymers with the method of Soskey and Winter,¹⁹ and it was applicable for all samples. When strain γ was smaller than 7, the edges of samples between parallel disks were not protruded. Step-shear deformation was applied both counterclockwise and clockwise. The obtained modulus was not influenced by either counterclockwise or clockwise. Consistency was not affected by whether samples were predeformed or fresh, if substantial waiting time between experiments was allowed. It required 0.1 to reach the stationary strain; data after 0.1 s are shown in each figure. Since parallel disks were used, obtained relaxation modulus was corrected with the equation proposed by Soskey and Winter.¹⁹ Applicability of this correction has already been demonstrated with former experiments.^{30,31} Each figure shows corrected relaxation modulus. To confirm linear relaxation modulus $G^o(t)$, we also present linear relaxation modulus predicted from G' and G'' . An approximate equation proposed by Schwarzl was used for the prediction.³⁵

Figures 8, 9, and 10 show stress relaxation modulus of EEA with different EA contents. Each predicted linear relaxation modulus was very close to experimental relaxation modulus at the smallest strain. Since G' and G'' of the three EEAs resemble one another in the EA content range from 9.0 to 25 wt %, it is safe to assume that linear relaxation moduli are also similar in the three EEAs. In addition, relaxation modulus at various strains was hardly affected by tested EA contents. The shape of

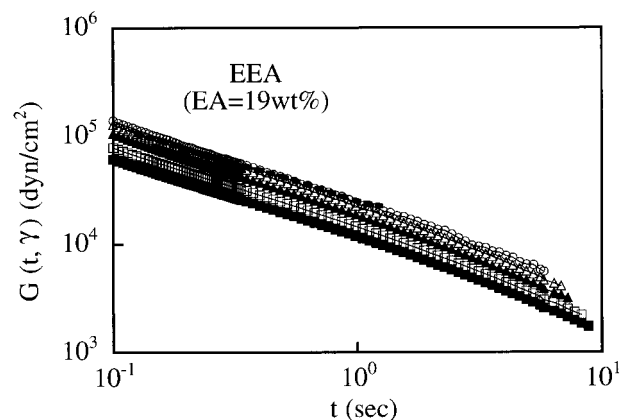


Figure 9 Stress relaxation modulus for EEA with 19 wt % of EA at 140°C under different step-shear strains: (○) 0.1; (△) 1.0; (▲) 2.0; (□) 3.5; (■) 5.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

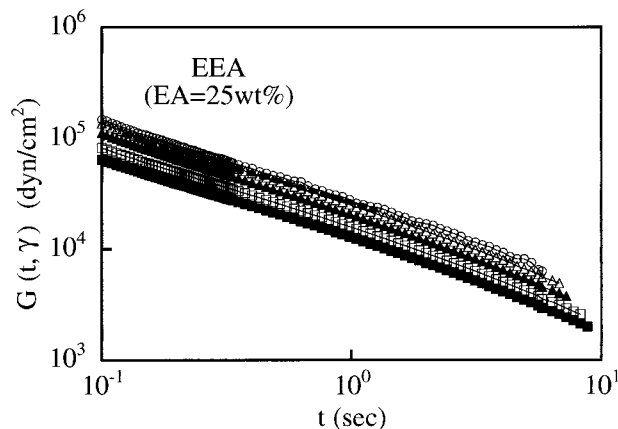


Figure 10 Stress relaxation modulus for EEA with 25 wt % of EA at 140°C under different step-shear strains: (○) 0.1; (△) 1.0; (▲) 2.0; (□) 3.5; (■) 5.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

relaxation modulus for EEA samples was quite similar to that of LDPE. Figures 11 and 12 show stress relaxation properties of AS and PS. Each predicted linear relaxation modulus was very close to experimental relaxation modulus at strain of 0.1. The shape of relaxation modulus for the AS sample is quite similar to that of linear polymer with relatively wide MWD. Stress relaxation modulus was measured for SEBS block copolymers at temperatures where slip between a sample and parallel disks does not occur. Figures 13 and 14 show stress relaxation properties of SEBS with different weight ratios. Each predicted linear relaxation modulus

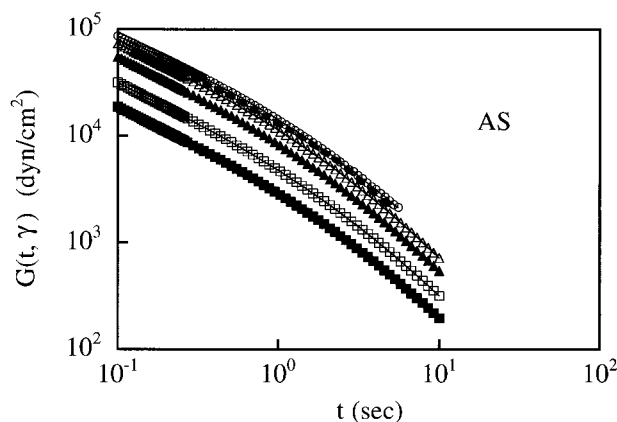


Figure 11 Stress relaxation modulus for AS at 185°C under different step-shear strains: (○) 0.1; (△) 1.0; (▲) 2.0; (□) 3.5; (■) 5.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

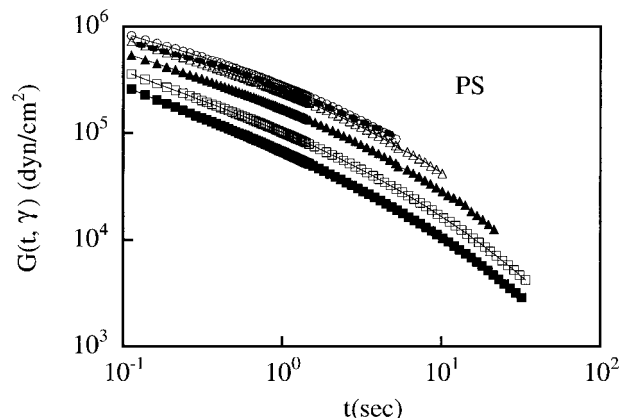


Figure 12 Stress relaxation modulus for PS at 160°C under different step-shear strains: (○) 0.1; (△) 1.0; (▲) 2.0; (□) 3.5; (■) 5.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

was close to experimental relaxation modulus at strain of 0.1.

Damping Functions

The damping functions were calculated based on the experimental relaxation modulus. Figure 15 illustrates the damping functions of all samples. Figure 15 confirms that damping functions of EEAs are not affected by EA contents in the range from 9.0 to 25 wt %, and that they are very close to that of LDPE. This is explained by the idea that EEA also has a comb-branched structure, like LDPE, and that short branching segments of EA

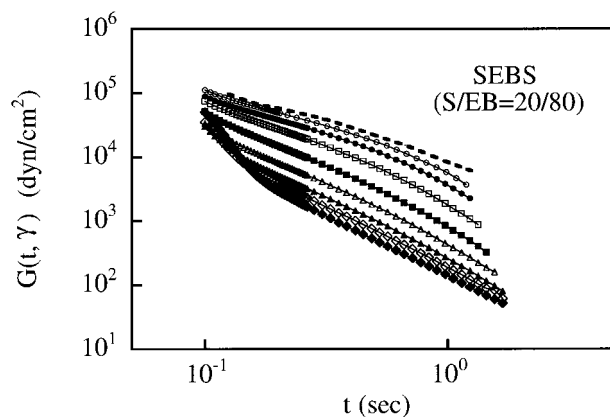


Figure 13 Stress relaxation modulus for SEBS (20/80) at 180°C under different step-shear strains: (○) 0.1; (●) 0.2; (□) 0.5; (■) 1.0; (△) 2.0; (▲) 3.5; (◇) 5.0; (◆) 7.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

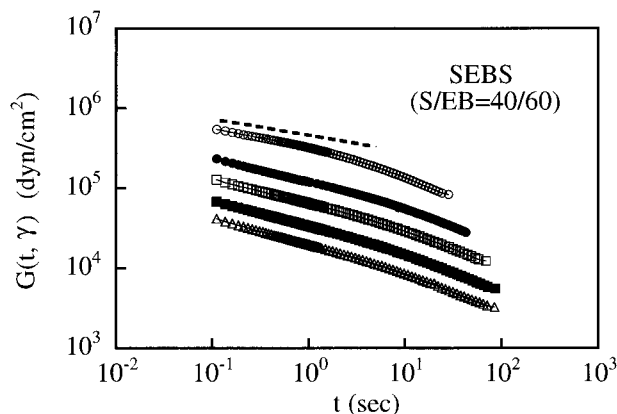


Figure 14 Stress relaxation modulus for SEBS (40/60) at 160°C under different step-shear strains: (○) 0.1; (●) 1.0; (□) 2.0; (■) 3.5; (△) 5.0. The dotted line is the linear relaxation modulus calculated from the equation proposed by Schwarzl.³⁵

hardly affect damping functions. Weaker damping functions of EEAs than Doi–Edwards prediction are explained by the same reason as that for LDPE, which was proposed by Larson.²³ The reason is that the strand of EEA is partially extended in step-shear deformation.

The relaxation spectra of the three EEAs are almost identical, and the damping functions of three EEAs are also similar to one another. Thus, the same strain-hardening property among the three EEAs was interpreted by almost the same relaxation spectrum with the same damping functions as the BKZ model.

Figure 15 also shows that the damping function of AS is very similar to that of PS, and both are close to that of Doi–Edwards prediction. It was confirmed that damping function of AS, like PS, is not influenced by temperature. The same strain-hardening property of AS and PS, when eliminating the influence of the relaxation speed, was interpreted by the same damping function of AS and PS. Figure 15 also suggests that the strain region which shows linear viscoelasticity is wider for EEA than for AS. This caused a smaller critical strain value in AS than that of EEA in the elongational viscosity.

Figure 15 reveals that SEBSs have stronger damping than do linear homopolymers. The damping function of SEBS (20/80) was stronger than that of SEBS (40/60). For SEBS (20/80), the damping function $h(\gamma)$ can be described as $1/\gamma$ above γ of 0.1, suggesting that stress stays constant above γ of 0.1. Strong damping functions of SEBS samples caused the strain-softening prop-

erty from the BKZ model, explained by the fact that strong damping functions make elastic modules smaller in large strain than do weak damping functions. There exists a critical damping function between the strain-hardening and -softening properties. The critical damping function is the function which is close to Doi–Edwards prediction. Earlier starting strains of damping for SEBS seem to be related to the small critical strain of SEBS in the elongational viscosity.

Next, we discuss strong damping functions from molecular dynamics. Meier interpreted melt-shear viscosity of SBS block polymer as a function of strain rates compared with homopolymer using the energy dissipation process.³⁶ He explained the viscosity under large strain rates with homogenization which occurs with the pulling out of S blocks from the original domain and their moving to another S domain. Watanabe and colleagues³⁷ also used the similar mechanism for plastic behavior of SBS solution assuming “bridged” structure of SBS. Even for the molten SEBS, this explanation should be applicable. SEBS chains are considered to be highly extended even before deformation because both ends form S domains, compared with linear homopolymers. Under large step-deformation, these S blocks should be easily pulled out of the S domain. These S blocks have no compatibility with B matrix, resulting in pulled S blocks going to S domains. Because these S blocks do not return to the orig-

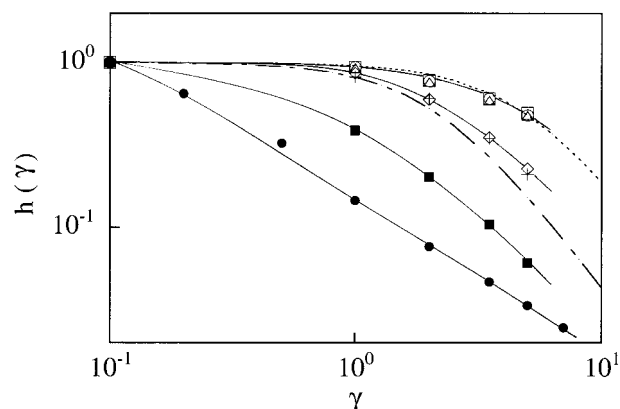


Figure 15 Damping functions, $h(\gamma)$, from step-shear stress relaxation modulus for various copolymers: (○) EEA (EA = 9.0 wt %); (□) EEA (EA = 19 wt %); (△) EEA (EA = 25 wt %); (+) AS; (◇) PS; (●) SEBS (20/80); (■) SEBS (40/60). The dotted line represents the damping function of LDPE from Soskey and Winter.¹⁹ The broken line represents the predicted damping function from Doi–Edwards theory.³⁴

inal S domain, the system loses elastic effect. This mechanism is regarded as the cause of stronger damping than Doi–Edwards prediction. Shorter S blocks ($S/EB = 20/80$) should be more easily pulled from S domains than longer S blocks ($S/EB = 40/60$), causing stronger damping.

CONCLUSION

The present study of the elongational viscosities of random and block copolymer melts has provided some new findings.

1. Random copolymers showed strain-hardening elongational viscosities. The strain-hardening property was little influenced by comonomer contents and depended on whether copolymers have linear or branched structures. To the contrary, block copolymers exhibited strain-softening elongational viscosities. The strain-softening properties were not affected by strain rates or block comonomer ratios.
2. The strain-hardening or -softening elongational viscosities were interpreted from relaxation spectrum and damping function using the BKZ model. It is worthy of note that the damping functions of linear and branched random copolymers are similar to those of linear and branched homopolymers, respectively. On the other hand, linear block copolymers exhibited stronger damping than did linear homopolymers, resulting in the strain-softening elongational viscosities. The smaller critical strains of elongational viscosities for block copolymers than those for random copolymers were explained by early starting strains for damping in $h(\gamma)$.

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