

Nonlinear Stress Properties of Poly(styrene-*block*-butadiene-*block*-styrene) Melt Under Elongational and Shear Deformation

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SYNOPSIS

Effects of block copolymerized structure on nonlinear stress properties under elongational and shear deformation were investigated. Samples used in this study were poly(styrene-*block*-butadiene-*block*-styrene) (SBS, weight rate of S/B = 40/60) and polystyrene (PS) as a reference. Tensile stress-strain and shear stress relaxation properties were measured at the molten state. SBS showed high elasticity after reaching the yield point under elongational deformation at room temperature. PS melt showed substantial tensile stress increase after the yield point as strain rates increased. However, SBS melt did not exhibit noticeable tensile stress rise at higher elongation, and this property was almost independent of strain rates. Stress relaxation experiments revealed that the damping function of SBS melt was more strain-softening than that of PS melt. The results suggested that the block copolymerized structure decreases melt elasticity under elongational and shear deformation. A transmission electron micrograph indicated that the lack of melt elasticity in SBS melt is caused by orientation of the lamellar structure toward the stretched direction during deformation. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Elastomeric properties of A-B-A-type block copolymers in the solid state have been investigated through tensile stress-strain properties.¹⁻⁶ A-B-A-type block copolymers exhibit high elasticity after plastic-to-rubber transition in stress-strain curves between the glass transition temperatures of A and B. Tensile stress-strain properties of A-B-A-type block copolymers show substantial stress increase at highly elongated conditions, when the strain exceeds the yield point. This property is almost independent of microdomain structures, such as spherical, cylindrical, and lamellar. Hashimoto et al.³ reported the origin of the high-elasticity phenomenon of poly(styrene-*block*-butadiene-*block*-styrene) (SBS) using a transmission electron micrograph and small-angle X-ray scattering (SAX).

The plastic-to-rubber transition in the stress-strain curve is a result of the structural change from alternating lamellar domains to fragmented polystyrene (PS) domains dispersed in polybutadiene (PB) matrix. Since SBS block copolymers are used as thermoplastic elastomers between the glass transition temperatures of two block segments, the tensile stress-strain properties of SBS block copolymers above the glass transition temperatures of both components have not been well-studied.

The tensile stress-strain properties of polymers at the molten state have been studied in terms of uniaxial elongational rheology of polymer melts. The elongational rheology gives basic data for the processability of polymer melts in blow molding, film molding, and melt spinning. The elongational rheology also provides the degree of melt elasticity. A number of experimental studies⁷⁻¹¹ on the uniaxial elongational rheology of polymer melts have been taken to clarify effects of molecular parameters, such as molecular weight distribution (MWD) and long chain branching. Elongational stress as a function

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of strain grows with two steps. The first step is the rapid stress growth. The second step is the noticeable stress rise after the yield point. The degree of stress rise in the second step is enhanced by wide MWD and long chain branching.^{8,11} However, few studies on effects of block copolymerized structure on the elongational rheology are published to date.

On the other hand, a strain-dependent function $h(\gamma)$, which is determined from stress relaxation experiments in step shear deformation, also describes the degree of melt elasticity. Extensive studies^{11–19} on the strain-dependent function have been done for homogeneous polymer melts and solutions, such as PS, polyethylene (HDPE, LDPE, LLDPE), and polydimethylsiloxane. Former studies revealed that polymers with long chain branching cause higher elasticity than linear polymers. Melt rheology of block copolymers under steady and dynamic shear flow has been well documented.^{20–25} However, effects of block copolymerized structure on the melt elasticity determined from the strain-dependent function have been unknown.

Here, we report effects of block copolymerized structure on nonlinear stress properties above glass transition temperatures of two block components. We compare the tensile stress–strain properties of SBS at the molten state with those at room temperature. We also discuss the difference of melt elasticity between SBS and PS under elongational and shear deformation.

EXPERIMENTAL

Poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymer (SBS, $M_n = 60,000$, $M_w = 80,000$, weight ratio $S/B = 40/60$) was used. We also used polystyrene (PS, $M_n = 110,000$, $M_w = 240,000$) as a reference. These samples were kindly supplied by Asahi Chemical Industry Co., Ltd. Rod-like samples were prepared through slow extrusion using a single-screw extruder. The diameter and the length were about 5 mm and 10 cm, respectively. Autograph (Shimadzu Seisaku-Sho Ltd.) was used to measure tensile stress–strain curves of rod-like samples, which were clamped between a pair of chucks set 50 mm apart, at 23°C. The stretching speed was 10 mm min⁻¹.

We used a Meissner elongational rheometer (Melten Rheometer, Toyo Seiki Seisaku-Sho Ltd.) to measure elongational stress as a function of strain at various constant strain rates. The rod-like samples with 5 mm of diameter and 10 cm of length were used for experiments. We use the Cauchy strain and

the Hencky strain rate in this paper, which are defined in eqs. (1) and (2):

$$\gamma = l/l_0 - 1 \quad (1)$$

$$\dot{\gamma} = dl/dt \quad (2)$$

where l_0 and l are initial and instantaneous length of rod-like samples, respectively. The reliability of the apparatus was described in the previous paper.⁹ A rod-like sample was immersed in a silicone oil bath heated to 140°C. Since samples were slightly shrunk by heating, 10 min of equilibrium time was allowed before experiments. The molten samples were stretched at constant strain rates by rotating a pair of gears. The homogeneity of elongational deformation was checked with a video camera. The actual strain rate was calculated from the decrease of rod diameter. The range of setting strain rate was from 0.005 to 0.5 sec⁻¹.

Experiments for oscillatory and stress relaxation in step–shear deformation were conducted using a rotational rheometer (Rheometrics RDA [II]). The geometries of test fixtures are parallel disks with a diameter of 8 mm. The measured angular frequency for oscillatory shear experiments is in the range from 0.1 to 100 (rad/sec).

Transmission electron microscopy (TEM) was used to observe the microdomain structure of samples before and after elongation at the centered cross-section which is parallel to the stretching direction. Samples were cryo-ultramicrotomed with a diamond knife to a thickness of 90 nm. The PB sections were selectively stained with OsO₄ vapor. Images were obtained using a JEOL 2000FX at 120 kV.

RESULTS AND DISCUSSION

A tensile stress–strain curve of SBS at 23°C is shown in Figure 1. The stress is the elongational force divided by the averaged cross-sectional area of the stretched rod-like sample. Rapid stress increase was observed within 0.08 of strain. After applied strain exceeded the yield point, necking suddenly appeared at a localized region and spread throughout the whole specimen. Further stretching caused substantial stress increase. These properties were very similar to those of the former studies.^{2,3} Elastic property comes from minimizing the free energy of boundary activated with fragmented PS, which are connected with bridge-like structures of SBS in PB matrix.^{2,3}

Figure 2 represents the tensile stress–strain properties of SBS block copolymer at 140°C under

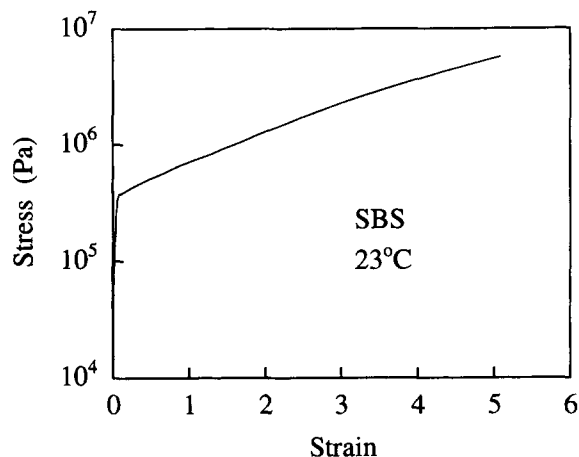


Figure 1 The tensile stress-strain property of SBS at 23°C.

various constant strain rates. The stress in Figure 2 is the elongational force divided by the actual cross section of the stretched rod-like sample. Homogeneous decrease of diameter along the rod-like samples was seen during measurement. The results of homogeneous decrease of diameter just before breakage of the samples were discarded. SBS melts showed the yield point at the strain of 0.5. After SBS melt was stretched beyond the yield point, no necking phenomenon was seen, and SBS melt did not exhibit substantial stress increase. This is quite different from the tensile stress-strain properties of SBS at room temperature. Lack of elastic characteristics of SBS at 140°C was observed in various elongational strain rates. The phenomenon that the yield stress was enhanced at higher strain rates suggests viscous characteristics of SBS melt. The strain reaching the yield point was about the strain of 0.5, and it was hardly affected by strain rates. We confirmed that the similar properties of SBS melt are observed in the temperature range from 120°C to 200°C.

We studied the origin of lack of high elasticity in SBS melt from three points of view. First is the comparison of tensile stress-strain properties between SBS melt and PS melt. Second is the order-disorder transition temperature of SBS melt. Third is the microdomain structural change during deformation.

Figure 3 shows that PS melt exhibits stress increase with two steps as a function of strain. The first region is rapid stress increase, and the second is noticeable stress increase after the yield point. The degree of stress rise in the second region became larger when strain rates increased. Takahashi et al.¹¹ reported that the strain rate where the degree of

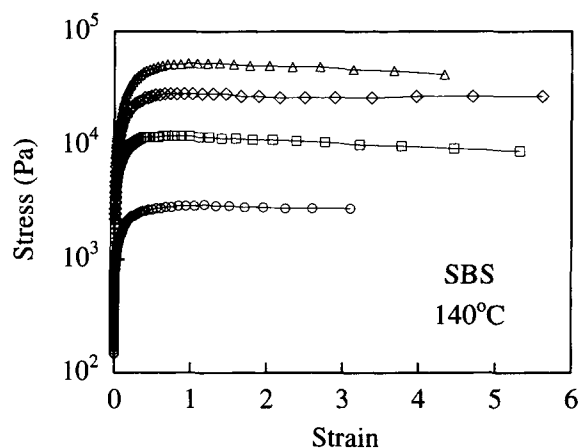


Figure 2 The tensile stress-strain property of SBS at 140°C in various strain rate conditions (sec^{-1}): (Δ) 0.351; (\diamond) 0.136; (\square) 0.0328; (\circ) 0.00373.

stress rise becomes large in the second region corresponds to the contraction rate of the polymeric chain. The tendency that the stress increase in the second region becomes larger at higher strain rate is consistent with former studies.^{8,11} Figure 3 reconfirms that linear polymers with homogeneous phase structures having relatively narrow MWD exhibit larger degrees of stress increase in the second region as strain rates increase. By contrast, the plateau stress in SBS melt after the yield point is observed in the strain rate range from 0.004 to 0.4 sec^{-1} . Thus, no rapid increase of SBS melt after the yield point seems to be associated with block copolymerized structure.

We examined whether SBS melt at tested temperatures shows the ordered or disordered molten

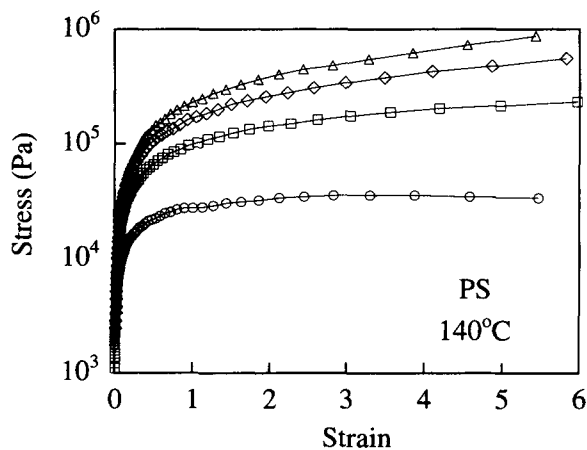


Figure 3 The tensile stress-strain property of PS at 140°C in various strain rate conditions (sec^{-1}): (Δ) 0.460; (\diamond) 0.163; (\square) 0.0407; (\circ) 0.00425.

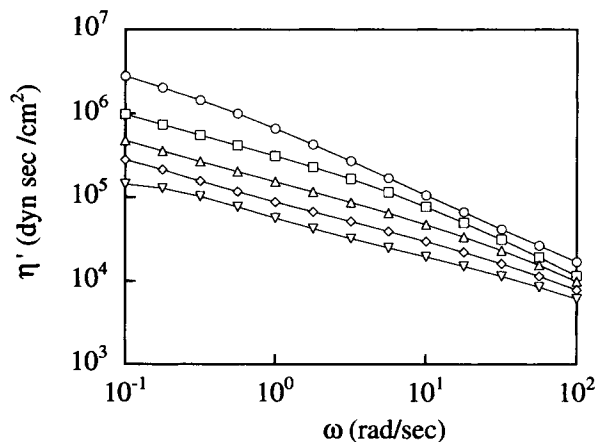


Figure 4 Dynamic viscosity of SBS as a function of angular frequency at various temperatures ($^{\circ}\text{C}$): (○) 120; (□) 140; (△) 160; (◇) 180; (▽) 200.

state. The temperature at which two phases of A-B-A-type block copolymer melts change to one phase of the copolymer melts is called the order-disorder transition temperature. There are basically two different methods, SAX²⁶ and a rheological method,²⁰⁻²⁴ to determine the order-disorder tran-

sition temperature. We used the rheological method, and dynamic viscosity is plotted as a function of angular frequency in Figure 4. Newtonian region was not observed below 200 $^{\circ}\text{C}$. Since effects of cross-linking and degradation of SBS appeared above 200 $^{\circ}\text{C}$ from differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), results above 200 $^{\circ}\text{C}$ are not discussed here. Nonexistence of the Newtonian region has been regarded as the presence of ordered microdomain structure of block copolymer melts from SAX study. Thus, Figure 3 suggests that the order-disorder transition temperature of SBS melt is higher than 200 $^{\circ}\text{C}$. The initial state of SBS melt in tensile stress-strain tests at 140 $^{\circ}\text{C}$ was found to be the ordered state.

In heterogeneous polymer systems, change of microdomain structure is important for melt rheology. We rapidly cooled samples in dry ice/ethanol solution, immediately after the strain reached 10 at the strain rate of 0.2 sec^{-1} . Figure 5 represents the microdomain structural difference between before (Fig. 5[a]) and after (Fig. 5[b]) tensile tests. Figure 5 suggests that lamellar structure is oriented toward the elongational direction after tensile tests. This microdomain structure of SBS melt after measurement

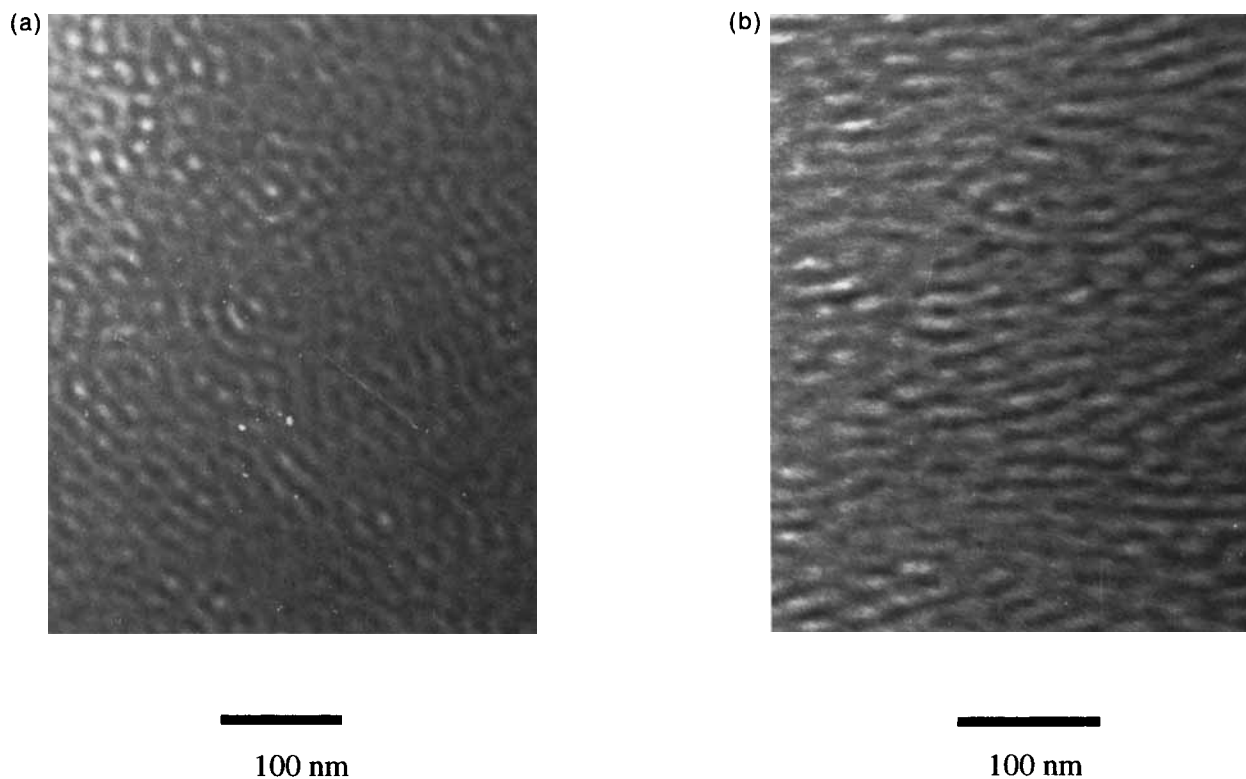


Figure 5 Transmission electron micrographs in the centered cross sections which are parallel to the stretched direction (horizontal direction in micrographs) before elongation (a) and after the strain reached 10 at the constant strain rate of 0.2 sec^{-1} (b).

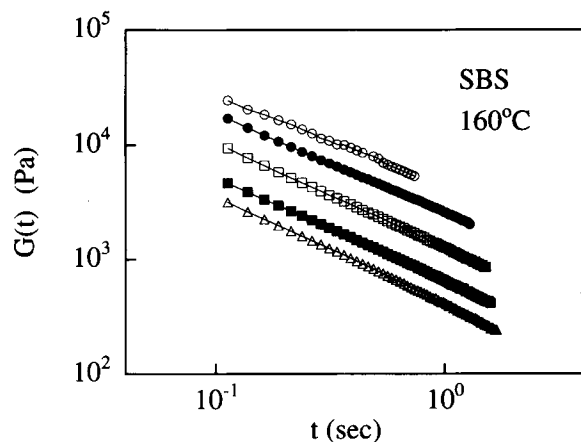


Figure 6 Stress relaxation modulus for SBS at 160°C in various step strains: (○) 0.1; (●) 1.0; (□) 2.0; (■) 3.5; (△) 5.0.

is distinguished from the SBS structure which exhibited fragmented PS domains in PB matrix after the elongation at room temperature. Hashimoto et al.³ reported that enormous increase of interfacial regions in the fragmented system caused high elasticity. In the molten SBS system, the amount of interfacial regions seems to be almost similar between the “before” and “after” elongation in Figure 5(a) and 5(b), respectively. On the other hand, weight-averaged molecular weight of PS in one part is 16,000, which is slightly smaller than M_e (entanglement molecular weight)^{27,28} of PS. Structural domain change during deformation easily occurs in PS phase, which has almost no entanglement points. Thus, TEM observation suggests that microdomain orientation toward the stretched direction, combined with keeping a similar interfacial region, results in the lack of high elasticity. It is interesting to note that rapidly cooled samples after tensile tests kept their length at room temperature for a month. This fact also supports the theory that oriented microdomain structure has no healing effect and that it lacks elasticity, since the free energy of boundary is not activated and stays constant. This contrasts with the phenomenon that the fragmented PS system formed by large elongational deformation at room temperature shows large recovery.^{2,3}

One question occurs in connection with the above interpretation, and that is whether or not the ordered microdomain structure of SBS melt is kept during elongation. The decrease of the order-disorder transition temperature induced by higher strain rate was reported.²⁹ The possibility of disordering induced by higher strain rates should be discussed. If higher strain rates induced complete dis-

ordered structure, stress-strain property should be influenced by elongational rates, and the behavior of SBS melt at higher strain rate should be similar to that of PS melt. However, no signs of high elasticity in SBS melt at higher strain rates were observed in the temperature range from 120°C to 200°C. Thus, it seems that the ordered microdomain structure presents even under large elongational deformation.

We examined whether the lack of melt elasticity of SBS is observed under shear deformation as well as elongational deformation. We performed stress relaxation experiments in step-shear deformation to characterize the effect of block copolymerized structure. When the strain γ was smaller than 5, the edge of the sample between parallel disks did not protrude. The displacement of the disk reached setting strain within 0.1 s. Since we used parallel disks, we corrected the stress relaxation modulus under heterogeneous strain with eq. (3), proposed by Soskey and Winter.¹⁶

$$G(t, \gamma) = G_a(t, \gamma)(1 + \partial \ln G_a(t, \gamma) / 4\partial \ln \gamma) \quad (3)$$

Applicability of this correction has been demonstrated in earlier experiments.¹⁶⁻¹⁸ Figures 6 and 7 show corrected results for SBS and PS, respectively. Storage modulus G' did not depend on a strain smaller than 0.5 for two samples. We regarded stress relaxation at $\gamma = 0.1$ as a linear relaxation modulus $G^\circ(t)$.

Experiments¹¹⁻¹⁹ on a variety of polymer liquids revealed that a shear relaxation modulus $G(t, \gamma)$ is factorized into a linear relaxation modulus $G^\circ(t)$ and a strain dependency function, i.e. a damping function

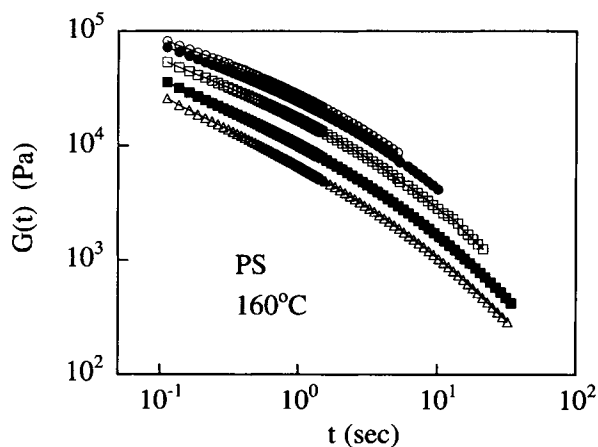


Figure 7 Stress relaxation modulus for PS at 160°C in various step strains: (○) 0.1; (●) 1.0; (□) 2.0; (■) 3.5; (△) 5.0.

$h(\gamma)$, in long time region. The Doi-Edwards theory³⁰ also supports the factored form (4).

$$G(t, \gamma) = G^{\circ}(t)h(\gamma) \quad (4)$$

Factorability was examined with the method of Soskey and Winter.¹⁶ Though eq. (4) was theoretically adapted to polymers with a homogeneous phase, it was applicable to not only PS but also SBS. The damping function $h(\gamma)$ was plotted as a function of strain γ for PS and SBS in Figure 8. The $h(\gamma)$ of PS shows slightly smaller dependence than that from the Doi-Edwards prediction. Takahashi et al.¹¹ reported that $h(\gamma)$ of PS with polydispersity of 1.2 fell very close to the curve from the Doi-Edwards prediction. Hence, slightly smaller dependence of PS melt than the prediction was regarded as the result of polydispersity.

On the other hand, Figure 8 shows that the damping function of SBS melt is more strain-softening than that of PS melts. Since SBS has a polydispersity of 1.3, the polydispersity does not make the damping function more strain-softening. Figure 8 allows us to interpret that the block copolymerized structure at the molten state shows less elasticity than PS under shear deformation. If one may assume complete disordered structure induced by step-shear deformation, $h(\gamma)$ should be similar to the Doi-Edwards prediction in Figure 8. If the assumption is true, the effect of the complete disordered structure induced should also appear in the shape of stress-relaxation modulus at high strain conditions. However, the large strain-softening property and the similar shape of stress relaxation in the strain range from 0.1 to 5 do not support the above assumption. Thus, the results of step-shear experiments also indicate that lamellar domains are oriented with keeping the ordered structure and similar boundary area during step-shear deformation.

Let us describe the strain-dependent function of tested samples with an approximation function. A good approximation function to fit the strain dependent function $h(\gamma)$ is eq. (5).^{13,14}

$$h(\gamma) = 1/(1 + a\gamma^2) \quad (5)$$

According to the Doi-Edwards theory, the parameter a is approximately 0.222. Figure 8 shows that the equation can fit the damping functions of PS and SBS. The parameters a for PS and SBS are 0.14 and 0.42, respectively. The fitted parameter for SBS confirmed that the block copolymerized structure makes the damping function more strain-softening.

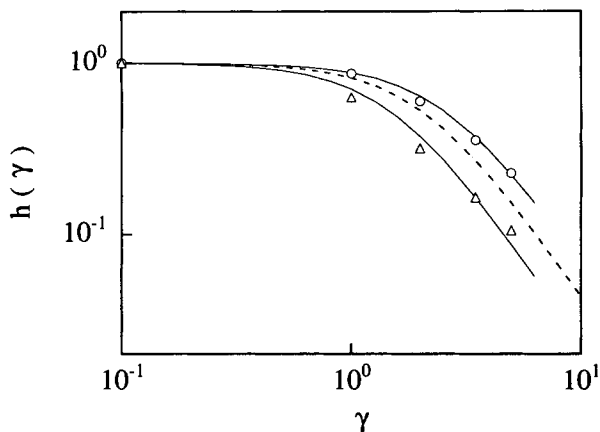


Figure 8 Damping functions for PS (○) and SBS (△). The solid curves are obtained from eq. (5) using the parameter “ a ” of 0.14 and 0.42 for PS and SBS, respectively. The broken curve represents the prediction from Doi-Edwards theory.

CONCLUSIONS

Our study of SBS melt provides the following new findings:

- (1) The effect of block copolymerized structure on nonlinear properties under elongational deformation was investigated. SBS showed high elasticity after reaching the yield point under elongational deformation at room temperature. PS melt gave substantial tensile stress increase after the yield point as strain rates increased. However, SBS melt did not exhibit noticeable stress rise at higher elongation, and this property was almost independent of strain rates and temperatures.
- (2) Stress relaxation of SBS melt in step-shear deformation was studied. The damping function of SBS melt was more strain-softening than that of PS melt. The results suggested that the block copolymerized structure in the ordered molten state decreases melt elasticity under shear deformation. TEM indicated that the lack of melt elasticity in SBS is caused by the orientation of the lamellar structure toward the stretched direction during deformation.

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