Stress Relaxation Behavior of Bidisperse Polystyrenes in Shear and Biaxial Extension

Takeharu ISAKI^{*†}, Masaaki TAKAHASHI^{**}, and Tomohiro DEGUCHI^{***}^{*}Mitsui Chemicals, Material Science Laboratory,
580-32, Nagaura, Sodegaura-City, Chiba 299-0265, Japan^{**}Department of Polymer Science and Engineering, Kyoto Institute of Technology,
Matsugasaki, Sakyo-Ku, Kyoto 606-8585, Japan^{***}Shimane Institute for Industrial Technology,
1, Hokuryou-cho, Matsumae-City, Shimane 690-0816, Japan

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Two bidisperse PS samples B1 and B2 (blend of monodisperse polystyrenes) are employed to investigate the effects of bimodal molecular weight distribution on damping behavior of stress relaxation in shear and biaxial extension. The order of characteristic relaxation times, reptation time τ_d and contraction time τ_s of each component, for B1 is ($\tau_{s,1} < \tau_{s,2} < \tau_{d,1} < \tau_{d,2}$) and that for B2 is ($\tau_{s,1} < \tau_{d,1} < \tau_{s,2} < \tau_{d,2}$), where suffixes 1 and 2 denote lower and higher molecular weight component respectively. Time dependent damping functions in shear $h(t, \gamma)$ and in biaxial extension $h_B(t, \epsilon_B)$ are employed to confirm the time-strain separability for bidisperse polymer systems. Time dependent damping functions of B1 are almost constant, but B2 vary with time in both shear and biaxial extension. To investigate effects of reptative constraint release (RCR) via double reptation scheme and convective constrain release (CCR) in shear and biaxial stress relaxation for bidisperse polymer systems, we use multi-mode extension of the Ianniruberuto and Marrucci (IM) model and the Mead-Larson-Doi (MLD) model. The model predictions of $h(t, \gamma)$ and $h_B(t, \epsilon_B)$ well describe experimental tendency. Time dependent damping functions become independent of time after contraction of long chain and the multi mode model prediction seems almost the same strain dependence. Effect of CCR is very important to describe damping behavior for bidisperse polymer systems.

Key Words: Bidisperse PS / Stress relaxation in biaxial extension / Time dependent damping function / CCR / Constitutive equations

1. INTRODUCTION

Molecular weight distribution (MWD) strongly affects shear and extensional flow behavior of polymer melts and the processability in various polymer processing operations. Many studies have been performed on the relationship between MWD and rheological properties of dynamic viscoelastic functions, relaxation spectrum, zero shear viscosity, steady state compliance and so on.¹⁾ Some theoretical blend rules were proposed^{2,3)} to describe the effect of MWD on linear viscoelastic properties. The effect of MWD on shear damping function in entangled polymer systems is reviewed and clarified by Osaki.⁴⁾ Polymer systems with broad MWD show somewhat weaker strain dependence of shear damping function.

Interesting experimental data are obtained by Mnstedt⁵⁾ concerning the effect of MWD on uniaxial extensional flow

behavior. A blend of lower molecular weight matrix and a substantially high molecular weight component shows very strong strain hardening behavior in uniaxial extension. The prominent effect of high molecular weight component on uniaxial extensional flow behavior has also been studied using blend samples with a small amount of ultra high molecular weight component to control the bimodal distribution.^{6,7)} The effect of MWD on biaxial extensional flow behavior was investigated by Takahashi et al.⁸⁾ Shear, uniaxial and biaxial damping functions of narrow- and broad-MWD polystyrene melts were reported.⁹⁾ However, two important unsolved problems still remain on the effects of MWD:

- (1) The effects of bimodal MWD on the shear and biaxial damping functions are not known.
- (2) No theoretical explanation is given for the effects of MWD on the damping functions.

In this study, two bidisperse polystyrene (PS) samples (blend of monodisperse PS samples, with 8 entanglement points per chain between long chains) are employed to investigate the

[†] Corresponding author
E-mail: Takeharu.Isaki@mitsui-chem.co.jp

effects of MWD on nonlinear viscoelastic properties. The shear and biaxial stress relaxation experiments were carried out to obtain the shear and biaxial time dependent damping functions $h(t, \gamma)$ and $h_B(t, \epsilon_B)$, where γ and ϵ_B are the step shear and biaxial extensional strains. The effects of entanglement between long chain and short chain in stress relaxation process seem to be very important for bidisperse polymer systems. Some important ideas such as double reptation^{2,3)}, convective constrain release (CCR)^{10,11,12)} and reptative constraint release (RCR) from double convection reptation (DCR)^{13,14,15,16,17)} have been presented. We also investigate the effects of molecular motions suggested by these ideas on shear and biaxial stress relaxation behaviors, using multi-mode CCR model of Ianniruberto and Marrucci (IM)¹⁵⁾ and multi-mode extension of the Mead, Larson and Doi (MLD)^{12,16,17)} model, to find out plausible explanation for the effects of bimodal MWD on the nonlinear viscoelastic properties. The objective of the present study is to solve the two important problems mentioned above.

2. EXPERIMENTAL

Two blend polystyrene samples (B1 and B2) are employed in this study. The weight-average molecular weight M_w and the polydisperse indices M_w/M_n and M_z/M_w are shown in Table I where M_n and M_z are number- and z- average molecular weights. The blend samples are prepared by mixing of two monodisperse polystyrenes by means of a solvent cast method. The sample B1 is a blend of 80 wt% of F20 and 20 wt% of F80. The blend B2 consists of 95 wt% of F20 and 5 wt% of F288. In Table II, the molecular weights and the weight fraction of components are summarized, where suffixes 1 and 2 denote lower and higher molecular weight components, respectively. In this Table, $w_2 M_2 / M_e$ denotes the number of entanglements between long chains per one long chain, and M_e is the molecular weight between entanglement points. In the blend samples B1 and B2, M_w and $w_2 M_2 / M_e$ are about the same but M_2 / M_1 is much different.

The storage modulus $G'(\omega)$ and loss modulus $G''(\omega)$ of F20, F80, B1 and B2 were already published in the reference.¹⁸⁾ The measurement temperature ranges from 110 to 280 °C depending on the samples. The step-strain stress relaxation experiments in shear were performed by RMS-605 with cone and plate geometry. Biaxial step-strain stress relaxation experiments of B1 and B2 were carried out by means of lubricated squeezing flow method at 160 °C and 145 °C, where details of experimental method were described in our previous study.^{8,9)}

3. RESULTS AND DISCUSSION

3.1 Relaxation Spectrum

Relaxation spectra $H(\tau)$ of four PS samples (F20, F80, B1 and B2) were calculated from dynamic viscoelastic data of the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$ by means of the 2nd order approximation equation proposed by Tschoegl.¹⁹⁾ Fig. 1 shows $H(\tau)$ plotted against relaxation time τ to compare the relaxation time distribution among the four samples (F20, F80, B1 and B2). In B1 a very small shoulder appears at the long time end of the spectrum, whereas somewhat more clear shoulder can be observed in B2.

A. Shear stress relaxation

Shear step-strain stress relaxation experiments for B1 and B2 were performed at 160 °C under shear to obtain the relaxation modulus $G(t, \gamma)$ as a function of time t at various strains γ . Figs. 2 shows the modulus $G(t, \gamma)$ of B1 (A) and B2 (B) respectively.

Table I. Average molecular weights, zero shear viscosity and steady state compliance of samples.

Sample	$M_w/10^5$	M_w/M_n	M_z/M_w	η_0/Pas (160 °C)	J_e^0/Pa^{-1} (160 °C)
F20	1.89	1.04	1.03	4.60×10^5	1.5×10^{-5}
F80	7.07	1.05	1.04	4.60×10^7	1.5×10^{-5}
F288	28.9	1.09			
B1	2.93	1.32	1.50	1.50×10^6	2.10×10^{-4}
B2	3.25	1.63	4.28	1.80×10^6	1.07×10^{-3}

Table II. Component molecular weights and weight fraction of blend samples.

Sample	w_2	M_1	M_2	M_2/M_1	$w_2 M_2 / M_e$
B1	0.20	1.89×10^5	7.07×10^5	3.74	7.8
B2	0.05	1.89×10^5	2.89×10^6	15.3	8.0

The suffixes 1 and 2 denote the lower and higher molecular weight components.

Fig. 1. Relaxation time spectra $H(\tau)$ plotted against relaxation time τ for four samples (F20, F80, B1 and B2).

Each solid line in the figure represents the relaxation modulus $G(t)$ of each sample calculated from the relaxation spectrum. Generally, torque is very small at small strains in stress relaxation experiments especially in long time region. The modulus $G(t)$ calculated from the relaxation spectrum well agrees with $G(t, \gamma)$ at small strain ($\gamma = 0.5$) in short time region, but small deviation is observed in long time region.

Relaxation modulus at various strains in long time region seems to be almost parallel and the time-strain separability does hold in experimental time ranges for B1, but small deviation is observed in the slope of $G(t, \gamma)$ at long times for B2. There may be a possibility that the damping behavior varies with time, and the damping function may be affected by combination of relaxation time of each component for the bidisperse polymer system. It is very interesting to confirm the time-strain separability for bidisperse polymer systems. We employed a time dependent damping function $h(t, \gamma)$ given by,

$$h(t, \gamma) = \frac{G(t, \gamma)}{G(t)} \quad (1)$$

Figs. 2. Relaxation modulus $G(t, \gamma)$ of B1 (A) and B2 (B) in shear at 160 °C as a function of time t at various strains γ .

Figs. 3. Time dependent shear damping function $h(t, \gamma)$ of B1 (A) and B2 (B) as a function of time t at various strains γ .

Figs. 3 shows $h(t, \gamma)$ of B1 (A) and B2 (B) as a function of time t at various strains. The time dependent damping function $h(t, \gamma)$ of B1 decreases slightly in short times and it becomes constant at long times. On the other hand, $h(t, \gamma)$ of B2 varies with time, showing a quite different behavior from that of B1.

3.2 Biaxial stress relaxation

Figs. 4 shows the biaxial relaxation modulus of B1 (A) and B2 (B), respectively. Each solid line in Figs. 4 is the relaxation modulus $G(t)$ of each sample, which is exactly the same line as the shear relaxation modulus at small strain. The modulus $G(t)$ agrees with $G_B(t, \epsilon_B)$ at small biaxial strain even in case of biaxial deformation. The biaxial relaxation modulus at various biaxial strains seems to be almost parallel for B1, and has a little different slope for B2. These tendencies are quite similar to the shear relaxation modulus. We also check the time-strain separability in the biaxial relaxation modulus for the bidisperse samples using a time dependent damping function $h_B(t, \epsilon_B)$ by

$$h_B(t, \varepsilon_B) = \frac{G(t, \varepsilon_B)}{G(t)} \quad (2)$$

Figs. 5 shows $h_B(t, \varepsilon_B)$ of B1 (A) and B2 (B) as a function of time t at various biaxial strains. The modulus $h_B(t, \varepsilon_B)$ of B1 is almost constant, while $h_B(t, \varepsilon_B)$ of B2 varies with time. These tendencies are very similar to the shear damping behavior. The difference in damping behavior between B1 and B2 will be discussed in the next section.

3.3 Stress Relaxation Behavior Predicted by the Constitutive Equations

Effects of convective constrain release (CCR) in situation of multiple modes are investigated in shear and biaxial stress relaxation for the bidisperse polymer system. The multiple-mode model is able to take into account the effect of constraint release due to relaxation of short chain's reptation motion, and CCR predicts that entanglement points decrease under large deformation. Marrucci¹⁰⁾, Mead, Larson and Doi (MLD)¹²⁾, Ianniruberto and Marrucci¹⁴⁾ proposed molecular constitutive models, taking into account the effects of CCR. Multi-mode

extension of the MLD model is introduced by Pattamaprom and Larson¹⁶⁾, and Ye et al.¹⁷⁾, while Ianniruberto and Marrucci (IM)¹⁵⁾ also extended their model for multi relaxation mode. The constitutive equation consists of stretch term, orientation term and relaxation time term. The multi-mode extension of the IM and the MLD models are the following.

$$\sigma = 5G_N^0 \sum_{i=1}^N w_i S_i \lambda_i^2 k_{s,i}(\lambda_i) \quad (3)$$

The stress tensor σ is given by the stretch λ_i of the primitive chain contour length and the orientation tensor S_i with the entanglement plateau modulus G_N^0 . The subscripts i and j denote components of the polymer with the weight fraction w_i . $k_{s,i}(\lambda_i)$ expresses the finite extensibility of polymer chain by a nonlinear spring effect.

Stretch term for IM

$$\frac{d\lambda_i}{dt} = \lambda_i \mathbf{K} : \mathbf{S}_i - \frac{\lambda_{\max}}{\tau_{s,i}} \frac{\lambda_i - 1}{\lambda_{\max} - \lambda_i} \quad (4)$$

$$k_{s,i}(\lambda_i) = \frac{\lambda_{\max} - 1}{\lambda_{\max} - \lambda_i} \quad (5)$$

Figs. 4. Biaxial relaxation modulus $G_B(t, \varepsilon_B)$ of B1 (A) and B2 (B) at 160 °C as a function of time t at various biaxial strains ε_B .

Figs. 5. Time dependent biaxial damping function $h_B(t, \varepsilon_B)$ of B1 (A) and B2 (B) as a function of time t at various biaxial strains ε_B .

Stretch term for MLD

$$\frac{d\lambda_i}{dt} = \lambda_i \mathbf{K} : \mathbf{S}_i - \frac{k_{s,i}(\lambda_i)}{\tau_{s,i}} (\lambda_i - 1) - \frac{1}{2} (\lambda_i - 1) \sum_{j=1}^N w_j \left(\mathbf{K} : \mathbf{S}_j - \frac{\dot{\lambda}_j}{\lambda_j} + \frac{1}{\lambda_j^2 \tau_{d,j}} \right) \quad (6)$$

$$k_{s,i} = \frac{(3 - \alpha^2)(1 - \beta^2)}{(1 - \alpha^2)(3 - \beta^2)}, \quad \alpha = \beta \lambda_i, \quad \beta = 1/\lambda_{\max} \quad (7)$$

Here $\lambda_{\max}$ is the maximum stretch ratio of polymer chain. $\mathbf{K}$ is the deformation gradient tensor, $\tau_{s,i}$ is a stretch relaxation time of polymer component i .

Orientation term

$$\mathbf{S}_i = \sum_j w_j \mathbf{S}_{ij} \quad (8)$$

$$\mathbf{S}_{ij} = \int_{-\infty}^t \frac{dt'}{\tau_{ij}(t')} \exp \left[- \int_{t'}^t \frac{dt''}{\tau_{ij}(t'')} \right] \mathbf{Q}(\mathbf{E}(t, t')) \quad (9)$$

Relaxation time for IM

$$\tau_{ij}(t) = \frac{1}{1/\tau_{d,i} + 1/\tau_{d,j} + |\mathbf{K} : \mathbf{S}_i| + |\mathbf{K} : \mathbf{S}_j|} + \tau_{s,i} \quad (10)$$

Relaxation time for MLD

$$\frac{1}{\tau_{ij}(t)} = \frac{1}{\lambda_i^2 \tau_{d,i}} + f(\lambda_i) \left(\mathbf{K} : \mathbf{S}_j - \frac{\dot{\lambda}_j}{\lambda_j} + \frac{1}{\lambda_j^2 \tau_{d,j}} \right) \quad (11)$$

$\tau_{d,i}$ is a reptation time of component i . τ_{ij} is an average relaxation time for entanglements between chains i and j . The switch function in Eq. (11) $f(\lambda_i) = 1/\lambda_i$ transfers from the tube shortening to the tube reorientation. $\mathbf{Q}$ in Eq. (9) is the universal tensor with the independent alignment approximation given by Doi and Edwards.²⁰⁾ $\mathbf{E}(t, t')$ is the deformation history and $\mathbf{u}$ is a unit vector which distributes randomly over the unit sphere and $\langle \rangle$ represents an ensemble average over all $\mathbf{u}$.

$$\mathbf{Q} \equiv \left\langle \frac{(\mathbf{E}(t, t') \cdot \mathbf{u})(\mathbf{E}(t, t') \cdot \mathbf{u})}{|\mathbf{E}(t, t') \cdot \mathbf{u}|^2} \right\rangle \quad (12)$$

According to Ye et al.¹⁷⁾, finite chain extensibility parameter $\lambda_{\max} = 17.85$ for polystyrene melt. Nonlinear spring coefficient of chain $k_{s,i}(\lambda_i)$ goes infinity at $\lambda_i = \lambda_{\max}$. The coefficient $k_{s,i}(\lambda_i)$ of polystyrene is almost unity in a range of stretch $\lambda_i < 8$, and we can neglect this parameter because initial stretch λ_0 is less than 3 at $\gamma = 6$ or $\varepsilon_B = 1.24$.

3.4 Model Parameters

For bidisperse polymer system, set of stretch relaxation time (or Rouse time) $\tau_{s,i}$, reptation time $\tau_{d,i}$ and weight fraction w_i of each component are necessary as parameters for the multi-mode IM model. For moderate molecular weight polystyrenes (F20 and F80), it is possible to determine relaxation times experimentally, but difficult for the high molecular weight sample (F288). Reliable rules are necessary to extrapolate characteristic times from information of molecular weight.

There are many methods to determine the characteristic times. Here we compare determination methods of characteristic times and investigate validity of the model parameters.

3.5 Evaluation of Rouse Time

The following four methods are examined. (A) The Rouse time τ_R is evaluated according to an equation proposed by Osaki et al.²¹⁾, and Menezes and Graessley.²²⁾

$$\tau_R = \frac{12\eta_0 M}{\pi^2 \rho RT} \left(\frac{2M_e}{M} \right)^{2.5} \quad (13)$$

Here, M_e is the molecular weight between entanglement points [$M_e = 16625$ by Fetters et al.²³⁾], ρ the density, R the gas constant and T is the absolute temperature. η_0 is the zero-shear viscosity, and another relation ($\eta_0 \propto M^{3.5}$) is necessary when experimental data is not available.

(B) The Rouse time from the storage modulus $G'(\omega)$ in the power law region using the Rouse theory [Osaki et al.²⁴⁾] is given by

$$\tau_R = \left(\frac{\alpha M}{1.111 \rho RT} \right)^2 \quad (14)$$

where $G'(\omega) = \alpha \omega^{1/2}$.

(C) The Rouse time from the tube theory can be written as

$$\tau_R = Z^2 \tau_e \quad (15)$$

Here $Z = M/M_e$ is the number of entanglements per molecule, and τ_e is the Rouse time of an entanglement segment. Evaluation of τ_e is a big problem. Ye et al.¹⁷⁾ obtained $\tau_e = 0.005$ s for PS solution by fitting with dynamic viscoelastic data using Milner-McLeish model.²⁵⁾ Sanchez-Reyes et al.²⁶⁾ obtained $\tau_e = 0.0036$ s for PS solution from Rouse time by method (B). We obtained $\tau_e = 0.257$ s for PS melts using Archer's strategy.²⁶⁾

(D) The Rouse time from the tube theory using reptation time is given by

$$\tau_R = \tau_d / 6Z \quad (16)$$

Evaluated values of the Rouse time by the methods (A) – (D) are compared in Table III.

3.6 Evaluation of Reptation Time

The following 5 evaluation methods are examined for the longest relaxation time (reptation time) τ_d .

(a) An experimental relation

$$\tau_d = 1.9\eta_0 J_e^0 [\text{Takahashi et al.}^{8)],} \quad (17)$$

(b) An experimental relation

$$\tau_d = \eta_0 J_e^0 [\text{Sanchez-Reyes et al.}^{26)],} \quad (18)$$

(c) The reptation time from the tube theory

$$\tau_d = 3Z^3 \tau_e \quad (19)$$

(d) Contour length fluctuation is taking into account by Milner-McLeish model²⁵⁾

$$\tau_d = 3Z^3 \tau_e (1 - 2s_d)^2 \quad (20)$$

(e) Ye et al. (2003) presented an equation in their reference (Eq. (25)).¹⁷⁾

The results are compared in Table IV.

3.7 Validity of the Model Parameters

According to the Milner and McLeish theory, the relaxation modulus $G(t)$ is expressed by

$$G(t) = G_{\text{Rouse}}(t) + G_{\text{reptate}}(t) + G_{\text{retract}}(t) \quad (21)$$

However, the effect of contour length fluctuations (retraction) does not take into account into the constitutive equations discussed here, and thus we neglect G_{retract} .

$$G(t) = G_{\text{Rouse}}(t) + G_{\text{reptate}}(t) \quad (22)$$

Short time Rouse process $G_{\text{Rouse}}(t)$ is given by

$$G_{\text{Rouse}}(t) = \frac{G_N^0}{Z} \left[\frac{1}{3} \sum_{p=1}^Z \exp\left(-\frac{p^2 t}{\tau_R}\right) + \sum_{p=Z+1}^{\infty} \exp\left(-\frac{2p^2 t}{\tau_R}\right) \right] \quad (23)$$

Long time relaxation process by reptation process²⁰⁾ $G_{\text{reptate}}(t)$ is given by

$$G_{\text{reptate}}(t) = G_N^0 \sum_{p \text{ odd}} \frac{8}{(\pi p)^2} \exp\left(-\frac{p^2 t}{\tau_d}\right) \quad (24)$$

We decided the best evaluation method by selecting best fit parameters for Eq. (22) to experimental data, and found that the method (C) (or (B)) is good for τ_R and the method (a) gives good estimation for τ_d .

Fig. 6 compares the relaxation modulus $G(t)$ of F20 and F80 obtained from relaxation spectrum with model prediction of Eq. (22). Model parameters are obtained by the method (C) for τ_R and the method (a) for τ_d . The reason for deviation from the experimental data may be neglect of contour length fluctuations and constraint release. Finally, we set the model parameters as follows.

$$\tau_{s,1} = \tau_R \text{ (low } M_w \text{ component)}, \tau_{s,2} = \tau_R \text{ (high } M_w \text{ component)}$$

$$\tau_{d,1} = \tau_d \text{ (low } M_w \text{ component)}, \tau_{d,2} = \tau_d \text{ (high } M_w \text{ component)}$$

Model parameters for the bidisperse PS samples B1 and B2 are listed in Table V.

Fig. 6. Relaxation modulus $G(t)$ of F20 and F80: Comparison between experimental data and calculated results based on Eq. (22) with the assigned relaxation times.

Table III. Evaluated Rouse time (sec)

Sample	(A)	(B)	(C)	(D)
F20	0.39	0.33	0.33	0.19
F80	6.38	4.66	4.64	5.13
F288	123.0	77.8	77.6	170.0

Table IV. Evaluated reptation time (sec)

Sample	(a)	(b)	(c)	(d)	(e)
F20	13.1	6.9	11.3	3.1	3.9
F80	1.31×10^3	6.90×10^2	5.92×10^2	2.50×10^2	2.73×10^2
F288	1.77×10^5	9.32×10^4	4.05×10^4	2.51×10^4	2.27×10^4

Table V. Parameters for the multi mode models.

Sample	$\tau_{s,1}/s$	$\tau_{d,1}/s$	w_1	$\tau_{s,2}/s$	$\tau_{d,2}/s$	w_2
B1	0.33	13.1	0.80	4.64	1.31×10^3	0.20
B2	0.33	13.1	0.95	77.6	1.77×10^5	0.05

3.8 Time Dependent Damping Functions

There are two possibilities of the combination of the relaxation times depending upon component molecular weights of the blend samples.

Case1: $\tau_{s,1} < \tau_{s,2} < \tau_{d,1} < \tau_{d,2}$ Case2: $\tau_{s,1} < \tau_{d,1} < \tau_{s,2} < \tau_{d,2}$

B1 is classified to the case1, and B2 corresponds to the case2. It is very interesting to compare the model prediction of case1 with that of case2, because the experimental data show different damping behavior between B1 and B2. Figs. 7 shows multi-mode model predictions of the IM ((A), (B)) and the MLD ((C), (D)) for the time dependent damping function $h(t, \gamma)$ of B1 ((A), (C)) and B2 ((B), (D)) at various strains. Model predictions for damping behaviors between B1 and B2 are quite different. For B1, both model predictions are similar to the experimental damping behavior. On the other hand, for B2 the MLD model prediction gives better agreement with the experimental data. Figs. 8 compares the chain contraction behavior of short and long chains in B1 and B2 predicted by the IM and MLD models. Solid lines represent long chain behavior and dashed lines denote short chain behavior. Contraction of the short chain is completed at the time around $t = 3\tau_{s,1}$. The long chain stretch does not change for the IM

model, while contraction of the long chain is accelerated for the multi-mode MLD model by constraint release due to short chain contraction, and long chain contraction finishes at $t = 2.5\tau_{s,2}$ for B1 and $t = 1.5\tau_{s,2}$ for B2.

In case of B1 ($\tau_{s,1} < \tau_{s,2} < \tau_{d,1} < \tau_{d,2}$), it is clear that $h(t, \gamma)$ is a decreasing function of time at $t < 2.5\tau_{s,2}$. After $t = 2.5\tau_{s,2}$, the time-strain separability holds and $h(t, \gamma)$ takes constant value $h(\gamma)$. Each multi-mode model gives almost the same strain dependence for $h(\gamma)$ as that of the single mode prediction. The strain dependence of damping function predicted by the MLD model is much stronger than the IM model. The MLD model gives stronger strain dependence for $h(\gamma)$ than the IM model. In case of B2 ($\tau_{s,1} < \tau_{d,1} < \tau_{s,2} < \tau_{d,2}$), $h(t, \gamma)$ shows complex behavior. The function $h(t, \gamma)$ once decreases at $t < 3\tau_{s,1}$, and after $t = 3\tau_{s,1}$, $h(t, \gamma)$ increases due to reptation relaxation of short chain around $t = \tau_{d,1}$. Then, $h(t, \gamma)$ decreases again at the time around $t = \tau_{s,2}$. After contraction of long chain component ($t = 1.5\tau_{s,2}$), $h(t, \gamma)$ takes constant value $h(\gamma)$. Each multi-mode model gives almost the same strain dependence for $h(\gamma)$ as that of the single mode prediction, just the same as in the case of B1.

Experimentally accessible time range was limited, but the damping behavior at $\tau_{s,1} < t < \tau_{s,2}$ can be observed. Although

Figs. 7. Multi-mode model predictions of the IM (A,B) and the MLD (C,D) on time dependent shear damping function $h(t, \gamma)$ for B1 (A,C) and B2 (B,D) as a function of time t at various strains γ .

both the IM and MLD models cannot give quantitative description of $h(t, \gamma)$ especially for B2, the time dependence of $h(t, \gamma)$ predicted by the MLD model is somewhat closer to the experimental data. This means that contraction of the long chain is somewhat accelerated by constraint release due to short chain contraction, with acceleration not so strong as predicted by the MLD model. After the longest chain contraction, $h(t, \gamma)$ becomes universal function and independent of molecular weight distribution. Damping behavior of bidisperse polymer melt is drastically changed by the combination of the relaxation times. The strain dependence of damping function predicted by multi-mode models, the IM model is much weaker, the MLD model is much stronger than experimental data. It is known that the MLD model prediction for damping function in shear shows has stronger strain dependence than the DE(IA) prediction.¹²⁾ However, the damping behavior (time dependence) predicted by the MLD model is closer to the experimental $h(t, \gamma)$ for bidisperse polystyrene melts.

Damping behavior in biaxial stress relaxation is almost similar to the shear. Figs. 9 shows multi-mode model

predictions of the IM ((A), (B)) and the MLD ((C), (D)) for the time dependent damping function $h(t, \gamma)$ of B1 ((A), (C)) and B2 ((B), (D)) at various strains. In B2, experimentally observed upturn of $h_B(t, \varepsilon_B)$ occurs at longer times than predicted by the MLD model. However, the MLD model prediction gives much better description of $h_B(t, \varepsilon_B)$ than the IM model, including the strain dependence. The effect of CCR is very important to describe the damping behavior for bidisperse polymer system.

4. CONCLUSIONS

Effects of molecular weight distribution on damping behavior of stress relaxation in shear and biaxial extension are investigated using two bidisperse PS samples B1 and B2 (blend of monodisperse samples). Two characteristic relaxation times, the reptation time τ_d and the Rouse time τ_R of each component, are evaluated experimentally. The order of relaxation times for B1 is $\tau_{s,1} < \tau_{s,2} < \tau_{d,1} < \tau_{d,2}$, while that for B2 is $\tau_{s,1} < \tau_{d,1} < \tau_{s,2} < \tau_{d,2}$. The time dependent damping functions in shear $h(t, \gamma)$ and in biaxial extension $h_B(t, \varepsilon_B)$ are

Figs. 8. Multi-mode model predictions of the IM (A,B) and the MLD (C,D) on the chain contraction of short and long chain components for B1 (A,C) and B2 (B,D). Solid and dashed lines respectively represent long chain and short chain behavior.

Figs. 9. Time dependent biaxial damping function $h_B(t, \varepsilon_B)$ predicted by multi-mode models of the IM (A,B) and the MLD (C,D) for B1 (A,C) and B2 (B,D) as a function of time t at various biaxial strains ε_B .

employed to confirm the time-strain separability at long times for the bidisperse polymer systems. At times $t > 3\tau_{s,1}$, the time dependent damping functions of B1 are almost constant, but those of B2 vary with time in both shear and biaxial extension.

The effects of convective constrain release (CCR) are investigated in shear and biaxial stress relaxation for bidisperse polymer systems. The multi-mode extensions of the IM and the MLD models are employed to investigate the damping behavior of the bidisperse polystyrenes. Although not quantitatively, the MLD model prediction with the CCR concept gives better description of $h(t, \gamma)$ and $h_B(t, \varepsilon_B)$ in the measured time region. In case of B1, $h(t, \gamma)$ and $h_B(t, \varepsilon_B)$ are decreasing functions before long chain retraction. The time-strain separability holds after completion of long chain contraction, where $h(t, \gamma)$ and $h_B(t, \varepsilon_B)$ take constant values, and the multi-mode models give almost the same strain dependences as those of the single mode models. In case of B2, $h(t, \gamma)$ and $h_B(t, \varepsilon_B)$ once decrease along with short chain retraction and after the retraction, $h(t, \gamma)$ and $h_B(t, \varepsilon_B)$ increase around reptation relaxation time of short chain. With contraction of long chain, $h(t, \gamma)$ and $h_B(t, \varepsilon_B)$ decrease again. The time dependent damping functions become independent

of time after completion of long chain contraction. The MLD model gives better prediction of time dependent damping function especially for B2 ($\tau_{s,1} < \tau_{d,1} < \tau_{s,2} < \tau_{d,2}$) due to CCR mechanism was taken into account in the stretch term of the model. The effects of CCR are very important to describe damping behavior for bidisperse polymer systems.

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