Macromolecules **1992,** *25,* 1824-1827

Cooperative Chain Relaxation in a Single-Phase Mixture of Dissimilar Polymers: Definition and Implication of the Cooperativity

Hiromu Saito, Hiraku Miyashita,[†] and Takashi Inoue[*]

Department of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Received October 3, 1991; Revised Manuscript Received December 10, 1991

ABSTRACT: We investigated, over a wide temperature range, the chain orientation relaxation in single-phase mixtures of polystyrene and poly(phenylene oxide) by the simultaneous measurement of stress (σ) and birefringence (Δn) after uniaxial stretching. The results could be represented by a master curve of σ with a single characteristic relaxation time τ_r intermediate between those of the component polymers. The master curve of birefringence $\Delta n(t/a_T)$ of the blend was very different from that estimated by the additivity of $\Delta n(t/a_T)$ of the component polymers. Only when the $\Delta n(t/a_T)$ curve of PPO (with short τ_r) was extended horizontally (along the time axis) while that of PS (with long τ_r) was shortened to result in $\tau_{r(PPO)}$ equal to $\tau_{r(PS)}$ did the $\Delta n(t/a_T)$ coincide with the sum of the two curves. This is clear evidence for the cooperative chain relaxation of dissimilar polymers. The nature of cooperative behavior was discussed in light of the many-body theory.

Introduction

Our preliminary interest was the design of birefringence-free plastics by blending positively and negatively birefringence polymers, so as to attain zero birefringence.[1] For the processing of birefringence-free plastics, the relaxation behavior of the dissimilar chains in a molten miscible polymer blend is of particular interest, because a complete compensation of birefringence would be achieved only when the dissimilar chains undergo an equivalent orientation accompanied by an equivalent relaxation.

Preliminary studies on the chain orientation relaxation behavior of dissimilar polymers used infrared dichroism and shear stress relaxation measurements for the single-phase mixture such as poly(methyl methacrylate) (PMMA)/poly(vinylidene fluoride) (PVDF).[2] The dissimilar polymers showed an identical time variation of the normalized Hermans orientation function. The mixture exhibited a relaxation spectrum with a single characteristic relaxation time, depending on the composition. The result suggests that the dissimilar polymers do not relax independently but cooperatively.

To obtain a deeper understanding of the cooperative relaxation, we carry out, over a wide temperature range, simultaneous measurements of stress and birefringence as a function of time after uniaxial stretching of a film specimen of a polystyrene (PS)/poly(phenylene oxide) (PPO) blend. Such blends are particularly suitable for this study, because (1) the polymers have birefringences of opposite sign (PS having negative and PPO positive birefringence) and (2) both PS and PPO are amorphous. The results are discussed on the basis of the many-body theory.

Experimental Section

Polymers used in this study: PS was supplied by Denka Co., Ltd.; GP-1, $M_w = 44.1 \times 10^4$, $M_n = 19.7 \times 10^4$. PPO was by Mitsubishi Gas Chemical Co., Inc.; $M_w = 5.7 \times 10^4$, $M_n = 1.6 \times 10^4$.

PS and PPO were dissolved at 10 wt % of the total polymer in chloroform. The solution was cast onto a glass plate. After the solvent had been evaporated at room temperature, the cast film was further dried under vacuum (10^{-4} mmHg) for 2 days at 120 °C. A stack of thin-cast films was compression-molded into a film about 0.5 mm thick. The film was then cut into rectangles of length 50 mm and width 3 mm. The rectangular specimens were kept at $T_g + 5$ °C for 1 day to dry further and remove frozen orientation, and then they were allowed to cool gradually to room temperature.

Figure 1 shows an apparatus for the simultaneous measurement of stress and birefringence relaxations after uniaxial stretching. In the tensile testing system (Far-East Manufacturing Inc.), two crossheads travel up and down at the same speed so that the light beam for Δn measurement irradiates the midpoint of the film specimen throughout the stretching and relaxation processes. The specimen was quickly stretched (90 mm/s) up to a draw ratio ϵ of 1.05. The stress was measured as a function of time after the deformation. The data were processed by a personal computer PC (PC-9801 VM, NEC Co., Ltd.) through an A/D converter CON (AD12-16, Contec Co., Ltd.; 12 bits).

The birefringence was measured by an optical system with a photoelastic modulator as shown in Figure 1. A 632.8-nm He-Ne laser (2 mW; GL G5370, NEC Co., Ltd.) was used as a light source. The light was passed through a Gran-Thomson polarizer and a photoelastic modulator (PEM).[3-5] The PEM (ADR-200, ORC Manufacturing Co., Ltd.) produces a sinusoidal retardation $\delta_0 = A_{PEM} \sin \omega t$ at a high frequency $\omega = 50$ kHz and adjustable amplitude A_{PEM}. The modulated light was applied to the specimen, leading to a retardation Δ. After passing through a Gran-Thomson analyzer, the light was detected by a photodiode (S1226-5BK, Hamamatsu Photonics Co., Ltd.). The detected photoelectric signal contains two components: ac amplitude E_{ac} with a frequency of 50 kHz modulated by PEM and dc amplitude (E_{dc}) which is independent of the ac signal. E_{ac} was measured by a two-phase lock-in amplifier (5610B, NF Electronic Instrument Co., Ltd.) as a function of time and was sent to the PC through CON. E_{dc} was measured directly by CON and sent to the PC. In the optical arrangement shown by arrows in Figure 1, the Δ by the specimen is given by[4]

$$\Delta = \sin^{-1}\left(\frac{E_{ac}}{2\,J_1(\delta_0)\,E_{dc}}\right) \tag{1}$$

where $J_1(\delta_0)$ is the first Bessel function which is experimentally

---

[*] To whom correspondence should be addressed.

[†] On leave from the Corporate Research Institute, Sekisui Chemical Co., Ltd., Osaka 618, Japan.

0024-9297/92/2225-1824$03.00/0 © 1992 American Chemical Society

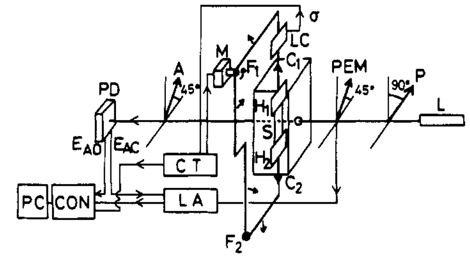

Figure 1. Apparatus for simultaneous measurement of stress and birefringence relaxation after uniaxial stretching: L, laser; P, polarizer; PEM, photoelastic modulator; S, specimen; H, crosshead; C, clamp; F, fulcrum; LC, load cell; M, motor; CT, controller; A, analyzer; PD, photodiode; LA, lock-in amplifier; CON, A/D converter; PC, personal computer.

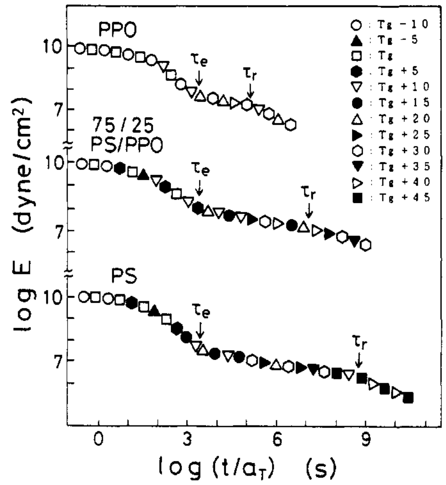

Figure 2. Master curves of the relaxation modulus $E(t/a_T)$ of PPO, 25/75 PPO/PS, and PS; reduced at each T_g. ($T_{g(PPO)}$ = 207 °C, $T_{g(blend)}$ = 116 °C, $T_{g(PS)}$ = 95 °C).

determined as a calibration constant. The birefringence Δn is then obtained from

$$\Delta n = \frac{\Delta \lambda d}{2\pi} \tag{2}$$

where λ is the wavelength of light and d is the thickness of the specimen.

The PEM system provides two advantages: the precise measurement of small Δn and the determination of the sign of Δn. The sensitivity of the PEM system is 3 orders of magnitude higher than that obtained by the transmitted light intensity method without PEM. The high sensitivity is attained by isolating the high-frequency (50-kHz) signal from low-frequency noise, since PEM plays the role of a chopper. The sign of Δn is judged from the phase difference between the reference signal through PEm and the ac one analyzed by the lock-in amplifier.

The glass transition temperature, T_g, was measured using a differential scanning calorimeter (DSC Model 910, E.I. du Pont de Nemours and Co., Ltd.).

Results and Discussion

The $E(t)$ curves obtained at various temperatures could be superimposed to a master curve by a horizontal shift. The master curves $E(t/a_T)$ reduced at each T_g, where a_T is the shift factor, are shown in Figure 2. The temperature dependence of a_T followed the WLF equation.[6,7] The relaxation time τ_e defined by the inflection point of the master curve is ca. $10^{3.2}$ s. The characteristic relaxation time τ_r defined by the end point of the rubbery plateau is short for PPO with a low molecular weight (M_w = 5.7 × 10^4), while that of PS with a high molecular weight (M_w = 44.1 × 10^4) is large. A 75/25 PS/PPO blend exhibits a single intermediate τ_r. This suggests a change in τ_r of the component polymers on blending; i.e., the τ_r of PPO increases, while that of PS decreases. That is, the dissimilar chains in the blend seem to relax cooperatively.

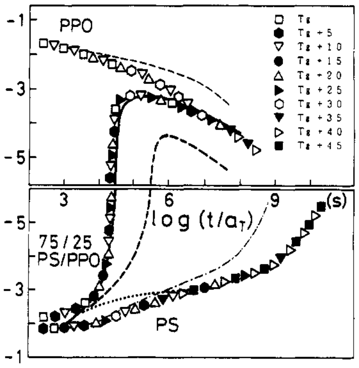

Figure 3. Master curves of relaxation birefringence $\Delta n(t/a_T)$ of PPO, 25/75 PPO/PS, and PS; reduced at each T_g. The dashed line was calculated by eqs 3 and 4, assuming $\tau_{r(PPO)} = 10^{6.3}$ s and $\tau_{r(PS)} = 10^{8.8}$ s; the broken line was calculated by assuming $\tau_{r(PPO)} = 10^{6.5}$ s and $\tau_{r(PS)} = 10^{7.5}$ s; the solid line was calculated by assuming $\tau_{r(PPO)} = \tau_{r(PS)} = 10^{7.0}$ s.

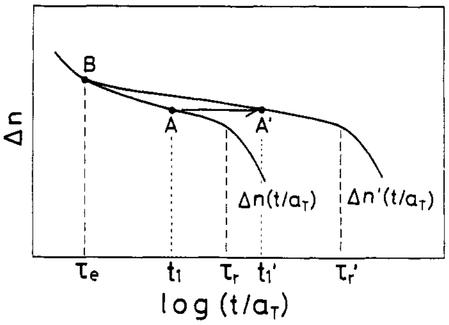

Figure 4. Schematic of the extension procedure.

The cooperative relaxation behavior can be characterized more quantitatively by birefringence relaxation. The master curves of birefringence relaxation $\Delta n(t/a_T)$ obtained by a procedure similar to that of $E(t/a_T)$ are shown in Figure 3. The data shown are birefringences divided by the draw ratio ϵ. Note that the component polymers have birefringences of opposite signs and that their relaxation rates are very different. The birefringence in the blend of polymers A and B may be described by

$$\Delta n(t/a_T) = \Delta n_A(t/a_T)\phi_A + \Delta n_B(t/a_T)\phi_B \tag{3}$$

where ϕ_i is the volume fraction of the ith component. First, we simply followed eq 3 and added the two curves of PS and PPO in Figure 3. The result is shown by the dotted line in Figure 3. It is very far from the observed $\Delta n(t/a_T)$ curve; the calculated one increases with time, maintaining a negative value, while the observed one is initially negative, changes sign from negative to positive, attains a maximum, and eventually starts to decrease. The simple summation by eq 3 implies that the values of τ_r of component chains A and B in the blend are equal to those in neat polymers A and B, respectively ($\tau_{r(PPO)} = 10^{5.3}$ s, $\tau_{r(PS)} = 10^{8.8}$ s; see Figure 2), i.e., that the dissimilar chains relax independently of each other in the blend.

Next, we assumed that PPO in the blend has longer τ_r than that of neat PPO and the master curve $\Delta n(t/a_T)$ was extended horizontally to $\Delta n'(t/a_T)$, as illustrated in Figure 4. The extension was carried out proportionally; for example, a certain point A on the $\Delta n(t/a_T)$ curve ($t/a_T = t_1$) is shifted horizontally to A' ($t/a_T = t_1'$) with a proportionality factor $(\tau_r' - \tau_e)/(\tau_r - \tau_e)$; i.e., $(t_1' - \tau_e)/(t_1 - \tau_e) = (\tau_r' - \tau_e)/(\tau_r - \tau_e)$. The extension procedure may be described by

$$\Delta n'(t/a_{\mathrm{T}}) = \Delta n\left(\frac{\tau_{\mathrm{r}} - \tau_{\mathrm{e}}}{\tau_{\mathrm{r}}' - \tau_{\mathrm{e}}}(t/a_{\mathrm{T}} - \tau_{\mathrm{e}}) + \tau_{\mathrm{e}}\right) \tag{4}$$

For instance, with $\tau_{\mathrm{r(PPO)}} = 10^{5.3}$ s and $\tau_{\mathrm{r'(PPO)}} = 10^{6.5}$ s (slightly larger than τ_{r}) in eq 4, the calculated $\Delta n'(t/a_{\mathrm{T}})$ curve is shown by a thin broken line in Figure 3. On the other hand, with $\tau_{\mathrm{r(PS)}} = 10^{8.8}$ s and $\tau_{\mathrm{r'(PS)}} = 10^{7.5}$ s (slightly smaller than τ_{r}), the $\Delta n'(t/a_{\mathrm{T}})$ for PS was similarly obtained and the calculated result is shown by a thin chain line in Figure 3. Next the two $\Delta n'(t/a_{\mathrm{T}})$ curves thus obtained were added by eq 3. The added curve is shown as a broken line in Figure 3. The shape of the broken line is now similar to that of the observed one.

The extension procedure implies that the τ_{r} values of component polymers approach each other; i.e., the relaxation of PPO is retarded while that of PS is accelerated by blending, indicating a weak cooperativity. The closer the τ_{r} values, the stronger will be the cooperativity. Thus, the closeness of the τ_{r} values of the component polymers should be a measure of the cooperativity.

The solid line in Figure 3 is the calculated $\Delta n(t/a_{\mathrm{T}})$ obtained by setting $\tau_{\mathrm{r'(PPO)}}$ exactly equal to $\tau_{\mathrm{r'(PS)}}$ ($=10^{7.0}$ s). It is very close to the observed one on the log time scale, suggesting a very strong cooperativity.

By contrast, in binary mixtures of homologous polymers, e.g., low and high molecular weight polystyrenes, stress relaxation studies by Watanabe et al.[8] found three peaks in the relaxation spectra, and these were assigned to entanglements between short chains (s–s), between long chains (l–l), and between short and long chains (s–l). The peak position for (l–l) was observed at short τ than for neat high molecular weight PS and that for (s–s) was at longer τ than for neat low molecular weight PS.[5] However, the positions were definitely apart. The result implies a very weak cooperativity, so that, the cooperativity in binary mixtures of homologous polymers seems to be much smaller than that for dissimilar ones.

The strongly cooperative relaxation behavior is inconsistent with the tube theory, in which a chain inside a tubelike region is assumed to move independently of the surrounding chains.[9–12] It can be discussed on the basis of the many-body theory as follows.

According to the many-body theory by Hess[13] and Skolnick et al.,[14] the center-of-mass diffusion constant D for a neat polymer system is given by

$$D = \frac{D_0}{1 + d_0\Psi/D_{\mathrm{eff}}} \tag{5}$$

where D_0 is the Rouse diffusion constant, $D_0 \propto (M\xi_0)^{-1}$, with M and ξ_0 being the molecular weight and the monomer friction constant, respectively, D_{eff} is the diffusion constant for the dynamical contact due to the entangle coupling between each chain, and Ψ is the entanglement parameter, $\Psi = M/M_{\mathrm{e}}$, M_{e} being the molecular weight between entanglements. In mixtures of dissimilar chains A and B, taking account of the dynamic contacts between dissimilar (A–B) and between similar chains (A–A, B–B), the diffusion constant of an A chain may be formulated by

$$D_i = \frac{(D_0)_{ii}}{1 + (D_0)_{ii}/[\gamma_{ii}(D_0)_{ii}/\Psi_{ii} + \gamma_{ij}(D_0)_{ij}/\Psi_{ij}]} \tag{6}$$

$$\gamma_{ii} + \gamma_{ij} + \gamma_{jj} = 1 \tag{7}$$

where γ_{ii} and γ_{ij} are the number fractions of the dynamical contacts between similar and dissimilar chains, $(D_0)_{ii}$ is the Rouse diffusion constant of one component i, and $(D_0)_{ij}$ is that affected by entangle coupling with a j chain.

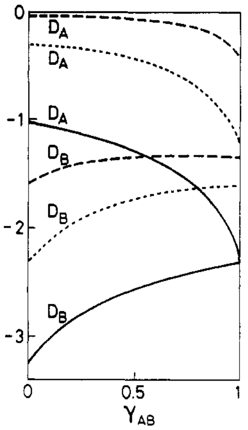

Figure 5. Calculated curves of log $[D_i/(D_0)_{\mathrm{AA}}]$ as a function of τ_{AB} by eqs 6 and 7: broken line, $\Psi_{\mathrm{AA}} = 0.05$ and $\Psi_{\mathrm{BB}} = 0.5$; dotted line, $\Psi_{\mathrm{AA}} = 0.5$ and $\Psi_{\mathrm{BB}} = 5$; solid line, $\Psi_{\mathrm{AA}} = 5$ and $\Psi_{\mathrm{BB}} = 10$. $(D_0)_{\mathrm{AA}}/(D_0)_{\mathrm{BB}} = 2M_{\mathrm{B}}/M_{\mathrm{A}}$.

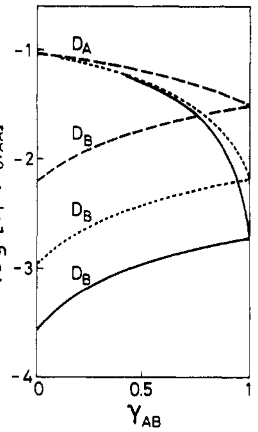

Figure 6. Calculated curves of log $[D_i/(D_0)_{\mathrm{AA}}]$ as a function of γ_{AB} by eqs 6 and 7: broken line, $\Psi_{\mathrm{AA}} = 5$ and $\Psi_{\mathrm{BB}} = 20$; dotted line, $\Psi_{\mathrm{AA}} = 5$ and $\Psi_{\mathrm{BB}} = 50$, solid line, $\Psi_{\mathrm{AA}} = 5$ and $\Psi_{\mathrm{BB}} = 100$. $(D_0)_{\mathrm{AA}}/(D_0)_{\mathrm{BB}} = M_{\mathrm{B}}/M_{\mathrm{A}}$.

The two diffusion constants, D_{A} and D_{B}, were calculated for a fixed $\Psi_{\mathrm{AA}}/\Psi_{\mathrm{BB}}$ by eqs 6 and 7, and the results are shown as a function of γ_{AB} in Figure 5. Similar results for various $\Psi_{\mathrm{AA}}/\Psi_{\mathrm{BB}}$ are also in Figure 6. Here, for simplicity, we assumed $\gamma_{\mathrm{AA}} = \gamma_{\mathrm{BB}}$, $\Psi_{\mathrm{AB}} = (\Psi_{\mathrm{AA}} + \Psi_{\mathrm{BB}})/2$, and $(D_0)_{\mathrm{AB}} = [(D_0)_{\mathrm{AA}} + (D_0)_{\mathrm{BB}}]/2$. The diffusion constant of the fast-moving component D_{A} decreases with increasing γ_{AB} while that of the slow-moving one D_{B} increases. Since D_i is inversely proportional to τ_{r}, the results indicate that the τ_{r} of the fast-moving component becomes larger with increasing τ_{AB} while that of the slow one becomes smaller. Thus, the values of τ_{r} of the components approach each other when τ_{AB} is close to 1, and the strength of cooperativity may be described by γ_{AB}.

Note that when M_{A} is smaller than M_{e}, D_{A} and D_{B} do not merge even at $\gamma_{\mathrm{AB}} = 1$ (as shown by dotted and broken lines in Figure 5), while they are equal at $\gamma_{\mathrm{AB}} = 1$ when $M_{\mathrm{A}} > M_{\mathrm{e}}$. The results suggest that the strongly cooperative relaxation behavior, observed in our binary mixture of dissimilar polymers, seems to arise when the dynamical contacts between dissimilar polymers are predominant over those between similar ones and the molecular weights of both components are larger than M_{e}.

As is well-known, the miscibility of the dissimilar polymers with high molecular weights arises from specific interactions between them, such as hydrogen bonding or the formation of a weak charge-transfer complex.[15] Hence, individual chains are expected to relax under a constraint due to such interactions. This constraint may make γ_{AB} equal to 1, resulting in the strongly cooperative relaxation.

Conclusion

The cooperative relaxation in the binary mixtures of dissimilar polymers was confirmed by the simultaneous measurements of stress and birefringence after the uniaxial stretching of the film specimen. In light of the many-body theory, the strong cooperativity seems to arise from two prerequisites; (1) both chains are long enough ($M > M_e$) and (2) the dynamical contacts are mostly between dissimilar polymers. This concept is consistent with the results of recent arguments based on the dynamic Monte Carlo simulations.[16,17]

Acknowledgment. We thank E. Mochida and N. Kiyomoto, ORC Manufacturing Co., Ltd., for the design of the PEM and helpful discussions. We are grateful to H. Nogami, Far East Manufacturing Ltd., for the design of the tensile testing machine.

References and Notes

(1) Saito, H.; Inoue, T. *J. Polym. Sci., Polym. Phys. Ed.* **1987**, *25*, 1629.
(2) Saito, H.; Takahashi, M.; Inoue, T. *J. Polym. Sci., Polym. Phys. Ed.* **1988**, *26*, 1761.
(3) Modine, F. A.; Major, R. W.; Sonder, E. *Appl. Opt.* **1975**, *14*, 757.
(4) Mochida, E. Technical Report of ORC Manufacturing Co., Ltd., 1987.
(5) Kornfield, J. A.; Feller, G. G.; Pearson, D. S. *Macromolecules* **1989**, *22*, 1334.
(6) Aoki, Y. *Polym. J.* **1984**, *16*, 431.
(7) Aoki, Y. *Macromolecules* **1990**, *23*, 2309.
(8) Watanabe, H.; Sakamoto, T.; Kotaka, T. *Macromolecules* **1985**, *18*, 1008.
(9) Edwards, S. F. *Proc. Phys. Soc.* **1967**, *92*, 9.
(10) de Gennes, P.-G. *J. Chem. Phys.* **1971**, *55*, 572.
(11) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818.
(12) Doi, M.; Edwards, S. F. *The Theory of Polymer Dynamics*; Oxford Science Publishers: London, 1986.
(13) Hess, W. *Macromolecules* **1986**, *19*, 1395.
(14) Skolnick, J.; Yaris, R.; Kolinski, A. *J. Chem. Phys.* **1988**, *88*, 1407.
(15) Olabisi, O.; Robeson, L. M.; Shaw, M. T. *Polymer–Polymer Miscibility*; Academic Press: New York, 1979.
(16) Kolinski, A.; Skolnik, J.; Yaris, R. *J. Chem. Phys.* **1987**, *86*, 1567.
(17) Pakula, T.; Geyler, S. *Macromolecules* **1987**, *20*, 2909.