Dielectric Relaxation in Polyisoprene/Poly(vinylethylene)/Toluene Ternary Solutions

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Introduction

The dynamical heterogeneity in miscible blends of polyisoprene (PI)/poly(vinylethylene) (PVE) was studied extensively by many authors[1] and explained recently in terms of a "self concentration model" proposed by Lodge and McLeish.[2] This model assumes that the difference of mobilities of PI and PVE in blends is due to the difference in local concentration arising from the chain connectivity. What happens if a diluent is added to PI/PVE blends? To examine this problem, we carried out dielectric measurements on PI/PVE/toluene (Tol) ternary solutions.

The effective local concentration ϕ_{eff} of a segment A in a blend A/B is given by

$$\phi_{\text{eff}} = \phi_s + (1 - \phi_s)\phi \tag{1}$$

where ϕ_s is the self-concentration and ϕ the average concentration of A.[2] Here all concentrations are given by volume fraction. Lodge and McLeish[2] calculated the values of ϕ_s of PI and PVE to be 0.45 and 0.25, respectively. Since ϕ_{eff} is always higher than average concentration, the components A and B exhibit different effective glass transitions which result in different friction coefficients for motions of the components.

When the blend A/B is diluted, ϕ_{eff} of the A segment may be rewritten by

$$\phi_{\text{eff}} = \phi_s + (1 - \phi_s)C\phi \tag{2}$$

where C is the factor representing the degree of dilution: $C = 1$ for the undiluted state and $C = 0$ for dilute solution. This equation indicates that with decreasing C the relative weight of ϕ_s increases. The strength of self-concentration effects may be assessed by ϕ_{eff} divided by the average concentration. The ratio of the strengths for a diluted blend ("soln") and the undiluted blend ("bulk") is given by $\phi_{\text{eff}}(\text{soln})/C\phi_{\text{eff}}(\text{bulk})$. This value increases with decreasing C, indicating that effects of self-concentration are enhanced by addition of a diluent. Strictly speaking, ϕ_s depends on C since the characteristic ratio changes by polymer−solvent interactions. Here we neglect this effect.

Experimental Section

Narrow distribution samples of PI and PVE were prepared by anionic polymerization in heptane by using *sec*-butyllithium as the initiator. Details of the preparation and characterization of the samples were reported previously.[3] In this study, PI-452 and PVE-602 were used where the code number indicates M_w in kg/mol. Toluene (Tol) with purity higher than 99% was obtained from Wako Pure Chemical Industries (Tokyo, Japan) and used without further purification. The method of dielectric measurements was also reported previously.[3]

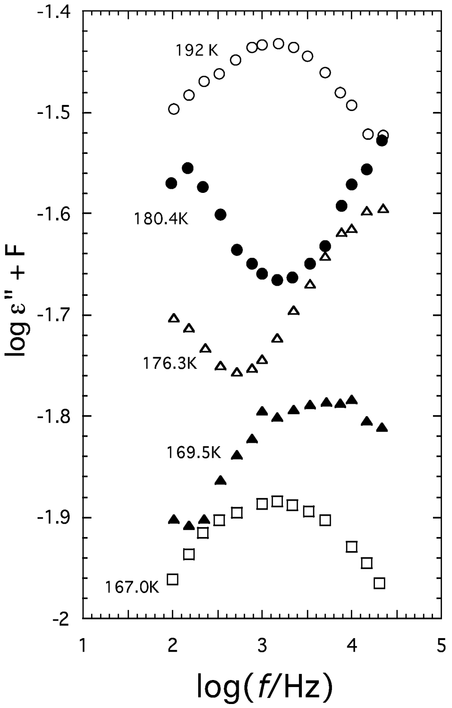

Figure 1. Representative ϵ'' curves of PI-452/PVE-602/Tol (37.5/12.5/50). The curves are shifted upward by $F = 0$, 0.1, 0.2, 0.3, 0.5, and 0.6 for the curves at 167.0, 169.5, 176.3, 180.4, and 192.0 K, respectively.

Results and Discussion

Figure 1 shows the representative ϵ'' curves of 50 wt % toluene solution of PI/PVE(75/25): specifically, the mixing ratio of PI-452/PVE-602/Tol is 37.5/12.5/50 by weight. Here the curves are shifted upward by F to avoid overlapping. At 167 K, a loss peak is seen at log $f = 3$. With increasing temperature this peak shifts to high frequency side. At 180 K the peak shifts to the range of log $f > 4.5$, and at the same time a new loss peak appears at log $f = 2$. At 192 K the newly appeared low-frequency peak is observed in the middle part of our experimental window, but the high-frequency peak locates completely outside of the window. These changes of the loss curves indicate that the relaxation process is bimodal. As reported by many authors, the low- and high-frequency loss peaks are due to segmental motions of PVE and PI, respectively.

From those data, the master curve of ϵ'' has been constructed. Figure 2 compares the master curves of ϵ'' in the segmental relaxation region between undiluted and 50 wt % solution of PI/PVE(75/25). The standard temperature of the undiluted blend is 273 K. For the sake of comparison, the ϵ'' curve for the 50% solution has been shifted so that the loss maximum frequencies of the low-frequency peaks coincide. It is seen that the separation between these peaks for the 50% solution is larger than that for the undiluted blend, indicating effects of dynamic heterogeneity are enhanced by ad-

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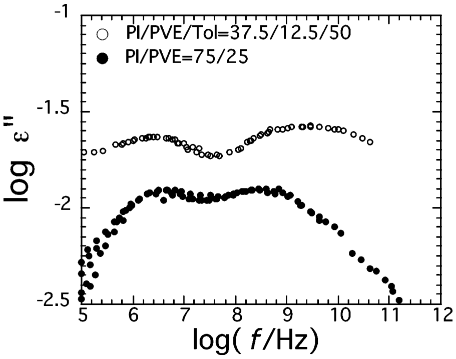

Figure 2. Comparison of the shapes of ϵ'' vs f curves between undiluted PI/PVE(75/25) and 50 wt % toluene solution of PI/PVE(75/25). The solution data are shifted along the abscissa so that the loss maximum frequency for the low-frequency peak coincides with that of the undiluted blend. Also shifted upward along the ordinate by 0.3 decade.

dition of toluene, in agreement with the expectation mentioned above.

Although the present results are consistent with the self-concentration model, the results can be explained alternatively by considering decoupling of cooperative motions. On account of weak interactions between the PI and PVE segments, cooperative motions between them are decoupled, and they move at different rates in the undiluted state. Diluents tend to weaken further the interactions between the PI and PVE segments, and hence decoupling of cooperative motions is enhanced by addition of a diluent. In dilute solution each component moves at different rates depending on the barrier heights for internal rotation of the chains. Therefore, the present result is consistent with the Lodge−McLeish model but does not give a positive evidence of the model.

References and Notes

(1) Haley, J. C.; Lodge, T. P.; He, Y.; Ediger, M. D.; von Meerwall, E. D.; Mijovic, J. *Macromolecules* **2003**, *36*, 6142 and references cited therein.
(2) Lodge, T. P.; McLeish, T. C. B. *Macromolecules* **2000**, *33*, 5278.
(3) Hirose, Y.; Urakawa, O.; Adachi, K. *Macromolecules* **2003**, *36*, 3699.

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