A Connection between the Modification of Solvent Dynamics by Polymer in Polymer Solutions and Component Dynamics in Miscible Polymer Blends

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ABSTRACT: In polymer solutions it has been established both theoretically and experimentally that the relative time scales for polymer and solvent motions are intimately related to the modification of solvent dynamics upon the addition of polymers. Using experimental data of miscible poly(vinylethylene)/polyisoprene blends, we show that a similar relation also holds in polymer blends. That is, the relative time scales for guest polymer and pure host polymer local motions are closely related to the modification of the host polymer dynamics by the presence of guest polymer. Dynamics in blends rich in polyisoprene resemble the behavior seen in Aroclor solutions of polystyrene. On the other hand, dynamics in blends rich in poly(vinylethylene) bear a strong resemblance to properties of Aroclor solutions of 1,4-polybutadiene or polyisoprene. As Gisser and Ediger have shown in Aroclor solutions of different polymers, one value of an adjustable scaling factor sufficed to bring together the rate at which the addition of guest polymer alters the relaxation time of the host polymer and the relative segmental relaxation times of guest and host polymers for both poly(vinylethylene)-rich and polyisoprene-rich blends. The value of the scaling factor for polymer blends is about a factor of 2 smaller than that found by Gisser and Ediger in Aroclor solutions of polymers.

Introduction

The fact that the presence of polymer chains changes the dynamics of the solvent in polymer solutions[1–5] has by now been firmly established by a number of experimental investigations,[6–13] using several different techniques. The mean solvent reorientation time, $\tau_s(c,T)$, can be significantly different from its value, $\tau_s(c=0,T)$, in neat solvent at finite polymer concentration c and temperature T. The ratio of these two times has been found experimentally to be an exponential function of c[6–13]

$$\zeta(c,T) \equiv \tau_s(c,T)/\tau_s(c=0,T) \simeq \exp(Ac) \qquad (1)$$

The coefficient A depends on the polymer and temperature and quantifies the rate at which the addition of the polymer changes the neat solvent reorientation time $\tau_s(c=0,T)$. The polymer solutions most studied have Aroclor 1248, a chlorinated biphenyl, as the solvent. The modifications of solvent dynamics by different polymers such as polystyrene(PS), polyisoprene (PI), 1,2-polybutadiene (1,2-PB), and 1,4-polybutadiene (1,4-PB) have been extensively studied and compared. A is positive for PS, close to zero for one 1,2-PBD[10] and slightly negative for another,[13] and negative for 1,4-PBD and PI. Its magnitude and temperature dependence vary with polymer (see Figure 1). These results are the subject of a recent review by Lodge.[2]

The physical understanding of this interesting effect has been considerably enhanced by recent works by Gisser and Ediger[11,12] which provide information of the mean relaxation time, $\tau_{\mathrm{poly}}(c\rightarrow 0,T)$, of the polymer local dynamics in dilute Aroclor solution from ^{13}C NMR relaxation data. Their results have been summarized as

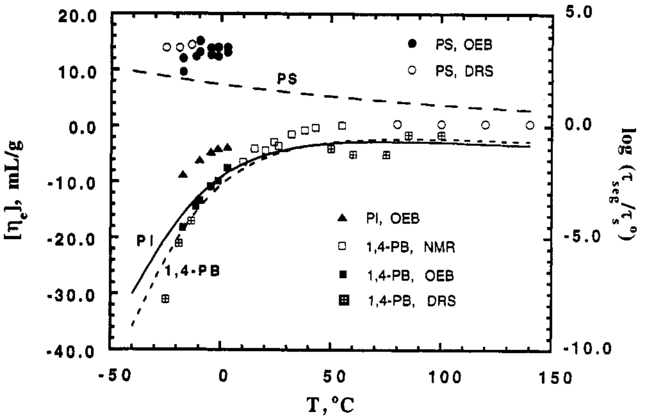

Figure 1. Temperature dependence of the modifications of Aroclor dynamics in polymer/Aroclor solutions (points, left axis) compared with the ratio of time scales for polymer segmental and solvent dynamics (smooth curves from eq 2, right axis). The data points were obtained by oscillatory electric birefringence (OEB), photon correlation spectroscopy (PCS), depolarized Rayleigh scattering (DRS), and nuclear magnetic resonance (NMR). Reproduced from ref 2 with permission.

$$\tau_{\mathrm{poly}}(c\rightarrow 0,T)/\tau_s(c=0,T) \approx (\eta_s{}^{\epsilon} \exp(E_a/kT))/(\eta_s/T) = \eta^{\epsilon-1} T \exp(E_a/kT) \qquad (2)$$

where E_a is the conformational transition energy barrier, η_s is the temperature-dependent shear viscosity for neat Aroclor 1248, and ϵ is an empirical constant. Values of $\epsilon \approx 1$ for PS, 0.41 for PI, and 0.3 for 1,4-PB have been reported. Using experimental values for all the quantities in eq 2, Gisser and Ediger[12] were able to calculate the ratio $\tau_{\mathrm{poly}}(c,T)/\tau_c(c=0,T)$ and find, for each of the three polymers, that it has a temperature dependence similar to that of A in eq 1. In other words

$$A \approx Q \log(\tau_{\mathrm{poly}}(c\rightarrow 0,T)/\tau_s(c=0,T)) \qquad (3)$$

where Q is an adjustable constant. Figure 1, reproduced

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from ref 2 with permission of the author, demonstrates the similar temperature dependences. The left-hand axis of this figure is labeled by the intrinsic effective solvent viscosity, $[\eta_e]$, which is exactly the quantity A here. The discrete points represent A as a function of temperature for Aroclor 1248 solutions of polystyrene, polyisoprene, and 1,4-poly(butadiene) obtained by several experimental techniques. The right-hand axis is labeled by $\log(\tau_{seg}/\tau_s^{\circ})$, which is exactly $\log(\tau_{poly}(c\rightarrow 0,T)/\tau_s(c=0,T))$ used here. The smooth curves represent the relative polymer segmental and solvation relaxation times from eq 3. It is remarkable that one value of Q is all that is needed to achieve correspondence between the two quantities on opposite sides of eq 3. The correspondence is not numerically exact but the trends are reproduced.

The experimental results of Gisser and Ediger indicate that the relative time scales for polymer and solvent motions are intimately related to the modification of solvent dynamics upon addition of the polymers. Such a relation is closely related to a suggestion made earlier by Lodge[14] and independently by Ngai[15] from arguments based on the coupling model.[16,17] Both Lodge and Ngai arrived at the conclusion that the sign and relative magnitude of A depend on the ratio $\tau_{poly}(c,T)/\tau_s(c=0,T)$. Parallel to the application of the coupling model to polymer solutions is the development of a theory for the component dynamics of miscible polymer blends[18-22] based on the same model and using the same concepts of constraint dynamics in mixtures. In polymer blends experimental techniques can resolve the segmental dynamics of one component[19,23] and, in some cases,[22,24] of both components in the blend. A wealth of information of the component dynamics in polymer blends acquired recently from experiments has verified many of the properties expected from the coupling model. Conventionally in the literature the problem of the modification of solvent by polymer in polymer solutions is not discussed in relation to the problem of component dynamics of polymer blends. However, Lodge[2] and Gisser and Ediger[12] have pointed out that such a relation may exist. The coupling model descriptions of both systems are based on essentially the same physics of constraint dynamics of mixtures and hence they come from the same vein. Thus it is interesting to investigate from an experimental standpoint whether the two problems are intimately related as suggested by the theoretical developments from the coupling model. In this work we shall reanalyze recent dielectric and mechanical data[22] of blends of PI with 1,2-PB (also known as poly(vinylethylene) (PVE)) along the lines of polymer solutions as outlined by eqs 1–3. This set of experimental data is chosen because the dynamics of the two components PVE and PI have been resolved, making an analysis of the blend data along the lines of polymer solutions possible. The findings will be reported in the sections to follow.

Correspondence between Polymer Blends and Polymer Solutions

To a large extent the segmental dynamics of miscible polymer blends are similar to those of polymer solutions. Addition of polymer A to polymer B modifies the segmental relaxation dynamics of each, and the dynamics of both components in the blend have been described satisfactorily by the coupling model.[18-22]

First let us make an analogy between polymer solutions in Aroclor and miscible polymer blends, using PVE/PI as an example. In blends richer in PVE, PVE and PI naturally play respectively the role of the "solvent" and the "polymer" of a polymer solution. Through this identification, PVE/PI blends richer in PVE mimic Aroclor solutions of PI, because the T_g of PVE, as with Aroclor, is higher than that of PI. Although we follow conventional wisdom here in using T_g to indicate which blends may correspond to which polymer solutions, these expectations are not guaranteed. Previous studies of polymer solutions including one sample of PVE in Aroclor[13] and poly(methylphenylsiloxane) in BMC[25] have in fact found the unusual situation that addition of a higher T_g component speeds up the solvent dynamics.

The dynamics of the PI component having been resolved, we can calculate the ratio $\tau_{PI}(c_{PI},T)/\tau_{neat\ PVE}(T)$ between the relaxation time of the PI component in the blend to that of neat PVE. This ratio for the blend data is the analog of $\tau_{poly}/\tau_s(c=0,T)$ for Aroclor solutions of PI, i.e.

$$\tau_{PI}(c_{PI},T)/\tau_{neat\ PVE}(T) \Leftrightarrow \tau_{poly}(c,T)/\tau_s(c=0,T) \qquad (4)$$

where $\Leftrightarrow$ is used to denote a correspondence between the two quantities appearing on both sides of the symbol. Similarly, we have the correspondence

$$\partial \ln(\tau_{PVE}(c_{PI},T)/\tau_{neat\ PVE}(T))/\partial c_{PI} \Leftrightarrow A(\text{for Aroclor solution of PI}) \qquad (5)$$

between the quantity on the left-hand side, which we can calculate from the blend data, and the parameter A of the Aroclor solution of PI defined in eq 1. To be clear, here $\tau_{PVE}(c_{PI},T)$ is the relaxation time of the majority PVE component in a blend with concentration of the minority PI equal to c_{PI}.

On the other hand, for blends richer in PI, the natural identification of PI as the "solvent" and PVE as the "polymer" brings them to perfect correspondence with Aroclor solutions of PS, because the T_g of PVE is higher than that of PI, in analogy to the relaxation of PS to Aroclor. From arguments similar to that given in the previous paragraph, we have the following correspondences between quantities of these blends and of the Aroclor solution of PS:

$$\tau_{PVE}(c_{PVE},T)/\tau_{neat\ PI}(T) \Leftrightarrow \tau_{poly}(c,T)/\tau_s(c=0,T) \qquad (6)$$

where $\tau_{PVE}(c_{PVE},T)$ is the relaxation time of the PVE component in blends richer in PI, and

$$\partial \ln(\tau_{PI}(c_{PVE},T)/\tau_{neat\ PI}(T))/\partial c_{PVE} \Leftrightarrow A(\text{for Aroclor solutions of PS}) \qquad (7)$$

where $\tau_{PI}(c_{PVE},T)$ is the relaxation time of the majority PI component in the blend with concentration of the minority PVE equal to c_{PVE} and A is the coefficient A for Aroclor solutions of PS.

An interesting question to ask is whether the quantities for the blends on the left-hand sides of the pair (4) and (5) and of the pair (6) and (7) are related in the same manner as in eq 3 for the corresponding quantities of the Aroclor solutions of polymers shown by Gisser and Ediger.[12] Specifically, the question is: can we find an adjustable scaling factor, Q_{blend}, such that

$$A_{PI} \equiv \partial \ln(\tau_{PVE}(c_{PI},T)/\tau_{neat\ PVE}(T))/\partial c_{PI} \approx Q_{blend} \log(\tau_{PI}(c_{PI},T)/\tau_{neat\ PVE}(T)) \qquad (8)$$

and

$$A_{PVE} \equiv \partial \ln(\tau_{PI}(c_{PVE},T)/\tau_{neat\ PI}(T))/\partial c_{PVE} \approx Q_{blend} \log(\tau_{PVE}(c,T)/\tau_{neat\ PI}(T)) \qquad (9)$$

hold simultaneously? If the answer is in the affirmative, then how does the value of Q_{blend} compare with the Q for Aroclor solutions of polymers? We shall have the answers in the next section.

Results

(a) Blends Richer in PI. In the remainder of this paper we shall focus our attention on blends of PVE and PI. The segmental dynamics of both components in these blends have been studied extensively by dynamic mechanical and dielectric relaxation techniques. The results reported[22] will be reanalyzed in this paper along the lines now generally adopted by workers in the dynamics of polymer solutions,[2,6-13] i.e., evaluations of the parameter A of eq 1, the relative time scales defined by $\tau_{poly}(c,T)/\tau_s(c=0,T)$, and the scaling factor Q in eq 3.

Blends rich in PI can be considered as analogs of Aroclor solutions of PS, with PI and PVE playing the role of Aroclor and PS, respectively. In these blends containing 20 and 25% of PVE, the dynamics of PI and PVE have been resolved by isothermal dielectric relaxation measurements.[22] The two resolved dielectric loss peaks observed enable the relaxation times, $\tau_{PVE}(c_{PVE},T)$ and $\tau_{PI}(c_{PVE},T)$, of the two components to be determined in blends with different concentration of PVE, c_{PVE}, as a function of temperature. Throughout the present work we shall use the Vogel–Fulcher equations obtained from fits to the temperature dependences of the experimentally determined relaxation times of the components instead of the actual experimental data themselves. The Vogel–Fulcher fits to the data allow us to extrapolate the relaxation times to temperatures lower than what were actually measured. The parameters of the Vogel–Fulcher equations were given in a table in ref 22. The ratio $\zeta_{PI}(c_{PVE},T) \equiv \tau_{PI}(c_{PVE},T)/\tau_{PI}(c_{PVE}=0,T)$, where $\tau_{PI}(c_{PVE}=0,T)$ is the relaxation time of neat PI at temperature T, calculated from dielectric data for the PVE/PI blends is the exact correspondent of $\tau_s(c,T)/\tau_s(c=0,T)$ for Aroclor solutions of PS. The limited data indicate that the dependence of $\ln[\zeta_{PI}(c_{PVE},T)]$ on c_{PVE} is also approximately linear, and thus

$$\zeta_{PI}(c_{PVE},T) \equiv \tau_{PI}(c_{PVE},T)/\tau_{PI}(c_{PVE}=0,T) = \exp(A_{PVE}c_{PVE}) \quad (10)$$

The dependence of the coefficient

$$A_{PVE} \equiv \partial \ln(\tau_{PI}(c_{PVE},T)/\tau_{PI}(c_{PVE}=0,T))/\partial c_{PVE} \quad (11)$$

on temperature calculated and shown as the solid curve in the upper part of Figure 2 bears a strong resemblance to A for Aroclor solutions of PS (see Figure 1). Both A_{PVE} and A for Aroclor solutions of PS are positive, have comparable magnitudes, and have mild temperature dependences.

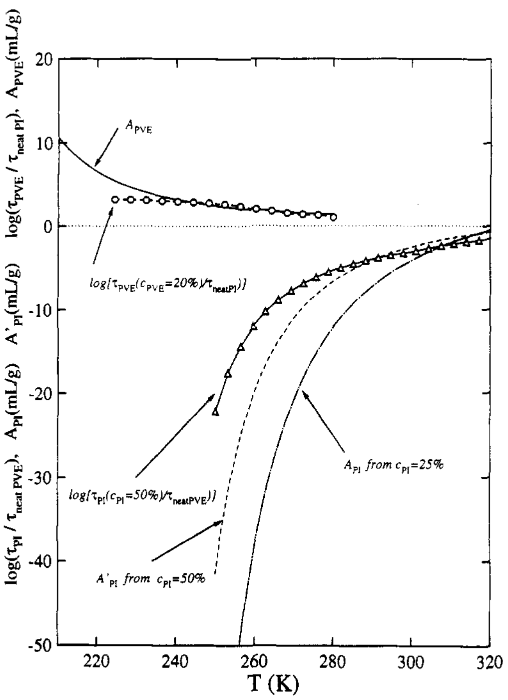

Figure 2. Temperature dependence of the modifications of host polymer segmental dynamics in PVE/PI polymer blends compared with the temperature dependence of the ratio of the time scales of segmental dynamics of guest polymer in the blend and of pure host polymers. The upper part of the figure contains data of PI-rich blends: solid curve represents A_{PVE} vs T, and dashed–beaded curve represents $\log(\tau_{PVE}(c_{PVE},T)/\tau_{PI}(c_{PVE}=0,T))$ vs T. Data in the lower part of the figure are from blends richer in PVE: dashed–dotted curve represents A_{PI} vs T, dashed curve represents A'_{PI} vs T, and the curve defined by a string of triangles represents $\log[\tau_{PI}(c_{PI}=50\%,T)/\tau_{PVE}(c_{PI}=0,T)]$.

Again in PVE/PI blends rich in PI, the difference in time scale, $\log(\tau_{PVE}(c_{PVE},T)/\tau_{PI}(c_{PVE}=0,T))$, obtained for the blends is the correspondent of $\log(\tau_{poly}(c,T)/\tau_s(c=0,T))$ for Aroclor solutions of PS. The dielectric and mechanical spectroscopies used in this work cannot resolve the dynamics of the PVE component in blends with $c_{PVE} < 20\%$. Comparison between the dielectric data for two different blends with c_{PVE} = 20 and 25% (see Figure 9 of ref 22) shows there is little change in $\log(\tau_{PVE}(c_{PVE},T))$ between these two blends. The temperature dependence of $\log(\tau_{PVE}(c_{PVE},T)/\tau_{neat\,PI})$ calculated from the dielectric data is shown also in Figure 2 (dashed–beaded curve in the upper part) and can be approximately represented by an expression of the form $\tau_{PVE}(c_{PVE}=20\%,T) \simeq (89.9)\tau_{PI}(c_{PVE}=0,T) \exp[(24\text{ kJ/mol})/RT]$. This is remarkably similar in form to the relation between τ_{PS} and τ_{Aro} (see eq 2) found by Gisser and Ediger in Aroclor solutions of PS, although we do not take the activation enthalpy of 24 kJ/mol obtained here too seriously to interpret it exactly as a conformation energy barrier. On close examination of Figure 2 to compare $\log(\tau_{PVE}(c_{PVE}=20\%,T)/\tau_{PI}(c_{PVE}=0,T))$ with A_{PVE}, we find these two quantities are roughly equal within a factor of 2 throughout the temperature range displayed. Thus a scaling factor

$$1 \le Q_{blend} \le 2\text{ mL/g} \quad (12)$$

will bring these two quantities into semiquantitative agreement with each other as indicated by eq 9. The Q_{blend} of the polymer blend is smaller than the value of 4 mL/g for Q found by Gisser and Ediger. This discrepancy is most likely due to the fact that we use $\tau_{PVE}(c_{PVE}=20\%,T)$ instead of $\tau_{PVE}(c_{PVE}\rightarrow 0,T)$, which is the exact correspondent of $\tau_{poly}(c\rightarrow 0,T)$ considered in polymer solutions, eq 3, by Gisser and Ediger. Certainly we expect a larger Q_{blend} than that given in eq 12 had we been able to obtain and use $\tau_{PVE}(c_{PVE}\rightarrow 0,T)$ to determine the relative dynamics.

(b) Blends Richer in PVE. PVE/PI blends richer in PVE are the analogs of Aroclor solutions of 1,4-PBD with PVE and PI in the blends playing the part of Aroclor and 1,4-PBD in the polymer solutions, respectively. In these blends, isothermal dielectric data show a single loss peak attributed to segmental dynamics of the majority PVE component. The dynamics of the minority PI component cannot be resolved by dielectric means. From the dielectric data[22] of pure PVE and a blend containing 25% PIP we have calculated the quantity

$$A_{\mathrm{PI}} \equiv \partial \ln(\tau_{\mathrm{PVE}}(c_{\mathrm{PI}},T)/\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=0,T))/\partial c_{\mathrm{PI}} \qquad (13)$$

which gives the modification of the PVE relaxation with the addition of PIP. The dependence of A_{PI} on T is shown as the dashed curve in the lower part of Figure 2. There is a remarkable similarity between the temperature dependence of A_{PI} for the blends in Figure 2 to that of A for Aroclor solutions of 1,4-PB shown in Figure 1. Both A_{PI} and A are negative in sign and undergo large changes in comparable temperature ranges.

Information on the dynamics of the PI component in blends richer in PVE cannot be obtained dielectrically because its contribution is overwhelmed by the host PVE, which has a larger dielectric strength. However, it can be resolved by isothermal dynamic mechanical spectroscopy,[22] in which the contribution of PIP to shear loss modulus can be detected. The mechanical loss peak associated with PI relaxation in a blend with 25% PIP is much broader than the experimental window of less than five decades, making it near impossible to obtain an estimate of $\tau_{\mathrm{PI}}(c_{\mathrm{PI}}=25\%,T)$ at any temperature. The mechanical loss peak associated with the PI component in 50/50 PVE/PI blends is not so broad as in 75/25 PVE/PI to make possible determination of $\tau_{\mathrm{PI}}(c_{\mathrm{PI}}=50\%,T)$ in a range of temperatures and a Vogel–Fulcher fit to the data. We then calculate the relative dynamics by the logarithm of the ratio of the segmental relaxation times of PI in the 50/50 PVE/PI blend and of PVE in neat PVE, i.e.

$$\log[\tau_{\mathrm{PI}}(c_{\mathrm{PI}}=50\%,T)/\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=0,T)] \qquad (14)$$

for a range of temperature. The results are shown in the lower part of Figure 2 as the curve formed by a string of triangles.

Returning to the isothermal dielectric measurements, in blends with $c_{\mathrm{PI}} = 50\%$ dielectric loss data show a loss peak contributed by the PVE component from which we can determine $\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=50\%,T)$. The relaxation times of neat PVE as a function of temperature, $\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=0,T)$, are also known from dielectric measurements. From these two sets of data we calculate the quantity

$$A'_{\mathrm{PI}} = (1/c_{\mathrm{PI}}) \ln[\tau_{\mathrm{PVE}}(c_{\mathrm{PI}},T)/\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=0,T)] \qquad (15)$$

where c_{PI} is 50% but now in eq 15 it is expressed in units of g/mL, in compliance with the convention used in polymer solutions. If there were no deviation of the experimental data from eq 13 even at the high concentration of $c_{\mathrm{PI}} = 50\%$, then A'_{PI} is exactly A_{PI}. From eq 16 the calculated dependence of A'_{PI} on temperature is shown as the dashed curve in the lower part of Figure 2. A'_{PI} is smaller than A_{PI} by less than a factor of 2 throughout this temperature range, and their overall temperature dependences remain similar. At high temperatures both A' and A reach the plateau value of about one. On decreasing temperature, initially there is a slow and then later a rapid decrease in both A'_{PI} and A_{PI} to large negative values. This behavior is remarkably similar to that exhibited in Figure 1 by the parameter A for Aroclor solutions of 1,4-PB.

It is appropriate to compare A'_{PI} of eq 15 with $\log[\tau_{\mathrm{PI}}(c_{\mathrm{PI}}=50\%,T)/\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=0\%,T)]$ of eq 14 because both quantities are determined from experimental data of the blend with $c_{\mathrm{PI}} = 50\%$, particularly when we examine the question of whether there is a scaling factor Q_{blend} that will bring them into agreement with each other, i.e.

$$A'_{\mathrm{PI}} \approx Q_{\mathrm{blend}} \log(\tau_{\mathrm{PI}}(c_{\mathrm{PI}}=50\%,T)/\tau_{\mathrm{PVE}}(c_{\mathrm{PI}}=0,T)) \qquad (16)$$

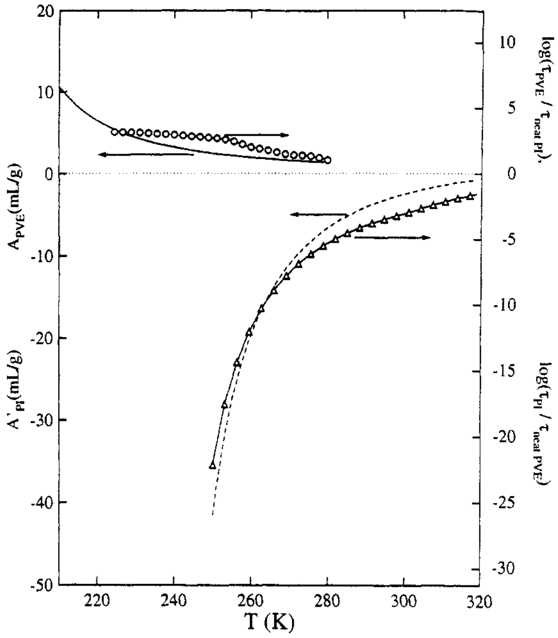

Figure 3. Temperature dependence of the modifications of the host polymer segmental dynamics in PVE/PI polymer blends (A_{PVE} and A'_{PI}, left axis) compared with the ratio of time scales of local segmental dynamics of guest polymer in the blend and of pure host polymer ($\log[\tau_{\mathrm{PVE}}/\tau_{\mathrm{neat\ PI}}]$ and $\log[\tau_{\mathrm{PI}}/\tau_{\mathrm{neat\ PVE}}]$, right axis).

By inspection of the two curves representing these two quantities in Figure 2 we see that eq 16 can be satisfied semiquantitatively over a major part of the temperature region by the choice of a constant Q_{blend} approximately the same as that found for blends rich in PI (see inequalities (12)). In Figure 3 we demonstrate this by the choice of

$$Q_{\mathrm{blend}} \approx 1.6 \text{ mL/g} \qquad (17)$$

This single value of Q_{blend} is sufficient to validate both eqs 8 and 9 at the same time. The value of Q_{blend} is smaller than $Q \approx 4$ mL/g obtained by Gisser and Ediger from data of Aroclor solutions of polymers.[12] The most likely cause of a smaller Q_{blend} is the use of $\tau_{\mathrm{PI}}(c_{\mathrm{PI}}=50\%,T)$ instead of $\tau_{\mathrm{PI}}(c_{\mathrm{PI}}\rightarrow 0,T)$ in eq 16.

Summary and Conclusions

In the preceding sections we have reanalyzed the component dynamics data of the PVE/PIP blends that have been reported in the preceding paper with the purpose of finding out whether there is an exact analogy between two problems: changes in segmental dynamics of components in blends and modifications of solvent dynamics in polymer solutions. PVE and PI in blends rich in PI play respectively the roles of PS and Aroclor in Aroclor solutions of PS. On the other hand, in blends rich in PVE the roles of the components are reversed, with PVE and PI corresponding to Aroclor and 1,4-PB, respectively, in Aroclor solutions of 1,4-PB. After these correspondences between blends and Aroclor solutions of polymers have been established, the analysis of the blend dynamics data remarkably show exactly the same pattern as in Aroclor solutions of polymers as evidenced by comparing Figures 1 and 2.

The coefficient A_{PVE}, which quantifies the rate at which the addition of PVE alters τ_{PI} in PI-rich blends, is found to have a small magnitude and a mild temperature dependence similar to that of the coefficient A for Aroclor solutions of PS. Likewise A_{PI}, which quantifies the rate at which the addition of PI modifies τ_{PVE} in PVE-rich blends, is found to have a large magnitude and a strong temperature dependence similar to that of the coefficient A for Aroclor solutions of 1,4-PB.

The difference in time scales between segmental motion of the guest polymer in a blend and segmental motion of the host polymer in its pure state is the analog of $\log(\tau_{\mathrm{poly}}(c,T)/\tau_{\mathrm{s}})$ for polymer solutions. For PI-rich blends, where PVE is the guest and PI the host, the difference in time scales is $\log(\tau_{\mathrm{PVE}}(c_{\mathrm{PVE}},T)/\tau_{\mathrm{neat\ PI}}(t))$, while for PVE-rich blends, where PI is the guest and PVE the host, the difference in time scales is now $\log(\tau_{\mathrm{PI}}(c_{\mathrm{PI}},T)/\tau_{\mathrm{neat\ PVE}}(T))$. We found these differences in time scales between guest-in-blend and pure host polymer segmental motions are strongly correlated with the changes in host-in-blend segmental relaxation times as the guest polymer concentration increases. Isothermal dielectric and mechanical relaxation data of the component dynamics and extrapolations to wider temperature ranges by using the Vogel–Fulcher equations which fit the experimental data were used to determine the quantities mentioned here. We find that one value of the scaling factor Q_{blend} with the value given by eq 17 can make simultaneously both eqs 8 and 9 to be valid semiquantitatively (see Figure 3). Although the correspondences between experiment and eqs 8 and 9 are not perfect, the broad features are well captured. Thus we have shown all the interesting results found in the modification of solvent dynamics in polymer solutions are reproduced in a polymer blend. This remarkably good correspondence between the experimental results of polymer solutions and polymer blends points to the fact that the underlying physics in both systems is the same. Theory proposed[15,16,18–20,26,27] to explain one problem must satisfy the requirement that it can also explain the other problem. The coupling model[15,16,18–22] is an example of such a theory, although it has not been developed to the stage that it can predict the polymer solution dynamics contained in eqs 8 and 9 quantitatively.

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