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Viscoelastic Properties of Homogeneous Polymer Blends in the Terminal Region

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ABSTRACT: Viscoelastic properties of homogeneous polystyrene/poly(vinyl methyl ether) (PS/PVME) blends were studied in terms of the zero-shear viscosity η^0 and the steady-state compliance J_e. The molecular weight and composition of PS (M_{PS} and ϕ_{PS}) were varied, whereas the molecular weight of PVME (M_{PVME}) was fixed, maintaining the condition $M_{PS} \gg M_{PVME}$. The behavior of η^0 and J_e was discussed as a function of M_{PS} and ϕ_{PS}. In the entangled region, η^0 can be explained by the scaling law, in the same way as in the semidilute polymer solutions, if $\phi_{PS} < 0.25$. The magnitudes of J_e and its M_{PS} and ϕ_{PS} dependences are comparable to those of polymer solutions in the nonentangled region. Therefore, it is concluded that the viscoelastic properties of homogeneous PS/PVME blends in the terminal region studied here are very similar to those of the polymer solutions if $M_{PS} \gg M_{PVME}$.

Introduction

Polymer blends can be classified into two regions, i.e., the homogeneous (one-phase) and phase-separated (two-phase) regions according to phase diagrams, and their viscoelastic properties exhibit different characteristics in these two regions.[1] Recently, moreover, the influence of flow field on the miscibility of polymer blends in the vicinity of phase separation has been extensively studied.[1−6] For further understanding the last problem, too, the viscoelastic properties of polymer blends in both the one- and two-phase regions, must be clarified.

In the one-phase region, the viscoelastic properties are determined by the composition ϕ and molecular weight M of the component polymers. Therefore, it is important to employ component polymers with narrow molecular weight distributions whose viscoelastic properties are well known. The simplest case of polymer blends is the binary blend of the same homopolymers (homopolymer blends), such as narrow molecular weight distribution polystyrenes with two different molecular weights, M_1 and M_2. The viscoelastic properties of homopolymer blends have been extensively studied, and the M_1 and M_2 dependences as well as the composition dependence have been elucidated.[7,8]

On the other hand, most viscoelastic studies of binary blends of different kinds of polymer have dealt with only the composition dependence, though a few works have examined the molecular weight dependence.[9,10]

There exist two kinds of interactions which may affect the viscoelastic properties of binary blends of different kinds of polymer: local nematic effects[11] and excluded volume effects.[12] To understand the viscoelastic properties of polymer blends in the one-phase region, therefore, we should carry out systematic studies on the molecular weight and composition dependences, considering the role of the above two effects.

Studies on local nematic effects[13−15] have revealed that the effects do not influence the longest relaxation process if the molecular weights of both components are much different as in this work.[15] On the other hand, the role of excluded volume effects in the viscoelastic properties of polymer blends has not been elucidated.

In this work, therefore, we examined the viscoelastic properties of polystyrene/poly(vinyl methyl ether) (PS/PVME) blends in terms of the zero-shear viscosity η^0 and the steady-state compliance J_e by varying the molecular weight and volume fraction of PS (M_{PS} and ϕ_{PS}), while the molecular weight of PVME (M_{PVME}) was fixed. In these blend samples, $M_{PS} \gg M_{PVME}$ was always preserved. According to studies on homopolymer blends,[8,16,17] PS/PVME blends,[18] and the PS/PVME/dibutyl phthalate system,[10,19] in which the molecular weight of one component is always much larger than that of the other, their viscoelastic properties in the terminal region are dominated by the component with the larger molecular weight. Therefore, we may discuss η^0 and J_e of the blends in terms of M_{PS} and ϕ_{PS}. For relatively low PS contents, moreover, excluded volume effects exist,[12] so that the region where PS chains overlap each other but PS contents are low corresponds to the semidilute region of polymer solutions.

As reported previously,[20−22] the zero-shear viscosity of polymers in the semidilute region where the concentration is lower than 0.2 g/cm^3 can be well explained by the following scaling law (1) if we use the empirical molecular dependence $\eta^0 \propto M^{3.4}$, though the applicability of the scaling law to self-diffusion coefficients in solutions may be questionable.[23−26]

$$\eta^0_{\ sp} \propto (C[\eta])^{3.4/(3\nu-1)} \tag{1}$$

It is to be noted that we should use high molecular weight samples to realize the semidilute region in polymer solutions and that the crossover concentrations from the dilute to the semidilute region depends on the physical properties of the polymers. In this work, therefore, we studied the viscoelastic properties of PS/PVME blends where the volume fraction of PS (ϕ_{PS}) is lower than about 0.2 in comparison with those of semidilute polymer solutions.

If the local friction coefficient varies with ϕ so as to give rise to the change in the glass transition temperature T_g, the viscoelastic data should be compared at the same free volume state. In PS/PVME blends, however, T_g remains almost constant up to around $\phi_{PS} = 0.20$[9] and the WLF equation for $\phi_{PS} = 0.20$[5] agrees with that of PVME.[27] Thus we can discuss our data at a constant temperature so as to reduce the ambiguity in the data analysis.

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Table 1. Molecular Characteristics of PVME and Polystyrenes

code	M_w	M_w/M_n
PVME	3.7×10^4	1.32
F-20	1.90×10^5	1.04
F-40	3.55×10^5	1.02
F-80	7.1×10^5	1.05
F-128	1.26×10^6	1.05
F-380	3.84×10^6	1.04

Experimental Section

The PVME sample was kindly supplied by BASF Japan Ltd. as a 70% toluene solution. The sample was fractionated in the same way as in a previous paper.[27] The weight-average molecular weight M_w and the molecular distribution M_w/M_n of the final fraction of PVME were determined by GPC, using a PVME calibration curve, and they are listed in Table 1. The zero-shear viscosity η^0 ($\log \eta^0 = 2.80$) and steady-state compliance J_e ($\log J_e = -5.97$) of this PVME sample at 80.6 °C almost agree with the data in the previous work.[27] The molecular weight between entanglements M_e of PVME was determined to be $1.2_4 \times 10^4$,[27] so that the PVME used in this study may be slightly entangled.

The PS samples used in this study were TOSOH standard polystyrenes with narrow molecular weight distributions: F-20, F-40, F-80, F-128, and F-380. The molecular characteristics of the PS samples are listed in Table 1.

The blend samples were prepared as follows: first, the prescribed amounts of PS and PVME were dissolved in benzene to give 5% polymer solutions. Then the uniform solutions were freeze-dried for 12 h at room temperature and dried for 12 h at ~80 °C under vacuum. If necessary, the samples were molded into disks of suitable size for the geometry of the rheometer.

Viscoelastic properties of the blends were measured in oscillation flow by using a Type RMS-800 (Rheometrics Inc.) mechanical spectrometer with a parallel plate geometry with a 2.5 cm diameter.

The measurements were carried out at several temperatures between 50 and 100 °C, always keeping the samples at temperatures lower than the phase separation temperatures. A few samples with high M_{PS} and high ϕ_{PS} were measured in steady flow by using a cone and plate geometry with a 2.5 cm diameter and 0.1 rad cone angle at 80.6 °C because their viscosities were too high to be measured in oscillation flow.

Dry nitrogen gas was introduced in the temperature control system of the RMS-800 to prevent the oxidation of PVME and also the absorption of moisture.

Results

All the dynamic shear moduli can be superimposed to generate master curves with respect to temperature for each M_{PS} and ϕ_{PS}. Figure 1 shows examples of the temperature dependence of the shift factor a_T for PS/PVME blends with various M_{PS} and ϕ_{PS}, where the reference temperature T_r is 80.6 °C. The solid line denotes the WLF equation 1 for PVME,

$$\log a_T = -C_1(T - T_r)/\{C_2 + (T - T_r)\} \qquad (2)$$

where C_1 and C_2 were determined to be 4.01 and 136.9, respectively.[27] Apparently, all the blend data are well represented by this equation within experimental error. Thus we can discuss the viscoelastic properties of the PS/PVME blends at a constant temperature (80.6 °C).

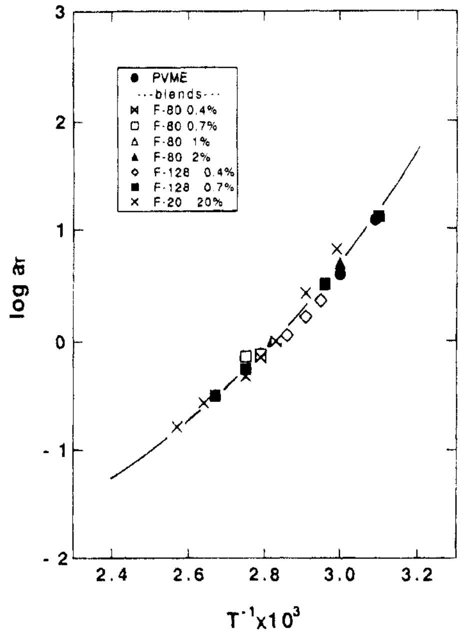

Figure 1. Temperature dependence of shift factor a_T. The reference temperature is 80.6 °C. The solid line represents the WLF equation for PVME, $\log a_T = -4.01(T - T_r)/(136.9 + T - T_r)$.

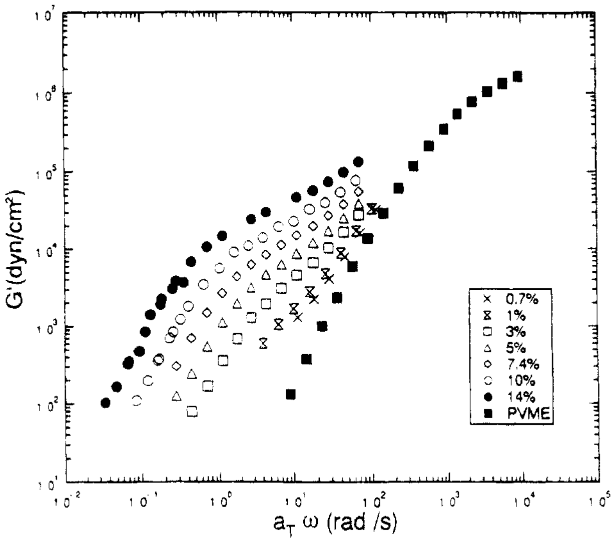

Figure 2. Examples of double-logarithmic plots of G' vs $a_T\omega$ for the blends of F-40 with different compositions. The data are shifted to the reference temperature, 80.6 °C.

Figures 2 and 3 show master curves of the storage modulus G' and the loss modulus G'' for F-40 blends with different compositions, respectively, shifted to the reference temperature 80.6 °C by using eq 2. It is noticed that the wedgelike shoulders appear at low frequencies, which become more prominent as ϕ_{PS} increases. These tendencies are qualitatively the same as those of homopolymer blends[7,8] and the PS/PVME/dibutyl phthalate system.[10] The low-frequency ends of the data reflect the relaxation of polystyrene, the longer chain. The slopes of G' and G'' at low frequencies are 2 and 1, respectively, so we can evaluate the zero-shear viscosity η^0 and the steady-state compliance J_e by using the following equations:

$$\eta^0 = \lim_{\omega \to 0}(G''/\omega) \qquad (3)$$

$$J_e = A_G/(\eta^0)^2 \qquad (4)$$

with $A_G = \lim_{\omega \to 0}(G'/\omega^2)$, where ω is the angular frequency.

To discuss the viscosity in terms of M_{PS} and ϕ_{PS}, the specific viscosity $\eta^0{}_{sp}$ is defined by

$$\eta^0{}_{sp} = (\eta^0 - \phi_{PVME}\eta^0{}_{PVME})/\eta^0{}_{PVME} \qquad (5)$$

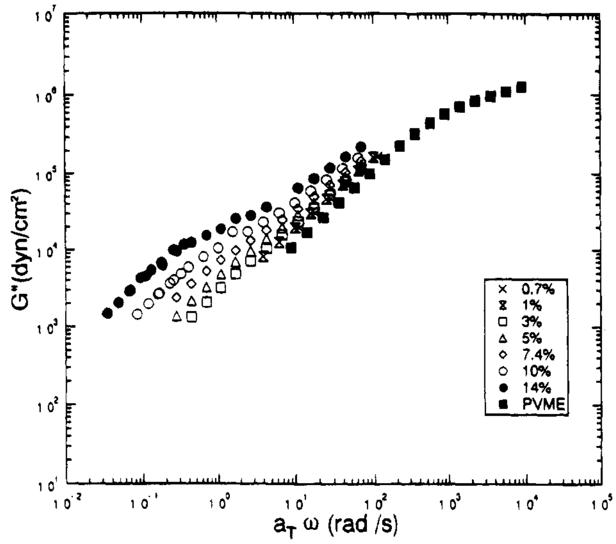

Figure 3. Examples of double-logarithmic plots of G'' vs $a_T\omega$ for the blends of F-40 with different compositions. The reference temperature is 80.6 °C.

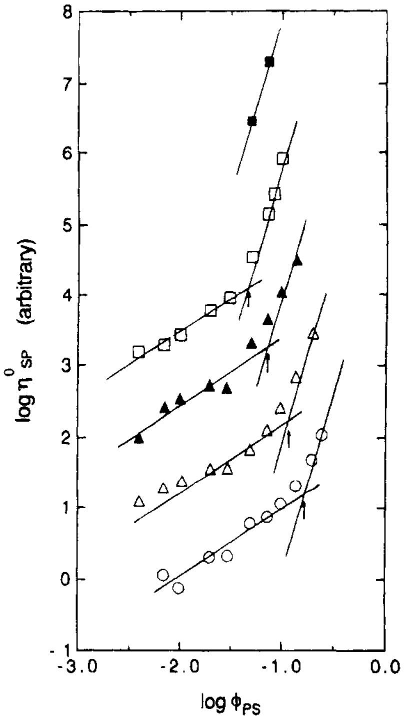

Figure 4. ϕ_{PS} dependence of η^0_{sp} for the blends of F-20 (○), F-40 (△), F-80 (▲), F-128 (□), and F-380 (■). The data of the blends of F-40, F-80, F-128, and F-380 are vertically shifted for clear representation. The arrows denote the critical volume fraction ϕ^*_{PS}.

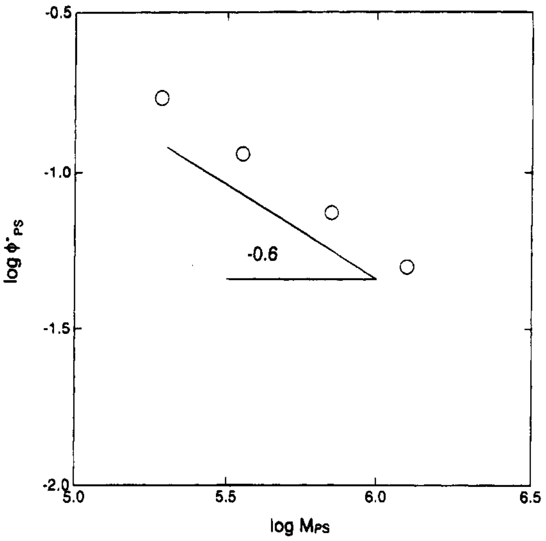

Figure 5. M_{PS} dependence of ϕ^*_{PS} determined in Figure 4. The solid line represents $\phi^*_{PS} \propto M_{PS}^{-0.6}$.

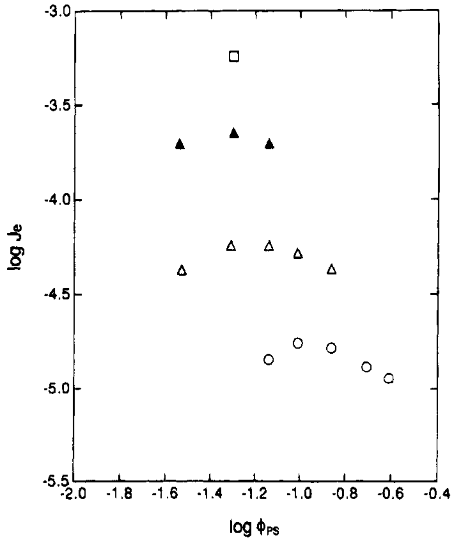

Figure 6. ϕ_{PS} dependence of J_e. Symbols are the same as in Figure 4.

where ϕ_{PVME} and η^0_{PVME} are the volume fraction and the zero-shear viscosity of PVME. Figure 4 shows the ϕ_{PS} dependence of η^0_{sp}. The figure reveals that the ϕ_{PS} dependence changes dramatically at a certain volume fraction denoted as ϕ^*_{PS}, which is determined as a crossing point of the different composition dependences in the low- and high-concentration regions. Here, we assumed that the composition dependences are independent of molecular weight in both regions. Comparing this result with the behavior of homopolymers, it is natural to say that ϕ^*_{PS} is the critical volume fraction at which PS chains begin to entangle with each other. That is, PS chains are isolated from other PS chains at $\phi_{PS} < \phi^*_{PS}$, while PS chains are entangled with each other at $\phi_{PS} > \phi^*_{PS}$. Hereafter, we call the former and the latter the "dilute" and "entangled" regions for η^0, respectively.

In the dilute region, the viscosity behavior may be similar to that in dilute polymer solutions.[28] As can be seen in Figure 4, however, the data in the dilute region are scattered so that we cannot discuss them in comparison with the dilute solution data. Therefore, we limit our discussion to the entangled region.

Figure 5 shows double-logarithmic plots of ϕ^*_{PS} against M_{PS}. The molecular weight dependence ϕ^*_{PS} determined from this figure is

$$\phi^*_{PS} \propto M_{PS}^{-0.6} \qquad (6)$$

where the absolute value of the exponent is smaller than those in homopolymer blends[8,16,17] and concentrated solutions of low molecular weight homopolymers[21,28] ($\phi^* \propto M^{-1}$).

Figure 6 shows double-logarithmic plots of J_e against ϕ_{PS}. The feature of this figure is practically the same as that reported for polymer solutions in the nonentangled region of J_e;[22,28,30,31] J_e shows a broad maximum at lower ϕ_{PS}, implying the transition between Rouse-like and Zimm-like behavior,[28,30] while J_e appears to be proportional to ϕ_{PS}^{-1} at higher ϕ_{PS}. Here, it should be

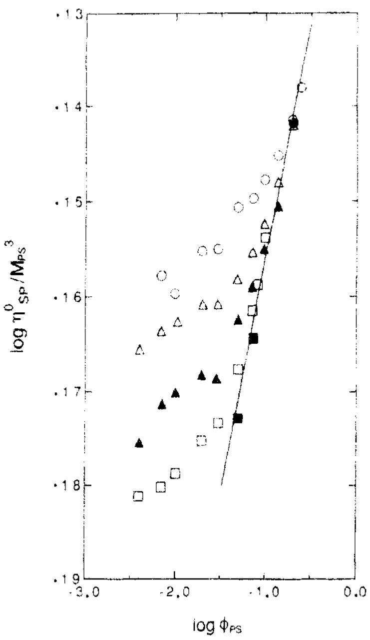

Figure 7. Double-logarithmic plots of $\eta^0{}_{sp}/M_{PS}{}^3$ vs ϕ_{PS}. The filled circle represents the datum of the blend F-20/PMVE (M_w = 40000) = 20/80.[24] Other symbols are the same as in Figure 4.

noted that the contribution of PVME on G' in the terminal region is negligible.

Discussion

The crossover from the dilute to the semidilute region of polymer solutions occurs at a certain degree of coil overlapping C/C^*.[21,22] Here, the critical concentration C^* at which polymer coils begin to overlap is defined by

$$C^* = 3M/4\pi\langle S^2\rangle^{3/2}N_A \tag{7}$$

where $\langle S^2\rangle$ is the mean square radius of gyration and N_A is Avogadro's number. Since $\langle S^2\rangle$ depends on molecular weight as $\langle S^2\rangle \propto M^{2\nu}$, where ν is the excluded volume exponent, eq 7 can be written as

$$C^* \propto M^{1-3\nu} \tag{8}$$

Consequently, the exponent of the molecular weight dependence of C^* varies with ν from -0.5 (Θ solvent; ν = 0.5) to -0.8 (good solvent; $\nu = 0.6$). It is to be noted that the exponent in eq 6 is between them.

As mentioned in the Introduction, it is reported that excluded volume effects exist in PS/PVME blends,[12] and thus the $M_{PS}{}^{-0.6}$ dependence of $\phi^*{}_{PS}$ may be due to excluded volume effects. If we assume that the same equation as eq 8 holds for $\phi^*{}_{PS}$, we have $\nu = 0.53$, which is an average value around the reference temperature, 80.6 °C, though. This value is very close to the value reported by Jelenic et al.[12] ($\nu = 0.52$), though they used deuterated PS instead of the ordinary PS used here.

Since the molecular weight dependence of the crossover concentration for the viscosity of PS/PVME blends is similar to those of polymer solutions as discussed above, we examine the applicability of scaling law[29] to the viscosity of polymer blends. To construct a scaling law to predict the volume fraction dependence of polymer blends, we determine the empirical molecular weight dependence of viscosity.

Figure 7 shows double-logarithmic plots of $\eta^0{}_{sp}/M_{PS}{}^3$ vs ϕ_{PS}, where the filled circle denotes the datum for PS/PVME blends,[5] in which PS is the same as in the other blends, but the molecular weight of PVME ($M_w = 4.0 \times 10^4$) is slightly different. If $\eta^0{}_{sp}/M_{PS}{}^{3.4}$ is plotted instead of $\eta^0{}_{sp}/M_{PS}{}^3$, the composition dependence in the entangled region is rather scattered. Thus we may assume that $\eta^0{}_{sp}$ of blends in the entangled region is proportional to $M_{PS}{}^3$.

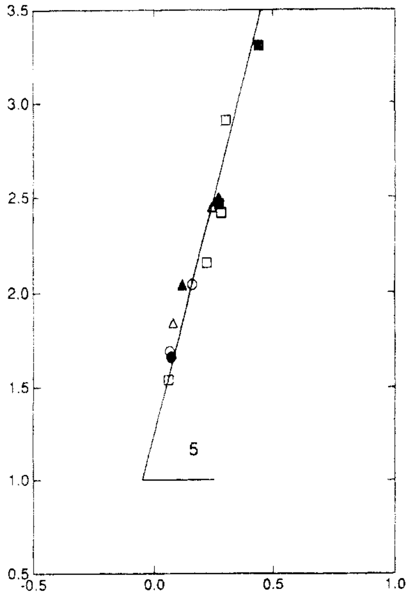

Figure 8. Double-logarithmic plots of $\eta^0{}_{sp}$ vs $\phi_{PS}/\phi^*{}_{PS}$. The solid line represents $\eta^0{}_{sp} \propto \phi_{PS}{}^5$ which is predicted by the scaling law. Symbols are the same as in Figure 7.

$$\eta^0{}_{sp} \propto M_{PS}{}^3 \tag{9}$$

Using eq 9 and the scaling method of de Gennes, we have the following equation for $\eta^0{}_{sp}$:

$$\eta^0{}_{sp} \propto (\phi_{PS}/\phi^*{}_{PS})^{3/(3\nu-1)} \tag{10}$$

where we assumed the same relationship for $\phi^*{}_{PS}$ as that for C^* in eq 8. Using the ν value described above (ν = 0.53), we can predict that $\eta^0{}_{sp}$ is proportional to $\phi_{PS}{}^5$. Figure 8 shows the double-logarithmic plots of $\eta^0{}_{sp}$ vs $\phi_{PS}/\phi^*{}_{PS}$ in the entangled region, where $\phi^*{}_{PS}$ of F-380 was evaluated by extrapolation to $M_{PS} = 3.84 \times 10^6$ in Figure 5. The solid line in the figure represents the predicted volume fraction dependence, $\eta^0{}_{sp} \propto \phi_{PS}{}^5$. Apparently, all the data fall on the solid line, so that the scaling law is valid to understand the viscosity of PS/PVME blends in the entangled region where $\phi_{PS} <$ 0.25, though the exponent in eq 10 is slightly different from that in eq 1 for polymer solutions.

Finally, we briefly discuss the steady-state compliance J_e. Figure 9 shows double-logarithmic plots of the reduced steady-state compliance, J_{eR}, against $\phi_{PS}M_{PS}$, where $J_{eR} = (J_e\phi_{PS}RT/M_{PS})[\eta^0/(\eta^0 - \eta^0{}_{PVME})]^2$. The solid and broken lines show the data for PS solutions in the nonentangled (Rouse) and entangled regions for J_e, respectively.[22] This figure indicates that all the J_{eR} values of the present polymer blends are comparable to those of polymer solutions in the nonentangled region.

From the above results we conclude that if $\phi_{PS} < 0.25$ and $M_{PS} \gg M_{PVME}$, the viscoelastic properties of PS/PVME blends are very similar to those of polymer solutions; $\eta^0{}_{sp}$ in the entangled region can be explained by the scaling law which is valid for semidilute polymer

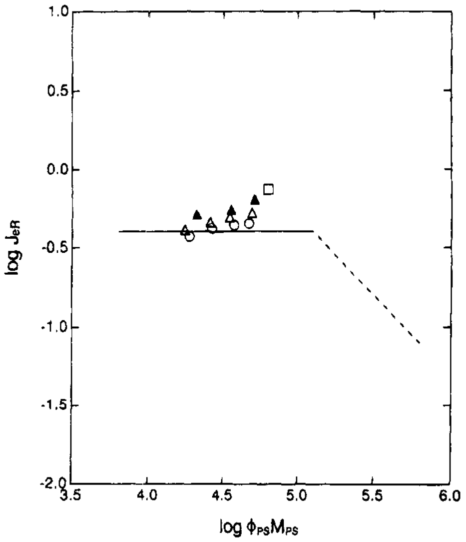

Figure 9. Double-logarithmic plots of J_{eR} vs $\phi_{PS}M_{PS}$. The solid and broken lines show the data of polystyrene solutions in the nonentangled and entangled regions,[23] respectively. Symbols are the same as in Figure 4.

solutions and J_{eR} is comparable to that of polymer solutions in the nonentangled regions for J_e.

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