Macromolecules **2002,** *35,* 9169−9175

Viscoelasticity of Polymers in Θ Solvents around the Semidilute Regime

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Received May 31, 2002

ABSTRACT: The complex shear modulus, G^*, was studied for polystyrene solutions in dioctyl phthalate (DOP); temperature = 22 °C (Θ) ∼ 50 °C; concentration = 59 kg m^{-3}; molecular weight range 200−20 000 kg mol^{-1}. The data were compared with those for PS in a good solvent, tricresyl phosphate (TCP). The solvent viscosity of the two neat solvents was found to be the same within experimental accuracy in the range of studied temperatures. For high-M samples, the rubbery plateau modulus of the two systems, in Θ and good solvents, agrees with each other. This result is inconsistent with the prediction of the original scaling theory, which predicts a lower rubber plateau modulus in a Θ solvent, but agrees well with the two-parameter scaling theory by Colby and Rubinstein [*Macromolecules* **1990**, *23*, 2753]. The location of the terminal flow region was almost the same for low-M samples, $M < M_e$. However, with increasing M, the terminal flow region in DOP was located at lower frequencies than in TCP. These results indicate that G^* in Θ and good solvents cannot be described with a universal function of $N_e = M/M_e$, as is usually assumed in scaling theories. We speculate that larger concentration fluctuation in Θ solutions may retard the entanglement dynamics.

Introduction

Viscoelastic properties of polymer solutions have long been studied extensively by many researchers. Owing to these efforts, effects of solvent quality on viscoelastic properties have been established for infinitely dilute solutions.[1−3] The basic idea for understanding effects of solvent quality for infinitely dilute solutions is chain dimension. The molecular weight, M, dependence of the radius of gyration, $\langle R_g^2\rangle$, in the infinitely dilute limit can be expressed as follows:

$$\langle R_g^2\rangle \sim M^{2\nu} \tag{1}$$

Here, ν is a characteristic exponent, $^1/_2$ in Θ solvents and $\sim^3/_5$ in good solvents. Viscoelastic properties of infinitely dilute polymer solutions can be interpreted through ν. For example, the molecular weight dependence of the intrinsic viscosity and frequency dependence of the intrinsic complex shear modulus can be related to ν.[4]

On the other hand, viscoelastic properties of semidilute solutions in Θ solvents are less understood compared with those in good solvents. For semidilute solutions, zero-shear viscosity, η, of well-entangled systems can be written as $\eta \sim M^\alpha$, where $\alpha = 3.4-3.6$.[5] Onogi and Masuda showed that concentration dependence of viscosity at a fixed molecular weight can be shifted on one curve with shift a factor C_C.[6] The molecular weight dependence of the shift factor, C_C, can be related to ν.

$$C_C \sim M^\nu \tag{2}$$

This result suggested that overlap of polymer coils is the origin of entanglement. This idea was succeeded by scaling theory proposed by de Gennes.[7] According to his scaling theory, the zero-shear viscosity and the rubbery plateau modulus, G_N, are assumed to be written with a universal function of the chain overlap ratio, c/c^*.

$$\eta \sim f(c/c^*) \sim M^\alpha c^{\alpha/(3\nu-1)} \tag{3}$$

$$G_N \sim c/M_e \sim g(c/c^*) \sim M^0 c^{1+1/(3\nu-1)} \tag{4}$$

Here, M_e is the entanglement molecular weight. c^* is the overlap concentration, which can be related to the intrinsic viscosity through the equation:

$$c^* \sim 2.5/[\eta] \sim M^{1-3\nu} \tag{5}$$

Equation 4 shows that, for the rubbery plateau modulus in a Θ solvent, $G_N \sim c^3$ ($\nu = {}^1/_2$) would be larger than that for good solvent systems, $G_N \sim c^{2.25}$ ($\nu = {}^3/_5$). Thus, once one assumes that the zero-shear viscosity or the rubbery plateau modulus can be written as a universal function of c/c^*, then this assumption leads us to the relationship, $M_e(\Theta) > M_e(\text{good})$.

The validity of the above scaling theory was examined by Takahashi et al.[8,9] They showed that concentration dependence of the zero-shear viscosity can be well described with the scaling theory. However, they also reported that the effect of solvent quality on the steady-state compliance, J_e, is smaller than expected by the scaling theory.

The inconsistency between the theory and experimental results was discussed by Colby and Rubinstein.[10] They proposed a new scaling theory considering the presence of two characteristic lengths: the correlation length for concentration fluctuation, ξ, and the tube diameter, a, which is responsible for entanglements. In good solvents, the tube diameter scales with the same way as ξ. However, in Θ solvents, the tube diameter follows a different scaling law from that for ξ. The new theory predicts that the rubbery plateau modulus is insensitive to solvent power. The experimental results on polybutadiene agrees well with the theory.[11] Later, Adam et al. extended this idea to derive a scaling law

10.1021/ma020849v CCC: $22.00

Table 1. Molecular Weight and Polydispersity Index for Polystyrene Samples

			c^*/kg m^{-3}	
PS code	M_w/10^3 kg mol^{-1}	M_w/M_n	Θ^a	good^b
F20	0.190	1.04	72	35
F40	0.427	1.02	48	19
F80	0.706	1.05	37	13
F128	1.09	1.08	30	9.5
F288	2.89	1.09	18	4.5
F550	5.48	1.15	13	2.8
F850	8.42	1.17	11	2.1
F2000	20.6	1.2	6.9	1.0

[a] Calculated from eq 5 with $[\eta] = 8.0 \times 10^{-2}$ M$^{-1/2}$ (ref 13). [a] Calculated from eq 5 with $[\eta] = 7.8 \times 10^{-3}$ M$^{-0.75}$ in benzene (ref 30).

for the temperature dependence of viscosity considering the effect of local viscosity.[12]

However, from an experimentalist's view, very limited data are available for the complex shear modulus, $G^*(\omega)$, at Θ temperature.[11] As far as we know, detailed comparison of $G^*(\omega)$ data in good solvents and Θ solvent have not been performed. In the present paper, we report G^* for polystyrene, PS, in dioctyl phthalate, DOP, and in tricresyl phosphate, TCP. DOP is a Θ solvent ($T_\Theta = 22$ °C) for PS, and TCP is a good solvent for PS. We will show that the rubbery plateau modulus is insensitive to solvent quality. On the other hand, the frequency dependence of G^* in the terminal flow region is not the same: G^* of a well-entangled system in DOP is broader than that for the TCP solution having the same molecular weight and concentration. As a result, the viscosity of the DOP solution shows stronger molecular weight dependence than in TCP. A possible explanation for this unexpected behavior is a large concentration fluctuation characteristic for Θ solutions. The present result indicates that some modification is needed for describing the viscoelasticity of polymers in Θ solvents.

Experimental Section

Materials. Polystyrene samples with sharp molecular weight distribution were purchased from Toso Co., Ltd. Molecular weight and polydispersity index of polystyrenes are summarized in Table 1. The Θ solvent for PS, dioctyl phthalate, and good solvent, tricresyl phosphate, were purchased from Nakarai Chemicals Co. and used as supplied. The Θ temperature of the polystyrene/DOP system is reported as 22 °C.[13] Most of measurements were performed at 59 kg m^{-3}. Weighed amounts of polymer and solvent were homogeneously mixed by addition of dichloromethane, and the latter was removed completely at 50 °C and lowered pressure. In evaluating volume fraction, the density of polystyrene and the two solvents are respectively $\rho_{PS} = 1.06$, $\rho_{DOP} = 0.9843$, and $\rho_{TCP} = 1.16$ g/cm^{-3}.

Measurements. A standard rheometer (ARES; Rheometrics Scientific Far East) was used for all the measurements. A cone–plate fixture with 25 mm diameter was used. The complex modulus was measured over a temperature range from 298.65 to 323.15 K.

Results

Viscosity of Solvents. Figure 1 shows the temperature dependence of solvent viscosity of neat DOP and TCP. Fortunately, the viscosity of the two solvents agreed with each other in the studied temperature range. In the following discussion, we compare data for TCP and DOP solutions at the same temperature and ignore the difference in viscosity of solvents.

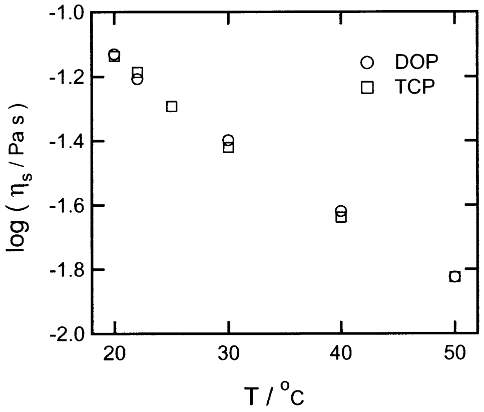

Figure 1. Temperature dependence of viscosity of the solvents, DOP and TCP.

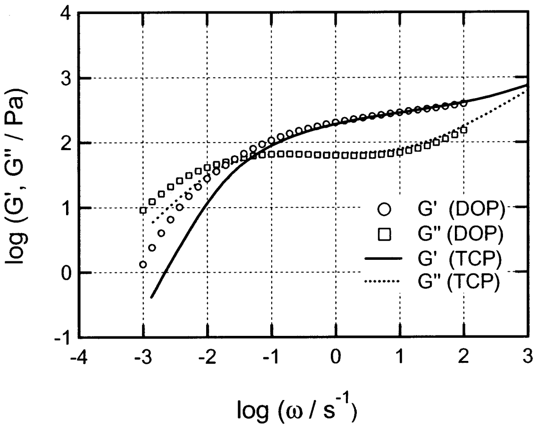

Figure 2. Comparison of G^* of F550 in DOP and TCP at 22 °C (Θ temperature for DOP) at $c = 59$ kg/m^{-3}. For TCP solution, data at ω/s^{-1} > 100 were obtained from the data at lower temperatures by using the method of reduced variables.

Comparison of G^* for Well-Entangled DOP and TCP Solutions. Figure 2 shows G^* of F550 in DOP with $c = 59$ kg m^{-3} at 22 °C (Θ temperature). Also included is the result for the TCP solution having the same volume fraction at the same temperature. The method of reduced variables (frequency–temperature superposition)[14] was used for TCP data measured at different temperatures.

First of all, we should note that the plateau modulus is identical for the two solutions.

$$G_N(\text{good}) \sim G_N(\Theta) \tag{6}$$

The G_N value can be determined by fitting of G^* with the equation composed of the bead–spring terms, $G^*_{BS}(\omega)$, and the entanglement terms, $G^*_{en}(\omega)$.

$$G^*(\omega) = G^*_{en}(\omega) + G^*_{BS}(\omega) + i\eta_\infty\omega \tag{7}$$

Here, η_∞ represents the effective solvent viscosity. $G^*_{BS}(\omega)$ was calculated assuming the Rouse–Zimm theory.[4]

$$G^*_{BS} = \frac{cRT}{M}\sum_i \frac{i\omega\tau_i}{1 + i\omega\tau_i} \tag{8}$$

$$\tau_p = \tau_R p^{-\beta} \tag{9}$$

In this calculation, β was 2. A more detailed description and an example of this fitting procedure were published elsewhere.[15] G_N can be calculated from $G^*_{en}(\omega)$[16]

$$G_N = \frac{2}{\pi}\int_{-\infty}^{\infty} G''_{en}(\omega)\ \mathrm{d}\ln\omega \qquad (10)$$

M_e thus calculated was 454 kgmol^{-1} following the equation $M_e = cRT/G_N$. This value is consistent with the calculated value using empirical equations for concentration dependence of M_e for good solvents, M_e/kg mol^{-1} = $7300\phi^{-1.4} = 422$[17] and M_e/kg mol^{-1} = $10200\phi^{-1.3} = 441$.[15] Thus, we may conclude that M_e is insensitive to solvent power. This result is in accord with that for polybutadiene systems.[11]

Second, we should discuss the difference in the frequency span of the rubbery plateau region. G^* of the two solutions is approximately identical at high frequencies where G' is proportional to $\omega^{1/2}$, which is characteristic for the Rouse mode. The agreement of G^* in the Rouse region suggests that the longest Rouse relaxation time, τ_R, of the two solutions would be comparable:

$$\tau_R(\mathrm{good}) \sim \tau_R(\Theta) \qquad (11)$$

A detailed comparison shows the Rouse mode ($G' \sim \omega^{1/2}$) in the Θ solvent locates at slightly higher frequencies. On the other hand, it is obvious that the terminal flow region of the DOP solution locates at lower frequencies. The averaged relaxation time, τ_w, for the Θ solution is larger than that for the good solution.

$$\tau_w(\mathrm{good}) < \tau_w(\Theta) \qquad (12)$$

Consequently, the ratio of the weight-averaged relation time, τ_w, to the longest Rouse relaxation time, τ_R, is larger than that for the TCP solution.

$$\tau_w/\tau_R(\mathrm{good}) < \tau_w/\tau_R(\Theta) \qquad (13)$$

In other words, the frequency span of the rubbery plateau region for the DOP solution is wider than that for the TCP solution. In modern theories for entanglement systems, the ratio τ_w/τ_R is assumed to be a unique function of number of entanglements, N_e ($=M/M_e$).[18] Thus, the behavior of the DOP solution does not satisfy the basic assumption of modern entanglement theories.

Temperature Dependence. Figure 3 shows a comparison of G^* for F550 in DOP and TCP solutions with c = 59 kg m^{-3} at 22, 27, 40, and 50 °C. Here, we used the frequency–temperature superposition principle to construct this figure. The superposition method works well for the TCP solution over a whole frequency region, and therefore data at different temperatures are superposed on one curve. For the DOP solution, G' and G'' data are shifted along the abscissa so that high-frequency data at high temperatures are superposed on the data at 22 °C. The temperature dependence of thus determined shift factor, A_T^{HF}, is close to the temperature dependence of the solvent viscosity. We will come back to the temperature dependence of A_T^{HF} later.

First, it is obvious that the two systems have the same height of the rubbery plateau modulus again at any studied temperature. Second, the shape of G^* for the DOP solution becomes closer to that for the TCP solution with increasing temperature. Note that solvent viscosity of the two systems is the same at the studied temperature. The location of the Rouse region is insensitive to the solvent power. On the other hand, the terminal flow region of the DOP solution is shifted to higher frequencies with increasing temperature, and its location is almost the same as that for good solvent at the highest temperature. Thus, the difference in the two systems becomes considerably smaller with increasing temperature. We conclude that the width of the rubbery plateau region of the DOP solutions varies with temperature. This means that the frequency–temperature superposition does not work for entangled DOP solutions.

Figure 4 shows the temperature dependence of zero shear viscosity and the shift factors of the two solutions.

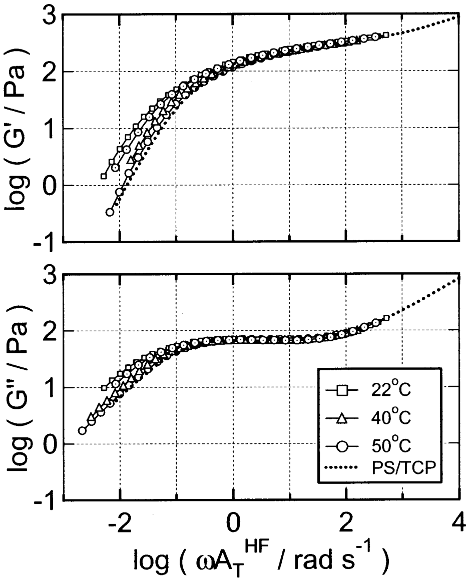

Figure 3. Temperature dependence of G^* for F550 in DOP (Θ solvent) and TCP (good solvent) at c = 59 kg/m^{-3}. Frequency scale was reduced so that data at high ω are superimposed.

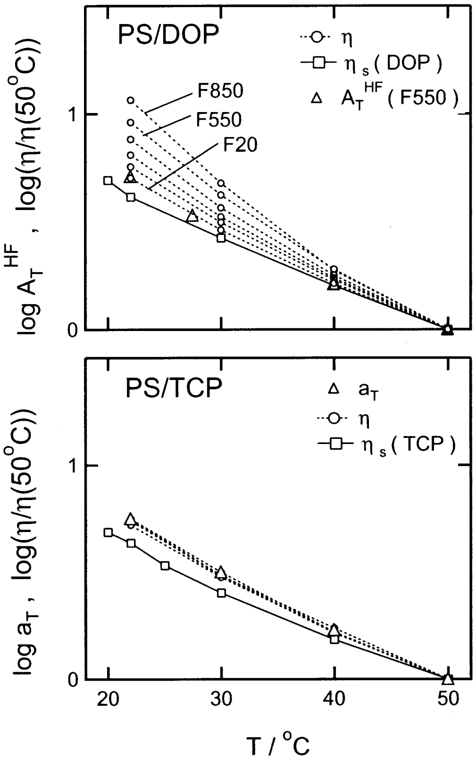

Figure 4. Temperature dependence of reduced viscosity, $\eta/\eta(50\ °\mathrm{C})$.

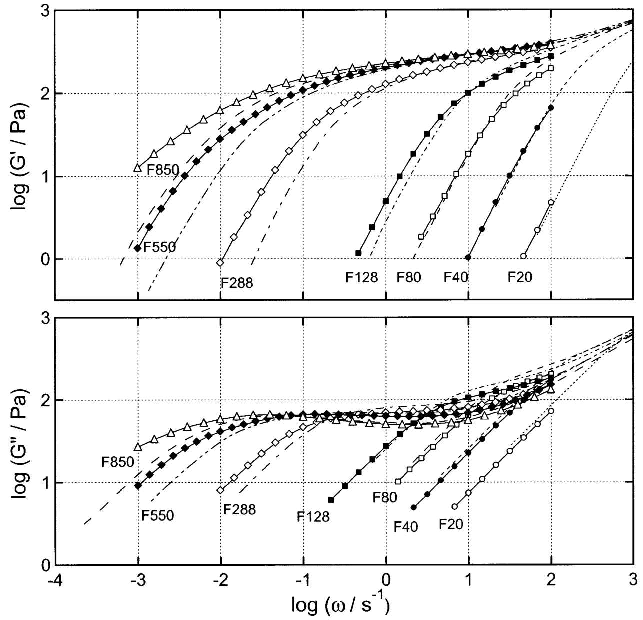

Figure 5. Comparison of G^* of PS in DOP and TCP at 22 °C (Θ temperature for DOP) at $c = 59$ kg/m^{-3}. For TCP solution, data at $\omega/\mathrm{s}^{-1} > 100$ were obtained from the data at lower temperatures by using the method of reduced variables. Lines with symbols and without marks respectively represent data for DOP and TCP solutions.

Here, data are reduced with the values at 50 °C. For the case of the TCP solution, the temperature dependence of the reduced zero-shear rate viscosity does not depend on molecular weight and agrees with the shift factor determined by the superposition of G^*. The temperature dependence of the viscosity or a_T is slightly stronger than that for viscosity of the pure solvent. The slightly stronger temperature dependence would be related to change of the effective solvent viscosity which is originated by modification of solvent dynamics by the presence of polymers having the high glass transition temperature ($T_g \sim 100$ °C) as discussed by Lodge et al.[19]

On the other hand, for the case of DOP, the temperature dependence of the viscosity is stronger than A_T^{HF}, which is determined by the superposition of G^* at high frequencies, reflecting the breakdown of the frequency–temperature superposition principle. The temperature dependence of A_T^{HF} is close to that for the neat solvent while temperature dependence of the viscosity increases with increasing molecular weight. The difference between the η for low-M PS and neat DOP is the same order of that between PS in TCP and pure TCP. Thus, in the terminal flow region, the high molecular weight samples show anomalous temperature dependence. These results suggest that the rate of polymer dynamics on short scales such as the bead–spring modes are governed by the effective solvent viscosity of DOP while the disentanglement process in DOP is not.

Molecular Weight Dependence. Figure 5 shows molecular weight dependence of G^* in DOP and TCP at 22 °C.

For the samples having low molecular weight (F20 ($N_e = 0.5$), F40($N_e = 1.1$), and F80 ($N_e = 1.9$)), G''/ω at low frequencies, which corresponds to the zero shear viscosity, for DOP solutions is slightly lower than that for TCP solutions. This may be natural because PS chain in DOP would have a more compact conformation. For F40 and F80 solutions, the shape of G' is slightly different between the two solvents: G' for DOP solutions crosses G' for TCP solutions. This means that the terminal relaxation spectra for the DOP solutions are broader than that for TCP solutions.

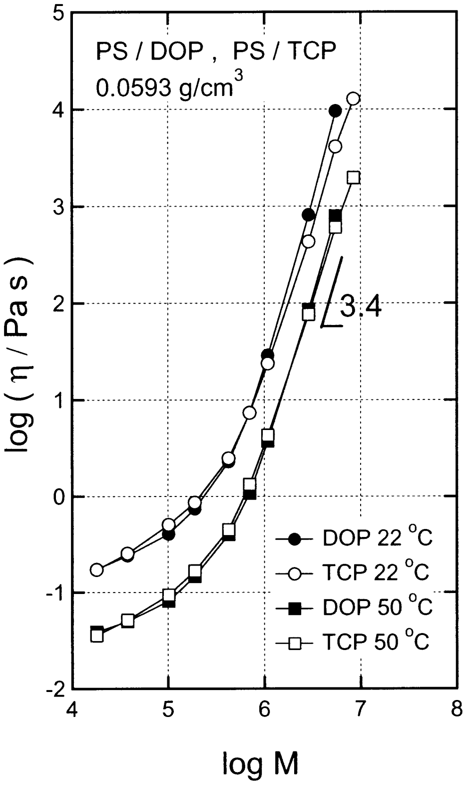

Figure 6. Molecular weight dependence of viscosity of PS in DOP (Θ solvent) and TCP (good solvent).

With increasing molecular weight (F288 and F550), the terminal flow region of DOP solutions locates at lower frequencies than that for the TCP solutions. For the case of F850, the shape of the terminal flow region is very different between the two systems. In the terminal flow region, G^* for the DOP solution becomes broader with increasing molecular weight. Thus, the difference between the DOP and TCP solutions becomes significant with increasing M.

Molecular Weight Dependence of Viscosity. Figure 6 shows molecular weight dependence of the viscosity at 22 and 50 °C. As expected from Figure 5, the viscosity of DOP solutions shows a stronger molecular weight dependence. The best fit to the power law for TCP solutions at high-M region resulted in $M^{3.4}$. For the case of DOP solutions at 22 °C, a slightly larger exponent, $\alpha = 3.6$ was obtained.

$$\alpha_\Theta > \alpha_{\mathrm{good}} \quad \text{(for well-entangled systems)} \qquad (14)$$

The difference between the two solvent systems becomes small at high temperatures.

Behavior at Low Concentration and High *M*. Figure 7 shows G^* of PS with $M_w = 20\,000$ kg mol^{-1} at $c = 0.0198$ g/cm^{-3}. At this concentration, G^* for the TCP solution is slightly higher than that for the Θ solution. More importantly, G' for the DOP solution crosses that for the TCP solution. This means that the frequency span of the rubbery plateau region is wider for DOP solutions although N_e is slightly lower for the DOP solution. This result is consistent with that at the high concentration.

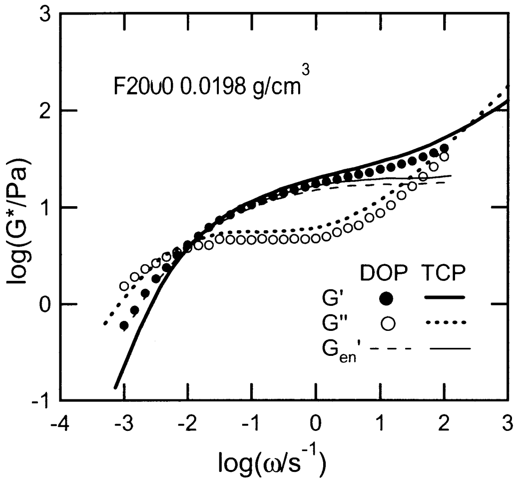

Figure 7. G^* of PS with $M_w = 20\,000$ kg mol^{-1} at $c = 19.8$ kg/m^{-3}. For TCP solution, data at ω/s^{-1} > 100 were obtained from the data at lower temperatures by using the method of reduced variables. The real part of entanglement term, G_{en}', in eq 7 was determined by subtracting the Rouse modes (eq 8) from G^*. See text for details.

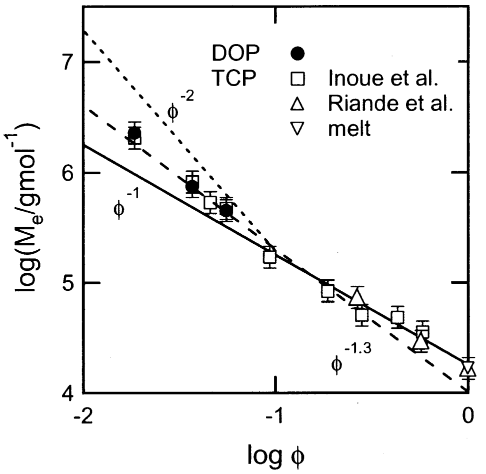

Figure 8. Concentration dependence of M_e for PS/TCP and PS/DOP systems. The lines indicate theoretical predictions and a reported empirical equation. The line for Θ solvent, ϕ^{-2}, is drawn by assuming that the difference in M_e would disappear at $\phi > 0.1$.

It may be worthwhile to note that the bead–spring modes for the DOP solution, which are observed at high-frequency region, ω/s^{-1} > 10, locates at higher frequencies than TCP. A similar but weak tendency is observed at high concentration ($c = 59$ kg/m^{-3}). For nonentangled systems with low molecular weight sample at the same concentration, the maximum relaxation time for DOP solution is shorter than that for TCP system, and therefore the bead–spring modes for the DOP solution locate at higher frequencies than that for the TCP solution. This can be explained from the difference in the radius of gyration in the two solvents. Slower bead–spring modes for the high molecular weight TCP solution would be related to the larger "blob size", and this effect would be more significant at lower concentrations where the difference in blob size is large.

Concentration Dependence of M_e. In Figure 8 M_e for polystyrene in the good and Θ solvents is plotted against volume fraction, ϕ. For the measurement of M_e at the lowest concentration, 2%, we used $M = 20\,000$ kg mol^{-1} sample. The G_N was determined by the fitting method described before. Also included are the data by other researchers.[20–22]

At the lowest concentration, M_e for DOP was found to be slightly larger than that for TCP but is still very close to that for TCP in view of the original scaling theory, predicting $\propto\phi^{-2}$. Thus, we can conclude that M_e of the two systems agrees with each other over a wide concentration regime. Note that the present data are in accord with the reported empirical equation, $M_e = 10200\phi^{-1.3}$ in the range of $\phi < 0.1$ In addition, it may be worthwhile to comment that for the case of the correlation length, ξ, the different concentration dependences ($\xi \sim c^{\nu/(1-3\nu)}$) are established for semidilute solutions of good and Θ solvents.[23,24]

Discussion

Comparison with Previous Studies. Colby et al. measured the complex shear modulus for high molecular weight polybutadiene, PB, in DOP (a near-Θ solvent for PB) and phenyloctane (a good solvent), and they compared concentration dependence of M_e.[11] They found that M_e is insensitive to solvent quality, and the relationship $M_e \sim c^{-1.3}$ holds well over a wide concentration regime from the melt to the semidilute regime. The present results are consistent with their results in the context that G_N is insensitive to solvent quality. However, Colby et al. did not make any comment on the difference of the frequency dependence of G^* in the terminal flow region. Unfortunately, they did not perform the measurements at the same concentration except for one sample having the lowest concentration ($\phi = 0.0214$, $N/N_e \sim 3.3$). Observing their published figures, we may conclude the frequency dependence of G^* in the terminal flow region would be identical at least for the solutions having the lowest concentration. This may possibly come from the fact that the temperature is about 12 °C higher than true Θ temperature. In addition, the glass-to-rubber transition region is not observed for PB solutions at 25 °C because of a higher rubbery plateau modulus by about 1 order of magnitude compared with the PS system. This makes it difficult to compare the frequency span of the rubbery plateau zone. Thus, the difference in ω dependence of G^* between the solvents has not been recognized so far.

It may be worthwhile to comment that both PS and PB have the identical concentration dependence of M_e in the semidilute regime. On the other hand, in the concentrated regime, they have the different exponents. For polystyrene solutions, $M_e \sim \phi^{-1.4}$ does not hold in the concentrated regime as shown in Figure 8. These results strongly suggest that the scaling rule for concentration dependence of M_e may not be universal in the concentrated regime. Sometimes the following equation has been used for the prediction of M_e for semidilute polystyrene solutions.

$$M_e/\text{kg mol}^{-1} = M_{e,\,\text{melt}}\phi^{-1.4} \sim 16.6\phi^{-1.4} \qquad (15)$$

This equation is based on the combination of $M_e \propto \phi^{-1.4}$, and the M_e value is 18 000 kg mol^{-1} for the melts. The present results indicate that it may give to about 1.6 times larger value for M_e. In calculation of $\tau_W \sim (N/N_e)^3$, it causes about $1.6^3 \sim 4$ times smaller values.

Molecular Origin of Anomalous Behavior of DOP Solutions. Broadening of G^* in the terminal flow region for F850 and its temperature dependence strongly suggest that the anomalous behavior of DOP systems

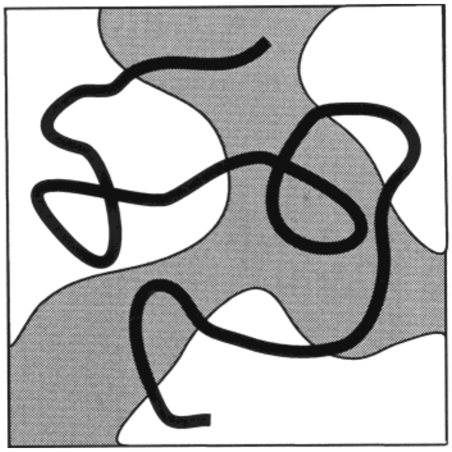

Figure 9. Concentration fluctuation in Θ solutions. The different shadows represent segment concentration fluctuations. In semidilute regime, local friction coefficient does not vary with the concentration, and therefore local modes such as bead−spring modes are insensitive to concentration fluctuation. On the other hand, the rate of disentanglement mode such as reptation mode depends on entanglement density, and motion of the whole chain is determined by the lowest rate in the concentrated region.

may be related to large concentration fluctuations. The characteristic size of concentration fluctuation can be measured by the scattering techniques. The estimated value of the correlation length for PS in cyclohexane at Θ is about 10 nm.[25,26] On the other hand, the radius of gyration for F850 is approximately 80 nm. [27] Here, we would like to use a very simple molecular model just to explain the different temperature dependence of the terminal zone and the rubbery plateau zone. Figure 9 shows a schematic diagram of an entangled chain in concentration fluctuation. With a large concentration fluctuation, local motions (bead−spring modes) of the polymer chain would not be affected so much because the relaxation times of local motions are relatively insensitive to concentration. The intensity of local modes would vary from place to place, but average spectra may not be changed significantly with concentration fluctuation. On the other hand, for an entanglement mode such as the reptation mode,[18] the motion of whole chain is cooperative, and hence the mobility of the whole chain is determined by the friction in the highest concentration region. Thus, global motions are expected to be very sensitive to the concentration fluctuation. The concentration fluctuation varies with temperature, and therefore only such global motion could show an anomalous temperature dependence.

It has been already pointed out that the dynamic asymmetry between constituent components in mixtures and solutions causes a coupling between stress and diffusion that is due to an asymmetric stress division.[28] This coupling effect causes a unique “viscoelastic effect” on not only the dynamics of the concentration fluctuations in phase separation processes in two-phase systems but also the dynamics of the concentration fluctuation in one-phase systems. The stress−diffusion coupling occurs when the growth rate of concentration fluctuation is faster than the relaxation rate of entangled polymer networks and suppresses the dynamics of concentration fluctuation. For concentration fluctuation with a characteristic length comparable with the entangled network, this criterion should be fulfilled and the growth of fluctuation is suppressed. However, for large length-scale concentration fluctuations, the growth rate is extremely small, and therefore such fluctuations will develop under a situation where the built-up local stress is completely relaxed, hence involving no such stress−diffusion coupling. Thus, we may define a screening length called the “viscoelastic length”. Recently, Toyoda et al. estimated the viscoelastic correlation length for PS in DOP in single phase. The estimated value for F550 in DOP at 59 kg m^{-3} is 1000 nm.[29] This size is about 10 times larger than the chain dimension. Thus, the effect of viscoelasticity on concentration fluctuations is well-recognized. On the other hand, the effect of concentration fluctuation on viscoelasticity or polymer chain dynamics, which possibly becomes significant under large concentration fluctuations, has not been formulated.

As described before, the anomalous behavior is not reported for PB/DOP systems. One other important difference between PS/DOP and PB/DOP systems is the difference of the glass transition temperature between the polymer and the solvent: The glass transition temperature of DOP is reported as 185 K.[11] This value is close to T_g of PB (174 K) but about 188 K lower than T_g for PS(373 K). T_g of PS/DOP solutions strongly depends on concentration, and therefore the friction coefficient is also sensitive to the concentration fluctuation. Thus, one possible origin for the anomalous behavior may be related to the difference of the glass transition temperature between polymer and solvent in addition to concentration fluctuation.

Conclusion

We compared G^* of entangled polymer systems in Θ and good solvents to investigate effects of solvent power in the semidilute regime. The height of the rubbery plateau modulus was found to be identical between good and Θ conditions. This result is in accord with the experimental results on PB systems and the two-parameter scaling theory. However, for the case of PS systems, the relationship $M_e \sim \phi^{-1.4}$ holds valid only for the limited low concentration regime, $\phi < 0.1$, contrary to PB systems. More importantly, for the case of PS systems, the frequency span of the rubbery plateau zone, which corresponds to the ratio of τ_w to τ_{Rouse}, is different between good and Θ solvent systems. The temperature dependence of τ_w did not follow temperature dependence of the effective solvent viscosity. Thus, τ_w/τ_{Rouse} at Θ is not a universal function of N/N_e as assumed in many molecular theories. This result may be related to the effect of large concentration fluctuations which are characteristic for Θ solvent systems.

Acknowledgment. This study was partially supported by a Grant-in-Aid for Scientific Research (No. 13450391) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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MA020849V