Viscoelastic and Diffusion Properties of Binary Blends of Monodisperse Polystyrenes

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ABSTRACT: Viscoelastic and diffusion properties of blends of short and long polystyrene (PS) chains (designated as 1- and 2-chains, respectively) with the molecular weights M_{w1} and M_{w2} were compared. The content of the 2-chains was small, and no entanglements between them existed in the blends examined. If $M_{w2} \gg M_{w1} > M_c°$ with $M_c°$ being the characteristic molecular weight, the relaxation time of the 2-chain in the blends was proportional to the diffusion time of the 2-chain evaluated from the diffusion coefficient data in the literature. Both times were almost proportional to $M_{w1}^3 M_{w2}^2$, suggesting that the 2-chain relaxed and diffused by the retarded Rouse-like mode due to tube renewal. However, the ratio of the two characteristic times did not coincide with that for the Rouse chain, indicating that the dynamics of the dilute 2-chain in the blends with $M_{w2} \gg M_{w1} > M_c°$ is not completely the same as that of the Rouse chain. If $M_{w2} \gg M_e° > M_{w1}$ with $M_e°$ being the entanglement spacing and if the 2-chains were not entangling but still overlapping with one another, their relaxation time ($\propto \zeta_0 M_{w1}^0 M_{w2}^2$ with ζ_0 being the monomeric friction coefficient) agreed reasonably well with the intrinsic Rouse diffusion time evaluated from the diffusion coefficient data for monodisperse PS. On the other hand, an analysis on the data of Green and Kramer suggested that the diffusion time of the infinitely dilute 2-chain was proportional to $\zeta_0 M_{w1}^0 M_{w2}^{1.5-1.6}$, and the Stokes-Einstein diffusion (having the characteristic time $\propto \zeta_0 M_{w1}^1 M_{w2}^{1.5}$) was not observed for the blends with $2100 < M_{w1} \lesssim M_e°$.

Introduction

The entanglement interaction is one of the most significant features in condensed long-chain polymer systems. The dynamics of such a chain molecule is strongly affected by the surrounding chains. Thus, binary blends composed of narrow molecular weight distribution (hereafter designated as *monodisperse*) polymers are a simple but very important model system for clarifying the entanglement effect on polymer dynamics. Viscoelastic as well as diffusion measurements are convenient for such studies.

We have examined the viscoelastic properties of blends of linear and monodisperse polystyrenes (PS) and found the following features.[1-3] If the weight-average molecular weight M_{w2} of the longer chain (hereafter designated 2-chain) is much larger than M_{w1} of the shorter chain (1-chain) while M_{w1} is still larger than the entanglement spacing $M_e°$ ($\cong 1.8 \times 10^4$)[4] and if the content w_2 of the 2-chain is smaller than a critical value $(w_2)_c \cong M_c°/M_{w2}$ corresponding to the onset of the entanglements between the 2-chains, the relaxation time of the 2-chain strongly increases with increasing M_{w1}. (Here, $M_c° \cong 3.1 \times 10^4$ is the characteristic molecular weight for bulk PS.[4]) In the framework of the generalized tube model, this relaxation process corresponds to tube renewal.[5-7]

The diffusion of PS chains either in the monodisperse state or in blends has also been examined.[8-16] In blends with $M_{w2} \gg M_{w1} > M_c°$ and with small w_2, the diffusion coefficient of the 2-chain strongly increased with decreasing M_{w1}.[11,13] Namely, the molecular motion attributable to tube renewal is observed also in diffusion measurements.

A comparison of the viscoelastic and diffusion data may provide more information on polymer dynamics. In this paper, we present the results of such a comparison and discuss the dynamic modes of the 2-chain in the blends.

Results and Discussion

Viscoelastic Data. We have already obtained viscoelastic data for PS/PS blends with $10^{-4}M_{w1}$ ranging from 0.52 to 17.2 and $10^{-4}M_{w2}$ from 31.5 to 281.[1-3] The viscosity ($\eta_{2,bB}$), elastic coefficient ($A_{2,bB}$), and compliance ($J_{2,bB}$) of the 2-chain in the blends with small w_2 were evaluated by[3]

$$\eta_{2,bB} = \eta_{bB} - w_1\eta_{1,m} \quad (1a)$$

$$A_{2,bB} = A_{bB} - w_1 A_{1,m} \quad (1b)$$

$$J_{2,bB} = A_{2,bB}/(\eta_{2,bB})^2 \quad (1c)$$

where the subscripts bB and 1,m respectively represent the quantities of the blend and monodisperse 1-chain and w_1 is the content of the 1-chain. The terms $w_1\eta_{1,m}$ and $w_1 A_{1,m}$ in eq 1a and 1b represent the contribution of the 1-chains to η_{bB} and A_{bB}.

As shown previously,[1] $\eta_{2,bB}$ and $A_{2,bB}$ were proportional to w_2, and hence $J_{2,bB}$ to w_2^{-1} (cf. eq 1c) for blends with $w_2 < (w_2)_c$, suggesting that no entanglement existed between the 2-chains, which thus behaved as in a dilute solution. We call such blends the *dilute* blends. For such blends, the quantities $J_{2,bB}\eta_{2,bB}$, the weight-average relaxation time of the 2-chain, and $w_2 J_{2,bB}$, the compliance of the 2-chain *reduced to its unit volume*, are independent of w_2. (We assumed the weight fraction w_2 to be equal to the volume fraction of the 2-chain in the blend.)

Figure 1 shows the M_{w2} dependence of (a) $J_{2,bB}\eta_{2,bB}$ and (b) $w_2 J_{2,bB}$ for the dilute blends. The open and filled circles are the data for the blends with large and small M_{w2}/M_{w1} ratios, and the triangles represent the data for the monodisperse PS. All these data are compared at an iso-free-volume-fraction (f_r) state with $f_r = 0.0644$. The reference temperatures are 146, 155, and 167 °C for the blends with $10^{-4}M_{w1} = 0.52$ and 1.05 and ≥ 2.34, respectively.[3]

As seen in Figure 1a, the relaxation time of the 2-chain in the dilute blends with $5200 \lesssim M_{w1} < M_e°$ is independent of M_{w1} and close to the *intrinsic* Rouse relaxation time (the solid line with the slope of 2) evaluated from the data for the monodisperse PS with small M_w. For $M_{w2} \gg M_{w1} > M_e°$, $J_{2,bB}\eta_{2,bB}$ strongly increases with increasing M_{w1} and is almost proportional to $M_{w1}^3 M_{w2}^2$, as shown previously.[3] This dependence may be explained by the tube renewal mechanism.[5-7,17] As M_{w1} approaches M_{w2}, $J_{2,bB}\eta_{2,bB}$ becomes more weakly dependent on M_{w1} and approaches the relaxation time of the monodisperse 2-chain (triangles).

The broken line in Figure 1a represents the *virtual* tube renewal time for monodisperse PS estimated from the data for the blends.[3] This virtual time is longer than the actual relaxation time (triangles) for the monodisperse PS with $M_w > M_c°$, and the difference between these times increases with increasing M_w. *As a crude approximation*, the tube may be assumed to be fixed in space for highly entangled monodisperse PS.[3]

In Figure 1b, we notice that $w_2 J_{2,bB}$ for the dilute blends with $M_{w2} \gg M_{w1}$ (open circles) is almost independent of

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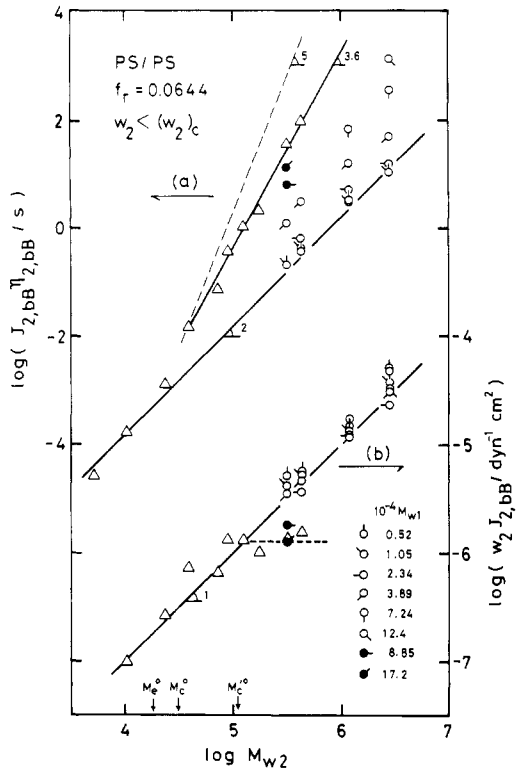

Figure 1. M_{w2} dependence of (a) $J_{2,bB}\eta_{2,bB}$ and (b) $w_2J_{2,bB}$ of the 2-chain in the dilute blends at an iso-f_r state with $f_r = 0.0644$. The open circles represent the data for the blends with a large M_{w2}/M_{w1} ratio, and the filled ones the data for those with smaller M_{w2}/M_{w1}. The direction of the pips attached to the circles specifies M_{w1}, as indicated in the figure. The triangles are (a) the weight-average relaxation time and (b) the compliance of monodisperse PS. The solid line for the compliance data represents the Rouse equation $J_2 = 0.4M_2/w_2\rho RT$. Note that the scales for the left and right axes are not the same.

M_{w1} and described approximately by the Rouse equation[4,20] (the solid line with the slope of unity)

$$J_2 = 0.4M_2/w_2\rho RT \quad (2)$$

with ρ ($\cong$1 g cm^{-3}) being the density of PS, R the gas constant, and T the absolute temperature. As M_{w1} approaches M_{w2}, $w_2J_{2,bB}$ (the filled circles) deviates downward from the Rouse line toward the compliance of well-entangled monodisperse 2-chains ($\cong 10^{-5.9}$ dyn^{-1} cm^2, represented by the horizontal broken line).

These results indicate that the 2-chain in the blend with $M_{w2} \gg M_{w1} > M_e°$ and $w_2 < (w_2)_c$ relaxes by the retarded Rouse-like modes (presumably due to tube renewal) *at low frequencies*. With decreasing M_{w2}/M_{w1} ratio below a certain critical value ($\cong$8 for the blends with $M_{w2} = 31.5 \times 10^4$; cf. Figure 1b), the slow relaxation modes of the 2-chain are no longer Rouse-like but become close to those of the monodisperse chain.

Diffusion Coefficient Data. Figure 2 summarizes the data for the self-diffusion coefficient D_m of monodisperse PS (open circles) taken from the literature.[8-11,15] Fleischer[10] reduced and compared the data for $M_w \lesssim M_e°$ at $T_g + 125$ °C with T_g being the glass transition temperature. The monomeric friction coefficient ζ_0 would be the same at his reference temperature. Thus, we compared the data of Fleischer[10] and other authors[8,9,11,15] at $T_g + 125$ °C (=225 °C for large M_w).

Antonietti and co-workers[15] reported the data for $M_w \gtrsim M_e°$ at 212 °C. They[14] showed that the temperature dependence of D_m agreed well with that of the viscosity η_m of monodisperse PS.[21] Thus, their data[15] were reduced by the WLF equation of Allen and Fox.[21] The data of

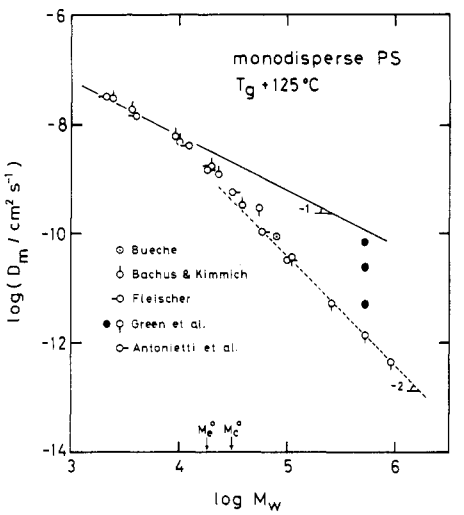

Figure 2. M_w dependence of the self-diffusion coefficient D_m of monodisperse PS taken from the literature[8-11,15] (open circles). The data reported by several authors are compared at $T_g + 125$ °C (the iso-ζ_0 temperature chosen by Fleischer[10]). The solid and broken lines respectively represent eq 3 and 4. Some data for the diffusion coefficient $D_{2,bB}$ of the 2-chain in the dilute 2/1 blends reported by Green and co-workers[11] are shown by the filled circles: M_{w2} for those blends is 52×10^4, and $10^{-4}M_{w1} = 3.6$, 5.4, and 11 from top to bottom.

Bachus and Kimmich[9] (for $M_w \lesssim M_c°$ at 230 °C) and Bueche[8] (for $M_w = 8 \times 10^4$ at 237 °C) were also reduced by that equation. The error due to these short extrapolations would be small.

The data of Green and co-workers[11] for $M_w > M_c°$ at 174 °C[13] were reduced to 225 °C by the Vogel equation given in the reference section of their paper.[12] (The temperature dependence of ζ_0 described by their Vogel equation agrees well with that obtained by the WLF equation of Allen and Fox.[21])

In Figure 2, we see that the D_m data reported by several authors agree well with one another. The M_w dependence of D_m at the iso-ζ_0 state may be summarized as follows. (a) For $M_w \lesssim 10^4$, D_m appears to be proportional to M_w^{-1}, as expected for the Rouse chain. (b) For $10^4 < M_w < (2\text{–}3)M_c°$, the M_w dependence of D_m becomes stronger. Antonietti and co-workers[15] reported that $D_m \propto M_w^{-(2.4\text{–}2.5)}$ in this region. (c) In the well-entangled region $M_w \gtrsim (2\text{–}3)M_c°$, the M_w dependence becomes a little weaker, and D_m is almost proportional to M_w^{-2}. We can see the transition from region b to region c even if we examine the data of Green and co-workers[11] alone. Thus, this transition is not due to some artifacts in our reducing and comparing the data of several authors at an iso-ζ_0 state.

The solid and broken lines in Figure 2 represent the empirical equations for the asymptotic regions a and c.

$$\text{(a) } D_m \cong 6.3 \times 10^{-5}M_w^{-1} \text{ (in cm}^2\text{ s}^{-1}\text{)} \quad \text{for } M_w \lesssim 10^4 \quad (3)$$

$$\text{(b) } D_m \cong 4.2 \times 10^{-1}M_w^{-2} \text{ (in cm}^2\text{ s}^{-1}\text{)} \quad \text{for } M_w \gtrsim (2\text{–}3)M_c° \quad (4)$$

Assuming that the intrinsic Rouse diffusion coefficient D_R is given by eq 3, we calculated the diffusion coefficient D_{rep} (in square centimeters per second) for the reptating chain as[22]

$$D_{rep}(M) = [3M/M_e°]^{-1}D_R(M)$$

$$D_{rep}(M) \cong 3.8 \times 10^{-1}M^{-2} \quad (\text{for } M_e° = 1.8 \times 10^4) \quad (5a)$$

$$D_{rep}(M) \cong 3.0 \times 10^{-1}M^{-2} \quad (\text{for } M_e° = 1.44 \times 10^4) \quad (5b)$$

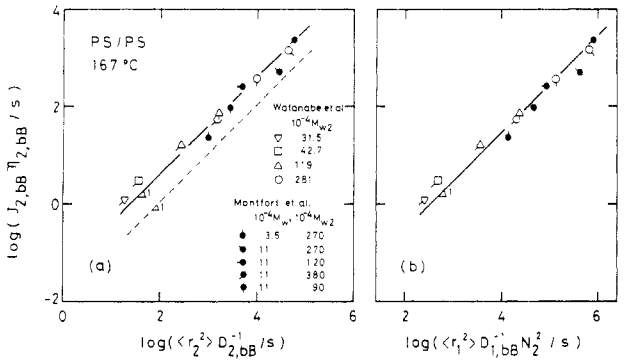

Figure 3. Comparison of the characteristic relaxation and diffusion times of the 2-chain in the dilute blends with $M_{w2} \gg M_{w1} > M_c°$ at 167 °C. The open symbols represent our data,[3] and the filled ones those of Montfort and co-workers.[19] The meaning of the pip for the open symbols is the same as in Figure 1.

Here, $M_e°$ is evaluated to be 1.8×10^4 by the relation of rubber elasticity,[4,20] $G_N^0 = \rho RT/M_e°$ and is found to be 1.44×10^4 by the Doi–Edwards relation[22] $G_N^0 = 4\rho RT/5M_e°$ with $G_N^0 = 2 \times 10^6$ dyn cm^{-2} being the plateau modulus. The result, especially eq 5a, agrees with eq 4 very well. Thus, not only the M_w dependence but also the magnitude of the D_m data (of Green and co-workers[11]) for well-entangled monodisperse PS appears to be described satisfactorily by the reptation mechanism alone.[23]

Green and co-workers[11] also reported the data for the diffusion coefficient $D_{2,bB}$ of the long diffusant (2-chain) in the short-matrix chains (1-chains) at 174 °C.[13] Some of their data for $M_{w2} \gg M_{w1} > M_c°$ reduced at 225 °C are shown by the filled circles in Figure 2. $D_{2,bB}$ is significantly larger than D_m of monodisperse 2-chain (open circles) and strongly increases with decreasing M_{w1}.

Comparison of Characteristic Relaxation and Diffusion Times. 1. Blends with $M_{w2} \gg M_{w1} > M_c°$. Here, we compare the relaxation and diffusion times of the 2-chain in the dilute blends with $M_{w2} \gg M_{w1} > M_c°$ at the reference temperature (167 °C) we employed in Figure 1a. For such blends, ζ_0 is practically constant and independent of M_{w1} and M_{w2} at a constant temperature (167 °C) well above T_g.

We defined two characteristic diffusion times, $\langle r_2^2\rangle/D_{2,bB}$ and $N_2^2\langle r_1^2\rangle/D_{1,bB}$. Here, $N_2 = M_{w2}/M_e°$ is the number of entanglements per 2-chain, $D_{i,bB}$ is the diffusion coefficient of the i-chain in the blend, and $\langle r_i^2\rangle$ is the mean-square end-to-end distance of the i-chain (i = 1, 2).

Green and co-workers[11] reported an equation, which described well their $D_{2,bB}$ data for $M_{w2} > M_{w1} > M_c°$ at 174 °C.[13] Reducing that equation by their Vogel equation,[12] we obtained

$$D_{2,bB} = 3.7 \times 10^{-3} M_{w2}^{-2} + 1.58 \times 10^{7} M_{w1}^{-3} M_{w2}^{-1} \quad \text{(in cm}^2\text{ s}^{-1}\text{)} \tag{6}$$

at 167 °C. (Note that $D_{2,bB} \propto M_{w1}^{-3}M_{w2}^{-1}$ for $M_{w2} \gg M_{w1}$. This dependence can be explained by the tube renewal mechanism.[5-7,11])

For the dilute blends, $D_{1,bB}$ should be very close to D_m of the monodisperse 1-chain. Thus, reducing eq 4 by the Vogel equation of Green and co-workers,[12] we evaluated $D_{1,bB}$ at 167 °C as[25]

$$D_{1,bB} \cong 3.8 \times 10^{-3} M_{w1}^{-2} \quad \text{(in cm}^2\text{ s}^{-1}\text{)} \tag{4'}$$

$\langle r_i^2\rangle$ (i = 1, 2) was evaluated by the empirical equation for PS chains at the Θ-condition[26]

$$\langle r_i^2\rangle = 52.8 \times 10^{-18} M_{wi} \quad \text{(in cm}^2\text{)} \tag{7}$$

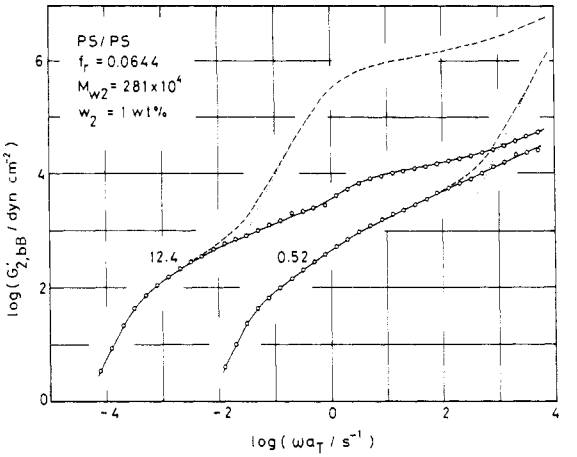

Figure 4. Comparison of the storage moduli $G_{2,bB}'$ of the 2-chain in dilute blends with $M_{w2} = 281 \times 10^4$ and w_2 = 1 wt % at an iso-f_r state with f_r = 0.0644 (circles and solid curves). The numbers attached to the $G_{2,bB}'$ curves indicate $10^{-4}M_{w1}$. The broken and dotted curves respectively represent the storage moduli of the blends (G_{bB}') and monodisperse 1-chains ($G_{1,m}'$).

Figure 3 compares the characteristic diffusion times evaluated by eq 6, 4', and 7 with our weight-average relaxation time $J_{2,bB}\eta_{2,bB}$ (open symbols). The $M_e°$ value used for the evaluation of N_2 was 1.8×10^4. Some data of Montfort and co-workers[19] are also shown by the filled circles. They evaluated the viscoelastic relaxation time $\bar{\tau}$ from Cole–Cole plots of the complex viscosity at 160 °C and reported that $\bar{\tau}$ was smaller by a factor of about 1.5 than the weight-average relaxation time for monodisperse PS.[19] Thus, we reduced their data to 167 °C by their WLF equation and plotted $1.5\bar{\tau}$ against the diffusion times. Their data agreed with ours fairly well.

In Figure 3, we find proportionality between the relaxation and diffusion times (the solid lines in the figure) described by

$$J_{2,bB}\eta_{2,bB} \cong 4.4 \times 10^{-2}\langle r_2^2\rangle/D_{2,bB} \quad (M_{w2} \gg M_{w1} > M_c°) \tag{8}$$

$$J_{2,bB}\eta_{2,bB} \cong 3.0 \times 10^{-3} N_2^2\langle r_1^2\rangle/D_{1,bB} \quad (M_{w2} \gg M_{w1} > M_c°) \tag{9}$$

The broken line in Figure 3a indicates the theoretical relation for the Rouse chain[20] (2-chain)

$$J_2\eta_2 = (1/90)\langle r_2^2\rangle/D_2 \tag{10}$$

The numerical factor in eq 8 is about 4 times larger than that in eq 10. One possible (but yet uncertain) interpretation for this difference can be obtained from Figure 4. Figure 4 shows the storage moduli $G_{2,bB}'$ of the 2-chain in the dilute blends with w_2 = 1 wt %, $10^{-4}M_{w2}$ = 281, and $10^{-4}M_{w1}$ = 0.52 and 12.4. These $G_{2,bB}'$ were obtained by

$$G_{2,bB}'(\omega) = G_{bB}'(\omega) - w_1 G_{1,m}'(\omega) \tag{11}$$

where G_{bB}' and $G_{1,m}'$ are the storage moduli of the blends and the monodisperse 1-chains, respectively (cf. eq 1).

As can be seen from Figure 4, no rubbery plateau appears in the $G_{2,bB}'$ curve for the blend with $M_{w1} = 0.52 \times 10^4$ ($< M_e°$), while the rubbery plateau and successive (wedgelike) shoulder are observed for the blend with $M_{w1} = 12.4 \times 10^4$ ($\gg M_e°$). These results indicate that the constraints on the 2-chain due to the surrounding 1-chains with $M_{w1} > M_e°$ are still effective at short time scales and released by the Rouse-like modes at long time scales. Namely, the dynamics of the 2-chain is not completely the same as that of the Rouse chain, suggesting that the numerical factor in eq 8 should *not necessarily* equal the

Rouse factor, $^1/_{90}$, given in eq 10. (Since $J_{2,bB}$ determined by eq 1c is insensitive to the behavior of the 2-chain at short time scales, the Rouse equation (eq 2) is approximately valid, as seen in Figure 1b.)

Now we analyze eq 9. This equation suggests that the diffusion of the 1-chain determines the rate of *mechanical* relaxation of the 2-chain. The comparison of eq 4 and 5 suggests that reptation is the dominant *diffusion* mechanism for the well-entangled 1-chains. Then eq 9 may be rewritten as

$$J_{2,bB}\eta_{2,bB} \cong 0.089N_2^2\tau_1^{rep} \qquad (9')$$

where $\tau_1^{rep} = \langle r_1^2\rangle/(3\pi^2 D_{1,bB})$ is the reptation time of the 1-chain.[22] Assuming the Rouse relation $J_{2,bB}\eta_{2,bB} = (\pi^2/15)\tau_{2,bB}$ with $\tau_{2,bB}$ being the longest relaxation time of the 2-chain in the blend, we can rewrite eq 9′ further

$$\tau_{2,bB} \cong 0.14N_2^2\tau_1^{rep} \qquad (9'')$$

On the basis of the random jump model, Graessley[7] calculated the time τ_t required for the tube renewal process as

$$\tau_t = (2\Lambda/\pi^2)N_2^2\tau_1^{rep} \qquad (12)$$

where $\Lambda = (\pi^2/12)^z/z$ is a factor determined by the number z of the local jump sites in an entanglement spacing. (Although Graessley used the Rouse equation similar to eq 10 in deriving eq 12, the comparison of eq 9″ and 12 seems to be reasonable because only the Rouse-like behavior of the 2-chain at long time scales is incorporated in the Graessley theory.) The numerical factor in eq 9″ is close to the Graessley factor $2\Lambda/\pi^2$ ($\cong$0.17) for $z = 1$ in eq 12. However, the factor in eq 9″ depends on the $M_e°$ value used for the evaluation of N_2. If we use $M_e° = 1.44 \times 10^4$ instead of 1.8×10^4 (cf. eq 5), the numerical factor in eq 9″ becomes 0.086, which is close to the Graessley factor ($\cong$0.069) for $z = 2$.

2. Blends with $M_{w2} \gg M_e° \gtrsim M_{w1}$. Here we turn our attention to the dilute blends with $M_{w2} \gg M_e° \gtrsim M_{w1}$, in which the 2-chain entangles neither with the 1-chains nor with the other 2-chains and ζ_0 depends on both temperature and M_{w1}. In Figure 1a, we showed the weight-average relaxation time of the 2-chain in such blends at the M_{w1}-dependent iso-ζ_0 temperatures. Those data were summarized as[3]

$$J_{2,bB}\eta_{2,bB} \cong (1.6 \pm 0.3) \times 10^{-12}M_{w1}^{0}M_{w2}^{2} \quad \text{(in s)} \qquad (13)$$

$$(M_{w2} \gg M_e° > M_{w1} \geq 5200;\ f_r = 0.0644)$$

First, we compare this relaxation time with the diffusion time evaluated from the D_m data. Applying the Vogel equation of Green and co-workers[12] to eq 3, we estimated the Rouse diffusion coefficient of the 2-chain at our iso-ζ_0 state as

$$D_{R2} \cong 5.7 \times 10^{-7}M_{w2}^{-1} \quad \text{(in cm}^2\text{ s}^{-1}\text{)} \qquad (3')$$

and the intrinsic Rouse diffusion time of the 2-chain as

$$(1/90)\langle r_2^2\rangle/D_{R2} \cong 1.0 \times 10^{-12}M_{w2}^{2} \quad \text{(in s)} \qquad (14)$$

This agrees with eq 13 reasonably well, suggesting that the dynamic modes of the 2-chain in our blends are close to the intrinsic Rouse modes.

Now we compare our relaxation time also with the diffusion time evaluated from the $D_{2,bB}$ data. Green and Kramer[13] examined the diffusion of the 2-chain in the blends with $M_{w2} \gg M_e° \gtrsim M_{w1}$. To compare the $D_{2,bB}$ data at an iso-ζ_0 state, they chose the M_{w1}-dependent reference temperatures $T_{r,GK}$ cited in Table I. They showed that $D_{2,bB} \propto M_{w1}^{-1}M_{w2}^{-(0.5-0.6)}$ at these $T_{r,GK}$ and concluded that the Stokes–Einstein diffusion[5] of the 2-chain was observed.

Table I
Reference Temperatures at Which the Dilute Blends with $M_{w2} = 52 \times 10^4$ and $M_{w1} \lesssim M_e°$ Have the Same Monomeric Friction Coefficient

M_{w1}	$T_{r,GK}$/°C[a]	$T_{r,AF}$/°C[b]
2100	90	83
4000	104	101
10000	116	115
20400	119	120

[a] Reported by Green and Kramer.[13] [b] $T_{r,AF} = T_g + 25$ °C;[21] T_g was evaluated by the empirical equation $T_g^{-1} = (1/373) + 0.72/M$ (in K^{-1}), which gave T_g values very close to those reported by Green and Kramer.[13]

Antonietti and co-workers[15] compared the $D_{2,bB}$ data for the blends with $M_{w1} \lesssim M_e°$ at a *constant temperature* 212 °C. They showed that $D_{2,bB}$ was almost proportional to M_{w2}^{-1} if M_{w1} was kept constant and that $D_{2,bB} \propto M_{w1}^{-\alpha}$ for constant M_{w2} with α being somewhat larger than unity. They also concluded that the Stokes–Einstein mechanism largely contributed to the diffusion of the 2-chain. Since ζ_0 at 212 °C would be the same for the *dilute* blends with the *same* M_{w1}, we may say that their relation $D_{2,bB} \propto M_{w2}^{-1}$ is the relation at an iso-ζ_0 state. (The M_{w1} dependence of their $D_{2,bB}$ data at an iso-ζ_0 state was still uncertain, however.)

The diffusion time $\langle r_2^2\rangle/D_{2,bB}$ evaluated from the data of Green and Kramer[13] is proportional to $M_{w2}^{1.5-1.6}$, while that from the data of Antonietti and co-workers[15] is proportional to M_{w2}^2. Our relaxation time (eq 13) is also proportional to M_{w2}^2 at an iso-ζ_0 state. This difference seems to be related, at least partly, to the difference in w_2: In most of the blends examined by Antonietti and co-workers[15] and also in our blends, the 2-chains were not entangling but still overlapping with one another. On the other hand, although not reported, Green and Kramer[13] seem to have examined the blends containing infinitely dilute 2-chain: They measured the concentration profile of the 2-chain diffusing from its *very thin* layer into a much thicker matrix of the 1-chains.

The polymer chains in a low molecular weight solvent exhibit Zimm-like behavior at infinite dilution, while Rouse-like behavior prevails when the chains overlap but do not entangle.[4] This Zimm–Rouse transition has been interpreted as due to the hydrodynamic screening that takes place as the polymer chains overlap.[4] Thus, we might *tentatively* explain the difference in the M_{w2} dependence of the characteristic times for the blends similarly as due to the difference in the magnitudes of the hydrodynamic interaction between the segments of the 2-chain. (However, this does not necessarily mean that the $D_{2,bB}$ data for the infinitely dilute 2-chain are explained by the Zimm theory, as shown later.)

Now we examine the M_{w1} dependence of the characteristic times at an iso-ζ_0 state: The diffusion time of Green and Kramer is proportional to M_{w1}, while our relaxation time is proportional to M_{w1}^0. To see whether this difference, which seems not to be related to the difference in w_2, is due to some artifacts in reducing the data to an iso-ζ_0 state or not, we reexamine the $D_{2,bB}$ data in Figure 5. (As shown previously,[27] our viscoelastic data were correctly reduced and compared at an iso-ζ_0 state.)

The filled circles in Figure 5a show the $D_{2,bB}$ data for the blends with $M_{w2} = 52 \times 10^4$ and $M_{w1} \lesssim M_e°$ at the Green–Kramer reference temperatures $T_{r,GK}$.[13] Certainly, $D_{2,bB} \propto M_{w1}^{-1}$ (and thus $\langle r_2^2\rangle/D_{2,bB} \propto M_{w1}$) at $T_{r,GK}$. However, as shown by the filled circles in Figure 5b, the viscosity $\eta_{1,m}$ of the matrix 1-chain (evaluated from the Allen–Fox article[21]) is not proportional to M_{w1} at $T_{r,GK}$.

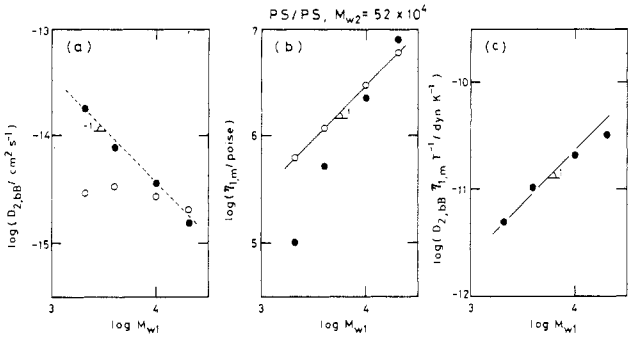

Figure 5. M_{w1} dependence of (a) $D_{2,bB}$ for the dilute blends with $10^{-4}M_{w2} = 52$ and $10^{-4}M_{w1} = 0.21$, 0.4, 1.0, and 2.04 reported by Green and Kramer,[13] (b) $\eta_{1,m}$ of the monodisperse 1-chain with M_{w1} as indicated above, and (c) the product $D_{2,bB}\eta_{1,m}T^{-1}$ evaluated for the dilute blends examined in Figure 5a. The filled circles indicate the data at the Green–Kramer reference temperature $T_{r,GK}$,[13] and the open ones the data at $T_{r,AF} = T_g + 25$ °C (cf. Table I).

Thus ζ_0 at $T_{r,GK}$ seems not to be the same for the blends examined in Figure 5a, because $\eta_{1,m} \propto \zeta_0 M_{w1}$ for $M_{w1} < M_c°$.[21]

For the Stokes–Einstein diffusion, we obtain[5]

$$D_{2,bB} \propto T\eta_{1,m}^{-1}\langle r_2^2\rangle^{-1/2} \quad (15)$$

with T being the absolute temperature. $\langle r_2^2\rangle^{1/2}$ would be almost the same for the blends examined in Figure 5a.[28] Thus, if the Stokes–Einstein diffusion takes place, the product $D_{2,bB}\eta_{1,m}T^{-1}$ should be independent of M_{w1}. Figure 5c shows the M_{w1} dependence of this product evaluated at $T_{r,GK}$ for the blends examined in Figure 5a. Clearly, $D_{2,bB}\eta_{1,m}T^{-1}$ is almost proportional to M_{w1}. This suggests that the Stokes–Einstein diffusion *does not* prevail for $0.21 < 10^{-4}M_{w1} < 2.04$ and leads to the relation $D_{2,bB} \propto \zeta_0^{-1}M_{w1}^0$ because $\eta_{1,m} \propto \zeta_0 M_{w1}$. Thus, the M_{w1} dependence of the diffusion time seems to be the same as that of the relaxation time.

Reducing the $D_{2,bB}$ data by the WLF equation of Allen–Fox[21] to an iso-ζ_0 state with a reference temperature $T_{r,AF}$ ($=T_g + 25$ °C), we also reach the above conclusion. As shown by the open circles in parts a and b of Figure 5, $\eta_{1,m} \propto M_{w1}$ and $D_{2,bB}$ is almost independent of M_{w1} ($\lesssim M_e°$) at $T_{r,AF}$.

$T_{r,AF}$ values are compared with $T_{r,GK}$ in Table I. The difference between $T_{r,AF}$ and $T_{r,GK}$ is not large for $M_{w1} \geq 4000$. However, since ζ_0 is strongly dependent on T if T is not much higher than T_g, these small differences in the reference temperatures may lead to a large difference in ζ_0.

Transition to Zimm Behavior. The analysis made in the previous section suggests that the infinitely dilute 2-chain in the blends with $2100 < M_{w1} \lesssim M_e°$ has the diffusion time

$$\langle r_2^2\rangle/D_{2,bB} \propto \zeta_0 M_{w1}^0 M_{w2}^{1.5-1.6} \quad (16)$$

Equation 16 suggests that the hydrodynamic interaction between the segments of the 2-chain, not screened by the 1-chains in such blends, is expressed in terms of a certain *local* viscosity being independent of M_{w1}: If the 1-chains behave as the Rouse chain, their *macroscopic* viscosity $\eta_{1,m}$ is represented as the product of the frictional and structural factors.[20,29] The former ($\propto\zeta_0$) represents the segmental friction, and the latter ($\propto M_{w1}$) is due to the large-scale normal modes of the 1-chain. Such 1-chains seem not to behave as a uniform medium with the viscosity $\eta_{1,m}$ for the segmental motion of the 2-chain as long as they are larger than the segment of the 2-chain. Then the dynamics of the 2-chain would not be completely the same as that of the (true) Zimm chain.

Table II
Comparison of the $D_{2,bB}$ Data for the Infinitely Dilute 2/1 Blends with $M_{w1} \lesssim M_e°$ and the Theoretical Diffusion Coefficient D_{Z2} of the Zimm Chain[a] at $T_{r,GK}$

	$D_{Z2}/D_{2,bB}$	
M_{w1}	$10^{-4}M_{w2} = 11$	$10^{-4}M_{w2} = 52$
2100	1.1_7	1.0_2
4000	0.5_0	0.4_9
10000	0.2_8	0.2_5
20400	0.1_3	0.1_6

[a] Calculated by eq 17; $\eta_{1,m}$ was evaluated from the Allen-Fox[21] article (cf. filled circles in Figure 5b), and $\langle r_2^2\rangle^{1/2}$ from eq 7.

However, if M_{w1} is sufficiently small, the 2-chain should exhibit Zimm behavior (essentially the same as Stokes–Einstein behavior). Table II compares the $D_{2,bB}$ data[13] and the theoretical diffusion coefficient of the Zimm chain[29] (2-chain)

$$D_{Z2} = 0.192kT/\eta_{1,m}\langle r_2^2\rangle^{1/2} \quad (17)$$

with k being the Boltzmann constant. We can check the validity of the Zimm theory at any temperature, because eq 17 does not include ζ_0 explicitly. Thus, we made the comparison at $T_{r,GK}$. We see that $D_{2,bB}$ is larger than D_{Z2} for $M_{w1} \geq 4000$. However, as first pointed out by Graessley,[30] $D_{2,bB} \cong D_{Z2}$ for $M_{w1} = 2100$. We expect that Zimm behavior is observed for $M_{w1} \lesssim 2100$.[31]

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(17) Very recently, Klein[18] showed that the tube renewal time may be proportional to $M_{w1}^{2.5}$ if the effective constraints are interdependent with one another. However, the assumption of this interdependence seems to be justified only for very large M_{w1}. The data[3,11,13] for blends with $M_{w2} \gg M_{w1} > M_c°$ seem to be better described by the original Klein theory[6] predicting M_{w1}^3 dependence. Because of the experimental restriction for M_{w2} ($\lesssim 3 \times 10^6$), one cannot choose very large M_{w1} to keep M_{w2} sufficiently larger than M_{w1}. Montfort and co-workers[19] reported that the relaxation time $\bar{\tau}$ of the 2-chain ($M_{w2} = 270 \times 10^4$) was proportional to $M_{w1}^{2.3}$ in the blends with $3.5 \leq 10^{-4}M_{w1} \leq 39$. However, the power-law type relation between M_{w1} and $\bar{\tau}$ is usually observed in a rather limited range of M_{w1} ($\ll M_{w2}$), and $\bar{\tau}$ becomes more weakly dependent on M_{w1} as M_{w1} ap-

proaches M_{w2}.[3] Thus, their exponent, 2.3, might increase if we evaluate it only from the data for the blends with $M_{w2} \gg M_{w1}$: If $M_{w2} = 270 \times 10^4$, the second term in eq 6 overwhelms the first term almost completely and the power-law type relation $\langle r_2^2 \rangle / D_{2,bB} \propto M_{w1}^3$ prevails in the range $M_{w1} \lesssim 10^5$. If we use the $\bar{\tau}$ data (Table II in ref 19) in this range of M_{w1}, the exponent becomes 2.7.

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(23) However, there still remains a crucial problem: Viscoelastic properties of well-entangled polymers cannot be described by the reptation mechanism alone. If we wish to explain the viscoelastic and diffusion properties of well-entangled polymers by the generalized tube model, we must assume some other mechanisms contributing largely to viscoelastic relaxation but only slightly to diffusion. Modified theories incorporating reptation and other mechanisms (such as contour length fluctuation) were proposed to explain the viscoelastic properties.[7,24] However, most of those theories assumed the independence of competing mechanisms and were not based on the Langevin equation describing the motion of the chain segments due to those mechanisms operating simultaneously. Thus, it cannot be concluded yet that the modified theories explain the diffusion and viscoelastic properties in a unified manner.
(24) Lin, Y.-H. *Macromolecules* **1984**, *17*, 2846.
(25) Although eq 4 was determined from the D_m data for $M_w > (2–3)M_c°$, the data for $M_c° < M_w < (2–3)M_c°$ are not largely different from those calculated by eq 4, as can be seen from Figure 2. Thus, we used eq 4 to evaluate $D_{1,bB}$ for $M_{w1} > M_c°$.
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(27) Watanabe, H.; Kotaka, T. *Macromolecules* **1986**, *19*, 2520.
(28) $\langle r_2^2 \rangle^{1/2}$ of the PS chain with $M_{w2} = 52 \times 10^4$ in a Θ-solvent (cyclohexane) is smaller by a factor of 30% than that in a good solvent (benzene).[26] Thus, the difference in the $\langle r_2^2 \rangle^{1/2}$ values for the blends examined in Figure 5 would be smaller than 30% and can be neglected.
(29) Yamakawa, H. *Modern Theory of Polymer Solutions*; Harper & Row: New York, 1971.
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(31) Smith and co-workers[32] examined the diffusion of the infinitely dilute 2-chain in the blends of poly(propylene oxide) (PPO): We found that the product $D_{2,bB}\eta_{1,m}$ (evaluated from the $\eta_{1,m}$ and $D_{2,bB}$ data in Table I and Figure 6 in their paper) was nearly the same for $M_{w1} = 1000$ and 1960. However, we also noted that $D_{2,bB}\eta_{1,m}$ for $M_{w1} = 4200$ ($< M_c° = 7000$ for PPO)[32] was significantly larger than those for $M_{w1} = 1000$ and 1960. Thus, for the PPO/PPO blends, Zimm behavior may have been observed for very small M_{w1} but not in the entire range of $M_{w1} < M_c°$. This result is consistent with those for the PS/PS blends shown in this paper (Table II).
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Entanglements in Binary and Ternary Blends of Narrow Molecular Weight Distribution Polystyrenes

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ABSTRACT: Viscoelastic properties of binary blends (bB) of monodisperse linear polystyrenes with low and intermediate molecular weights M_1 and M_2 (designated 1- and 2-chain, respectively) were examined and compared with those of ternary blends (tB) composed of the same 1- and 2-chains plus a third high molecular weight M_3 component (3-chain). In tB, the 3-chain content w_3 was so small that no 3–3 entanglements existed. If the content of the 2-chain w_2 was sufficiently large, the compliance J_2 and viscosity η_2 of the 2-chain in bB were proportional to w_2^{-2} and $w_2^{3.5}$, as in the case of concentrated solutions of the 2-chain in a low molecular weight solvent. The range of w_2 where these relations were observed was wider for bB with larger M_2/M_1 ratio. The relaxation time τ_3 of the 3-chain in tB was proportional to w_2^3 if M_2/M_1 and w_2 were large; this relation was not observed for small M_2/M_1 and w_2. To describe the slow relaxation behavior of the 2- and 3-chains in a unified way, we evaluated an effective entanglement spacing $\tilde{M}_{e2}$ characterizing the terminal relaxation modes of the 2-chain. $\tilde{M}_{e2}$ increased with decreasing w_2 and increasing M_2/M_1 ratio. A universal relation $\tau_3 \propto \tilde{M}_{e2}^{-3}$ with $\tilde{M}_{e2}$ being determined for the corresponding bB was found for tB with large and small M_2/M_1 ratio. Thus, bB and tB respectively could be regarded in the long-time region as the concentrated solution of the 2-chain and 3/2 blend having the effective entanglement spacing $\tilde{M}_{e2}$. These results were interpreted on the basis of the tube renewal concept.

Introduction

The effect of entanglement on the viscoelastic properties of flexible linear polymers is one of the central problems in polymer rheology. Extensive data have been accumulated for entangled polymers with both narrow and broad molecular weight distribution (MWD).[1,2] However, the detailed relaxation mechanisms of entangled polymers are not yet fully understood.

Blends composed of narrow MWD polymers are simple but important model systems for understanding this problem because such blends often exhibit relaxation modes not observable in narrow MWD polymers. Recently, we carried out a series of systematic studies[3–6] on binary blends (bB) of narrow MWD linear polystyrenes (PS) with low and high weight-average molecular weights (M_{w1} and M_{w2}, respectively). The results obtained were as follows.[3–6]

The relaxation modes of the short-chain component (hereafter designated the 1-chain) were affected by blending only slightly, while those of the long-chain component (2-chain) were strongly dependent on M_{w1} and M_{w2} as well as on the composition w_i (i = 1, 2) of the blend.

When M_{w1} was larger than the entanglement spacing M_e, a power-law type dependence of the relaxation time of the 2-chain on M_{wi} and w_i was observed for the blends under the following *extreme* conditions.

(a) If $M_{w2} >> M_{w1} > M_e$ and $w_2 < (w_2)_c$ with $(w_2)_c$ being the critical 2-chain content for onset of entanglements between the 2-chains (2–2 entanglements), the retarded Rouse-like relaxation of the 2-chain was observed at low frequencies, and its characteristic time was[5,6]

$$\tau_{12} \propto \zeta_0 w_2^0 M_{w1}^3 M_{w2}^2 M_e^{-3} \quad (1)$$

Here ζ_0 is the monomeric friction coefficient.

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