(31) Kurata, M.; Yamakawa, H. *J. Chem. Phys.* **1958**, *29*, 311.
(32) Daoud, M.; Jannink, G. *J. Phys. (Paris)* **1976**, *37*, 973.
(33) Onogi, S.; Kimura, S.; Kato, T.; Masuda, T.; Miyanaga, N. *J. Polym. Sci., Part C* **1966**, *15*, 381.

(34) Masuda, T. Dissertation, Kyoto University, Kyoto, Japan, 1973.
(35) Johnson, M. F.; Evans, W. W.; Jordan, I.; Ferry, J. D. *J. Colloid Sci.* **1951**, *6*, 377.

Viscoelastic Properties of Binary Blends of Narrow Molecular Weight Distribution Polystyrenes. 2

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ABSTRACT: Viscoelastic properties of binary blends of narrow distribution polystyrenes with low and high molecular weight (designated as 1-chain and 2-chain, respectively) were examined. In the blends the 2-chains entangle with themselves, only when the weight fraction w_2 of the 2-chain has exceeded a critical value w_c. Then, such blends exhibit a boxlike relaxation spectrum with the characteristic time τ_{22} and intensity P_{22} at the long-time end. For the blends with the molecular weight of the 2-chain M_2 sufficiently larger than that (M_1) of the 1-chain, the τ_{22} is proportional to $w_2^{1.5}M_2^{3.5}$ and P_{22} to w_2^2. The behavior is similar to that of ordinary concentrated solutions. In such blends, a wedgelike spectrum with the characteristic time τ_{12} ($\propto w_2^0 M_1^3 M_2^2$) appears on the intermediate time scale. In terms of the concepts of reptation and tube renewal, this process may be attributed to the renewal of the tubes composed of the 1-chains. On the other hand, for the blends with M_2 close to M_1, the τ_{22} and P_{22} become proportional to $w_2^0 M_2^{3.5}$ and w_2^1, respectively, and the wedgelike spectrum on the intermediate time scale becomes less prominent. Namely, the 2-chains relax before the renewal of the tubes composed of the 1-chains completes.

Introduction

Binary blends of polymers having narrow molecular weight distributions (MWD) are one of the simplest model systems for examining the effect of polydispersity on the viscoelastic properties. Extensive studies have been carried out by various authors on such binary blends, and some of the earlier results were summarized, for example, in the monograph by Ferry[1] and in the review by Graessley.[2] Recently, some workers[3–5] including ourselves[6] reexamined this problem on the basis of the "tube model"[7–11] and proposed some new blending laws.[3–6,12]

In such an attempt,[6] we described linear viscoelastic properties of binary blends consisting of narrow MWD polystyrenes of short and long chains (hereafter designated as 1- and 2-chains, respectively) with molecular weights M_1 and M_2 differing at least 10 times. For such blends, there was a critical value w_c for the content w_2 of the 2-chain corresponding to the onset of entanglements among the 2-chains. Thus, in what we called *dilute* blends[6] with w_2 below w_c, first the relaxation of entanglements among 1-chains took place, and that of entanglements among the 1- and 2-chains prevailed at long times. Then, the blends behaved as dilute solutions of 2-chains dissolved in 1-chains. On the other hand, in *concentrated* blends with w_2 well above w_c, the relaxation of 1–2 entanglements appearing at intermediate times was followed by the relaxation of entanglements among the 2-chains at sufficiently long times. Then, the blends behaved just as concentrated solutions of 2-chains.

We interpreted these results on the basis of the tube model incorporating not only the concept of *reptation*,[7–11] but also *contour length fluctuation*,[13,14] and *tube renewal processes*.[14,15] On this basis we concluded that the relaxation of the 1–2 entanglements appearing at intermediate times is due to the renewal of tubes composed of 1-chains to release the constraints imposed on 2-chains. We also concluded that the relaxation of the 2–2 entanglements at long times proceeds by reptation accompanying contour

length fluctuation of the 2-chains, while the 1-chains are simply acting as solvent at this stage.

To generalize the above-mentioned tube-theory concept on the relaxation modes in binary blends,[6] we extended this study to the blends having relatively small M_2/M_1 ratio. To this end, we prepared a series of binary blends consisting of monodisperse polystyrenes with M_2/M_1 ratio ranging from 2 to 8 and with varying blending ratio. Then, we studied their linear viscoelastic properties. In this paper, we present the results and discuss possible relaxation mechanisms on the basis of the tube model employed in the previous study.[6]

Experimental Section

Anionically polymerized narrow MWD polystyrene (PS) samples were used. The characterization of the samples was carried out on a gel permeation chromatography (GPC; Toyo Soda, Ltd., Model HLC-801A) equipped with a triple-detector system consisting of a built-in refractometer, a UV monitor (Toyo Soda, Ltd., Model UV-8), and a low-angle laser light scattering photometer (Toyo Soda, Ltd., Model LS-8). Chloroform was the elution solvent, and commercially available narrow MWD PS (Toyo Soda, Ltd., TSK PS samples) were used as elution standards. Table I shows the characteristics of the samples. Each sample has an approximately logarithmic-normal MWD.

To prepare binary blends, we chose an L294 sample as component 2 (longer chain) and others as component 1 (shorter one). Prescribed amounts of the two PS samples were dissolved in benzene to make a 5 wt % solution. The solution was freeze-dried for 12 h and further dried at about 80 °C under vacuum for 24 h. The dried blend was then molded at about 170 °C with a
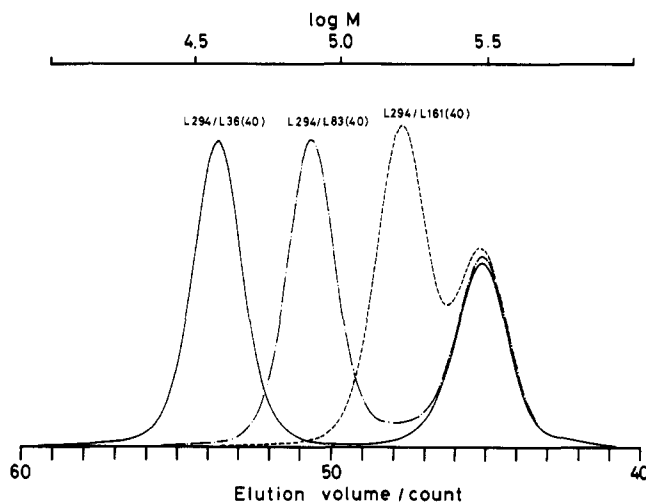
**Table I
Characteristics of Polystyrene Samples**

code	$10^{-3}M_n$	$10^{-3}M_w$	$10^{-3}M_z$	$10^{-3}M_{z+1}$
L36	36.3	38.9	41.6	44.6
L83[a]	82.7	88.6	96.1	107
L161[a]	161	172	183	197
L294[a]	294	316	341	373

[a] Supplied from Toyo Soda Mfg. Co., Ltd.

Figure 1. Gel permeation chromatograms of 40 wt % L294/L36, L294/L83, and L294/L161 blends obtained by a UV detector.
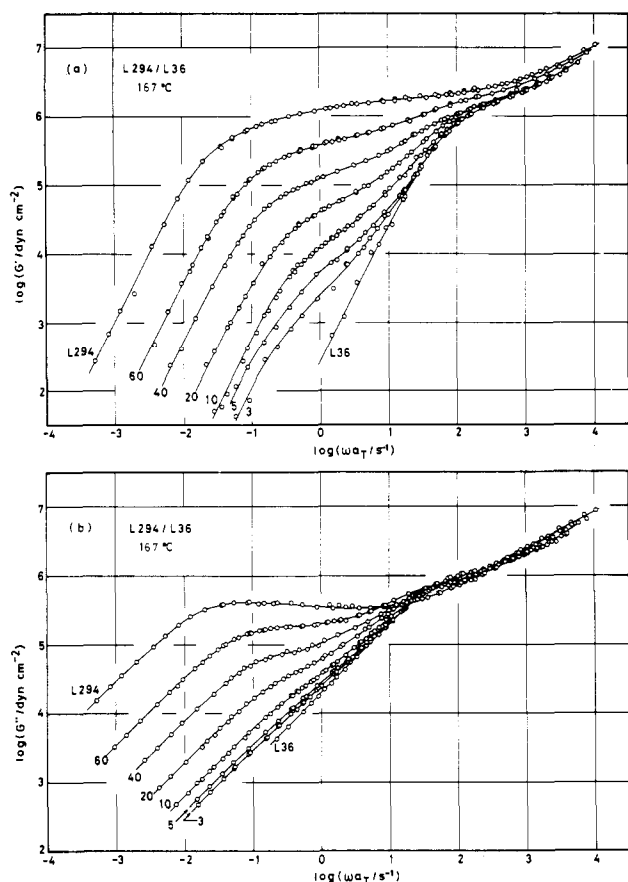

Figure 2. Master curves of (a) the storage modulus G' and (b) loss modulus G'' for L294/L36 blends reduced at 167 °C. The numbers represent the content w_2 of L294 in weight percent.

laboratory hot press into disks of about 26-mm diameter and 1.3-mm thickness. For reference, the component PS samples were also examined. Figure 1 shows GPC chromatograms for 40 wt % blends of L294/L36, L294/L83, and L294/L161 obtained by the UV monitor. The molecular weight distribution is bimodal even for the L294/L161 blend with the ratio M_2/M_1 close to 2. In the following, subscripts 1 and 2 refer to the quantities for the 1- and 2-chains, respectively.

Dynamic measurements were carried out on these disk samples at several temperatures between 128 and 195 °C with a conventional cone-and-plate rheometer (Autoviscometer L-III, Iwamoto Seisakusho, Kyoto). The radius of the cone was 15.0 mm and the angle between the cone and plate was 3.68°. The storage G' and loss G'' moduli were determined by the Markovitz equation.[16]
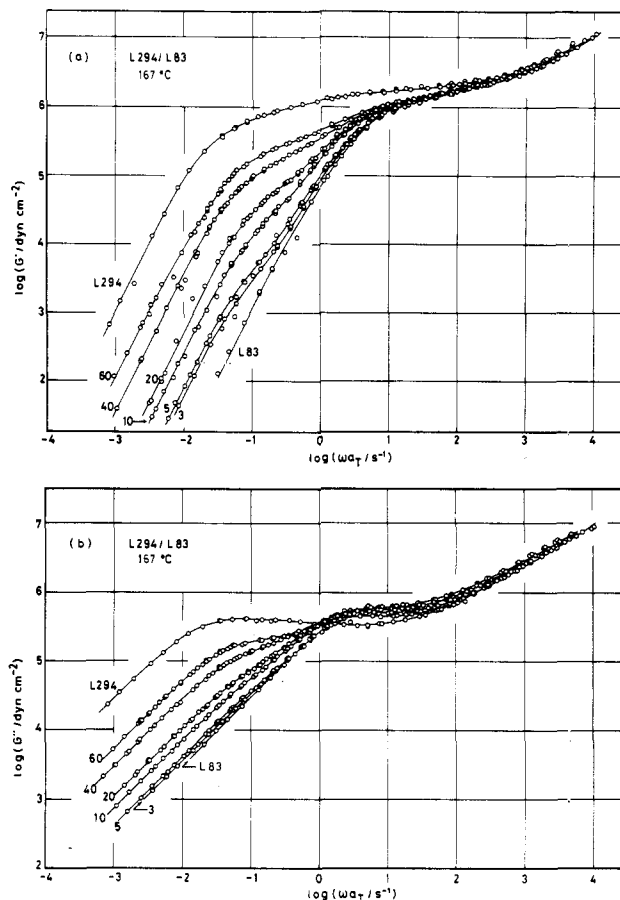

Figure 3. Master curves of (a) the storage modulus G' and (b) loss modulus G'' for L294/L83 blends reduced at 167 °C. The numbers represent the content w_2 of L294 in weight percent.

The time–temperature superposition principle[1] was applicable.

Results and Discussion

Master Curves, Viscosity, and Compliance. Figures 2–4 show the master curves of G' and G'' reduced at 167 °C for L294/L36, L294/L83, and L294/L161 blends, respectively. The numerical values in these figures represent the content w_2 in weight percent of the 2-chain (L294 sample). All the PS samples have molecular weights larger than that between entanglement points, M_e^0 ($\cong 18 \times 10^3$),[1,2] determined for narrow MWD PS samples. Thus, the G' and G'' curves of the component PS samples exhibit a rubbery plateau.

The G' and G'' curves for L294/L36 and L294/L83 blends exhibit a shoulder, although the G'' curves less prominently. The position of the shoulders depends little on w_2, but the height increases with increasing w_2 until w_2 reaches 10 wt %.

For the L294/L36 and L294/L83 blends with w_2 above 10 wt %, the shoulder becomes a plateau. With further increasing w_2, this plateau extends to the lower frequency side, and its height also increases. However, for the L294/L161 blends with a small M_2/M_1 ratio (more precisely, the weight-average molecular weight ratio M_{w2}/M_{w1}) this two-step rubbery plateau merges into a single broad plateau.

Figure 5 shows the temperature dependence of the shift factor a_T for all the blends including the component PS samples examined here. The solid curve represents the WLF equation[1] with the reference temperature $T_r = 167$ °C. All the systems exhibit the same a_T vs. T relation within experimental errors. In other words, we may conclude that all the systems examined have the same mo-
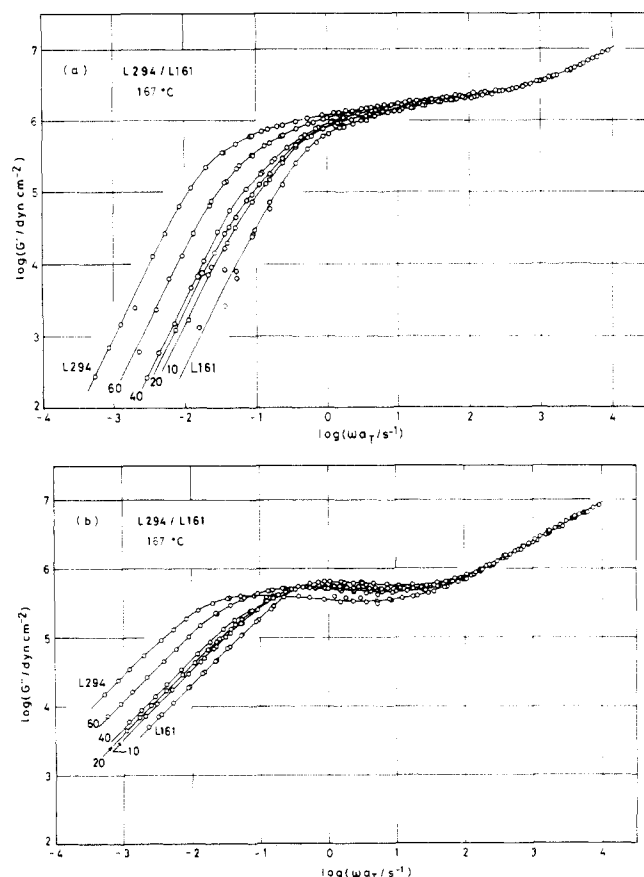
Figure 4. Master curves of (a) the storage modulus G' and (b) loss modulus G'' for L294/L161 blends reduced at 167 °C. The numbers represent the content w_2 of L294 in weight percent.
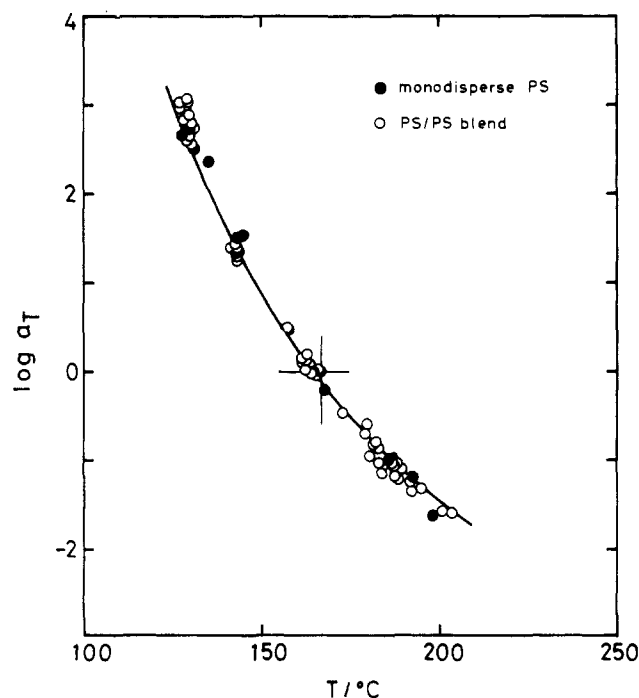

Figure 5. Plots of the logarithm of the shift factor log a_T of the blends and component PS samples against temperature. The solid curve indicates the WLF equation with the reference temperature $T_r = 167$ °C.

nomeric friction coefficient at 167 °C.

Figure 6 shows the dependence of the zero-shear viscosity η_0 at 167 °C on the weight-average molecular weight M_w $(=w_1M_{w1} + w_2M_{w2})$ for all the blends and component
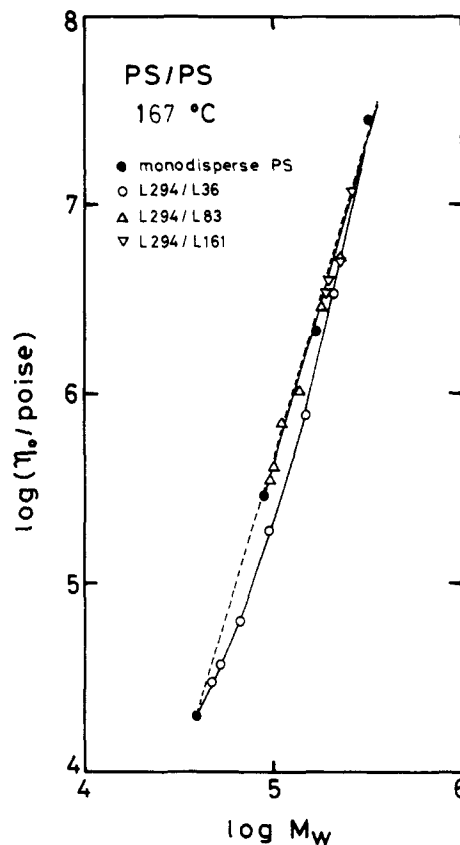

Figure 6. Dependence of the zero-shear viscosity of the blends at 167 °C on their weight-average molecular weights.

PS samples examined here. The relation between η_0 and M_w for L294/L83 and L294/L161 blends having a M_{w2}/M_{w1} ratio smaller than 4 agrees with the 3.5th power law for monodisperse PS samples (broken line in the figure), but that for L294/L36 blends having a M_{w2}/M_{w1} ratio as large as 8 obviously does not obey this relation. In other words, η_0 of binary blends generally cannot be described by M_w alone.[6]

Figure 7 shows the dependence of the steady-state recoverable compliance J_e^0 at 167 °C on w_2 for all the blends. For L294/L161 blends, J_e^0 seems to obey the relation proposed by Mills[17] (eq 1) or Agarwal[18] (eq 2). However,

$$J_e^0 \propto (M_z/M_w)^{3.7} \tag{1}$$

$$J_e^0 \propto (M_zM_{z+1})/(M_nM_w) \tag{2}$$

in the entire range of w_2, this system does not obey eq 3.

$$J_e^0 \propto w_2^{-2} \tag{3}$$

On the other hand, both eq 1 and 2 become unsatisfactory for L294/L83 blends with $M_{w2}/M_{w1} \cong 3.6$, and especially with small w_2. However, eq 3 becomes valid for these blends with $w_2 \geq 60$ wt %. Finally, for L294/L36 blends with $M_{w2}/M_{w1} \cong 8$, eq 1 and 2 are unsatisfactory in the entire range of w_2 examined, but eq 3 becomes valid in a much wider range of w_2, say, ≥ 40 wt %, as reported previously.[6] Any average molecular weights such as M_w, M_z, etc., or their combinations are inadequate as a single, unique parameter describing viscoelastic properties of all types of blends.

Relaxation Spectra. Figure 8 shows the relaxation spectra H of all the blends determined by the second-order Tschoegl approximation[19] from the G' and G'' master curves at 167 °C. The numerical values in the figure represent w_2 (in weight percent). We see that the H cal-
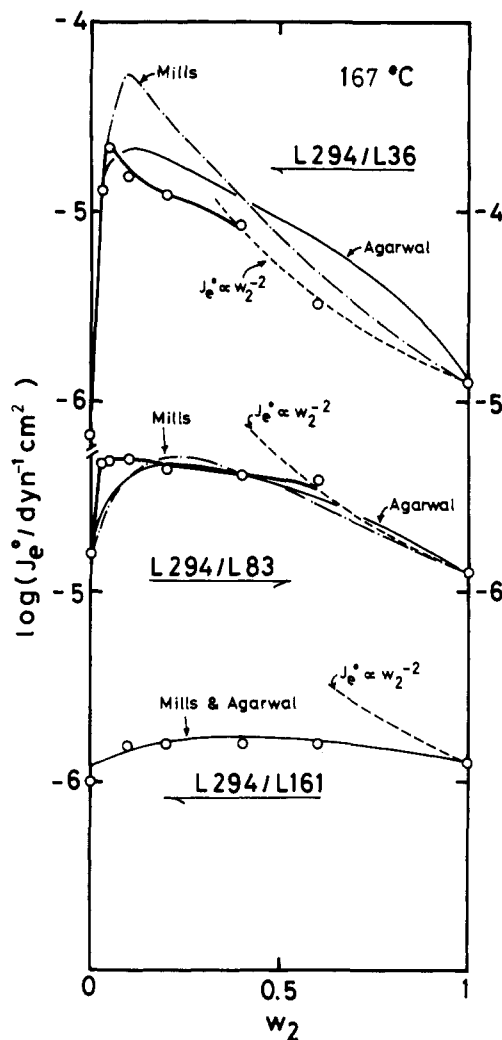
Figure 7. Dependence of the steady-state recoverable compliance of the blends at 167 °C on the content w_2 of the L294 sample.
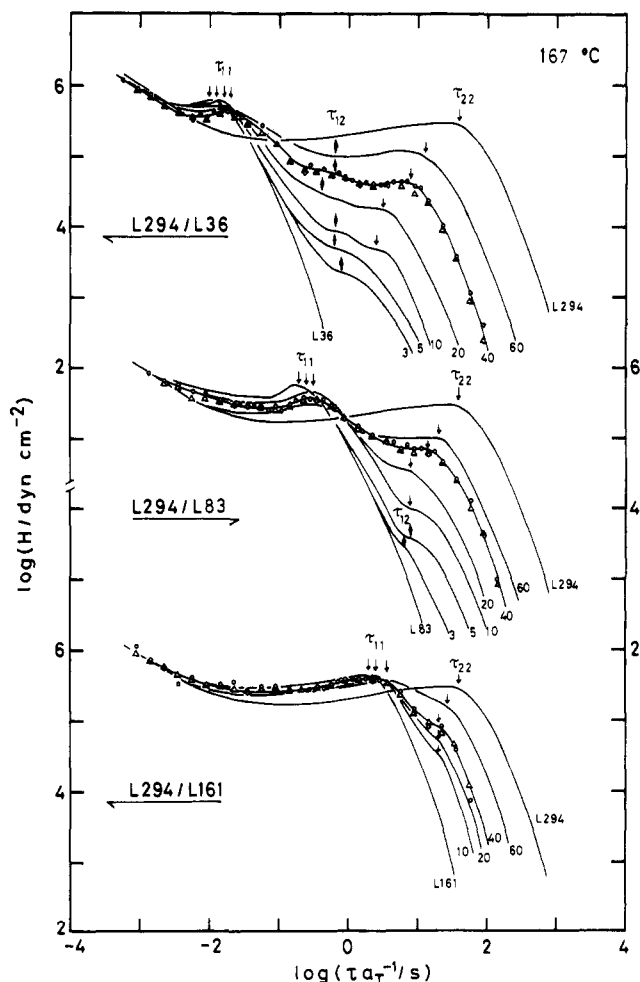

Figure 8. Relaxation spectra calculated for the blends at 167 °C by the second-order Tschoegl approximation. The numerical values in the figure represent the content w_2 of the L294 sample in weight percent.

culated for 40 wt % blends from the G' (represented by circles) and G'' (triangles) curves coincide with each other within the accuracy of the Tschoegl approximation. This was true for all other blends examined here.

In this figure, we notice the following features. Each component PS sample exhibits a box-type spectrum. The L294/L36 blends have a critical content w_c of 10 wt %: For those with $w_2 < w_c$, only a wedgelike shoulder appears after the box-type spectrum due to the 1-chain. The position of this shoulder depends little on w_2, but its height increases as w_2 is increased. When w_2 exceeds w_c, the wedgelike end of the spectrum becomes boxlike, and its end extends to the longer time side with further increase in w_2. However, a small maximum still remains in the H at approximately the same position as that of the shoulder for the blends with $w_2 < w_c$. This small maximum becomes less significant as w_2 is further increased. Since the G' and G'' curves give an identical H, this small maximum should not be an artifact.

By analogy with concentrated solutions,[1,2] the characteristic molecular weight M_{c2} for the 2-chain in the blends can be estimated as

$$M_{c2} \cong M_c{}^0 / w_2 \qquad (4)$$

where $M_c{}^0$ ($\cong 36 \times 10^3$)[1,2] is the value for bulk monodisperse PS. For L294/L36 blends at $w_2 = w_c$ ($\cong 10$ wt %), M_{w2} is close to M_{c2} determined by eq 4. Thus, the w_c seems to correspond to the onset of entanglements among the 2-chains. Hence, its value ($\cong 10$ wt %) should be inde-

pendent of M_{w1}. Thus, all the blends with w_2 below w_c may be classified as *dilute* blends in which the 2-chains do not entangle with each other, while those with w_2 above w_c may be regarded as *concentrated* blends.

For L294/L83 blends with $w_2 \leq w_c$ (10 wt %) also, a shoulder appears after the box-type spectrum corresponding to that of the 1-chain, and for those with $w_2 > 10$ wt %, a box-type spectrum emerges at the longer time end. However, we cannot clearly identify a small maximum at the intermediate time scale for these blends.

For L294/L161 blends with $w_2 \geq w_c$, we observe a broad box-type spectrum at the long-time end, presumably because the box-type spectrum of the 1-chain overlaps that of the 2-chain to some extent even on this time scale.

Characteristic Relaxation Time and Intensity. We estimated characteristic relaxation times τ_{ii} (i = 1 or 2) and τ_{12} from the position of the peaks in the box-type spectrum and/or wedgelike portion of the spectrum H, as indicated in Figure 8 by usual and diamond-shaped arrows, respectively. The intensities P_{ij} were estimated from the height of H at τ_{ij}. Figures 9 and 10 show plots of these τ_{ij} and P_{ij} vs. w_2, respectively.

As can be seen in Figure 8, we found two characteristic times τ_{11} and τ_{12} for L294/L36 blends with $w_2 < w_c$, while for those with $w_2 > w_c$ we found three of them designated as τ_{11}, τ_{12}, and τ_{22} from the short-time side. Since the maxima in the H at intermediate times were small and broad for these blends, we divided, by employing the blending law proposed previously,[6] each spectrum into the
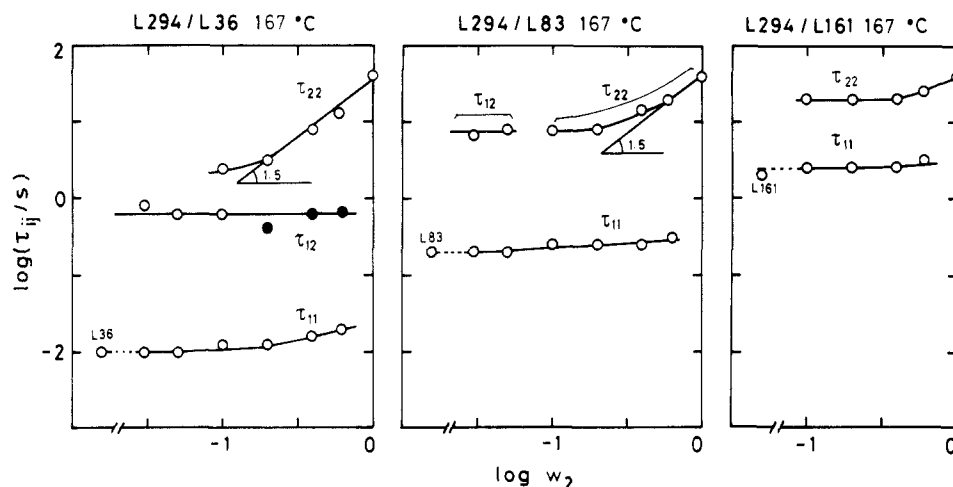
Figure 9. Dependences of the characteristic times τ_{ij} of the blends at 167 °C on the content w_2 of the L294 sample. The filled symbols represent τ_{12} obtained by applying the blending law proposed previously.[6]

Figure 10. Dependence of the intensities P_{12} and P_{22} of the blends at 167 °C on the content w_2 of the L294 sample. The filled symbols represent P_{12} obtained by applying the blending law proposed previously.[6]
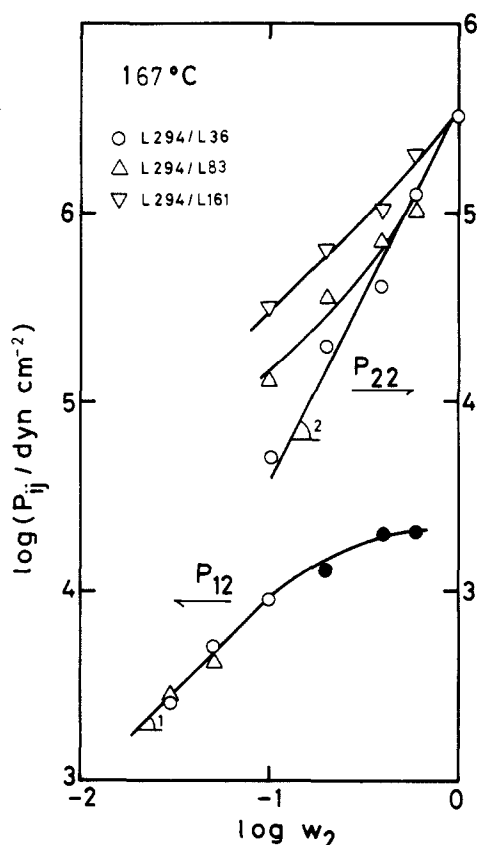
Rouse wedge portion at short times and three other portions corresponding to the characteristic times τ_{11}, τ_{12}, and τ_{22}. Then, we estimated τ_{12} and P_{12} from the corresponding portion of the spectrum. The τ_{12} estimated by this way roughly coincides with the position of the small and broad maximum in the H shown in Figure 8.

For L294/L83 blends with $w_2 < w_c \cong 10$ wt %, we also found two characteristic times. We assigned them as τ_{11} and τ_{12} from the short-time side, as shown in Figure 8. This is because the relaxation mode with the characteristic time τ_{22} should not appear in these *dilute* blends with $w_2 < w_c$, as reported previously.[6]

As can be seen in Figure 8 for L294/L83 and L294/L161 blends with $w_2 > w_c$, we identified only two characteristic

times. Since these blends are *concentrated* ones, we designated them as τ_{11} and τ_{22}.

The w_2 dependence of τ_{ij} and P_{ij} shown in Figures 9 and 10 may be summarized as follows. For all the blends, the τ_{11} are almost independent of w_2 and coincide with the characteristic relaxation time τ_1 of the component 1-chain in its bulk. With increasing w_2, the τ_{11} slightly increase. However, other (12 and 22) modes are significantly different from one blend to another.

For *dilute* blends of L294/L36 and L294/L83 with $w_2 < w_c$, the τ_{12} are almost independent of w_2, while the P_{12} are proportional to w_2. Figure 11 shows the plots at small w_2 of $P_{12}M_{w2}/w_2$ and $\tau_{12}M_{w1}^{-3}M_{w2}^{-2}$ against M_{w2}. The different symbols represent the data for different blends including some previous data (open symbols).[6] Obviously, these two quantities are almost independent of M_{w1} and M_{w2}. Thus, the following equations hold for τ_{12} and P_{12} of L294/L36 and L294/L83 blends with $w_2 < w_c$:

$$\tau_{12} \propto w_2^0 M_{w1}^3 M_{w2}^2 \tag{5}$$

$$P_{12} \propto w_2^1 M_{w1}^0 M_{w2}^{-1} \tag{6}$$

For the *concentrated* blends of L294/L36, the τ_{12} are still almost independent of w_2, while P_{12} deviate downward from the proportionality observed for small w_2 ($<w_c$), as already demonstrated in our previous paper.[6] The τ_{22} and P_{22} satisfy the following equations in the range of $w_2 \geq 20$ wt %:[20]

$$\tau_{22} \propto w_2^{1.5} M_{w1}^0 M_{w2}^{3.5} \qquad (\tau_{22} \gg \tau_{12}) \tag{7}$$

$$P_{22} \propto w_2^2 M_{w1}^0 M_{w2}^0 \tag{8}$$

These equations are obeyed by usual concentrated solutions.

For the *concentrated* blends with the smaller M_{w2}/M_{w1} ratio, eq 7 and 8 are valid only for those in a narrow range of w_2 far above w_c. Finally, with decreasing the M_{w2}/M_{w1} ratio close to unity, the τ_{22} becomes independent of w_2, and the w_2 dependence of P_{22} seems to reduce from eq 8 to

$$P_{22} \propto w_2 \tag{9}$$

Molecular Picture and Blending Law. From the dependence of J_e^0, the characteristic times τ_{ij} and intensities P_{ij} ($i, j = 1$ or 2) on w_2, M_{w1}, and M_{w2}, we conclude that the blends with a small M_{w2}/M_{w1} ratio do not behave as *ordinary* solutions of the 2-chain even at the longest time end, contrary to those with a large M_{w2}/M_{w1} ratio.[6]
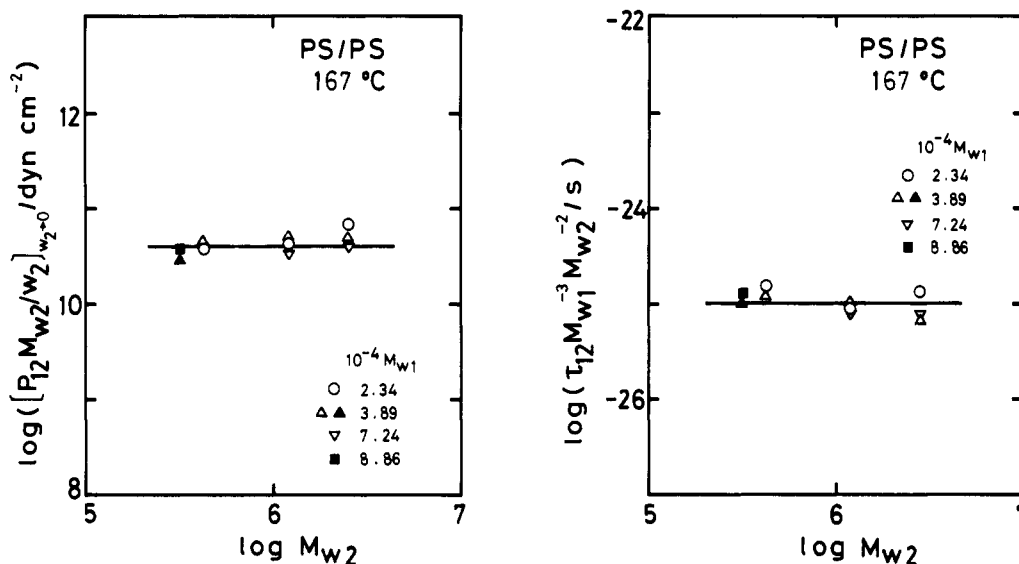
Figure 11. Double logarithmic plots of $P_{12}M_{w2}/w_2$ and $\tau_{12}M_{w1}^{-3}M_{w2}^{-2}$ vs. M_{w2} for the blends at 167 °C. The difference in the symbol corresponds to the difference in M_{w1}. The data obtained in the present study are represented by the filled symbols, while the previous data by the open ones.

Although this change of the behavior of the blends is rather gradual and the critical M_{w2}/M_{w1} value for this change depends on w_2 (cf. Figures 7, 9, and 10), we may assign this critical value to $M_{w2}/M_{w1} \cong 8$.

Now, we may extend our tube model picture[6] on the relaxation mechanisms in binary blends with a large M_{w2}/M_{w1} ratio to more general cases as follows.

First of all, in any binary blends with any w_2, the relaxation mode of the 1-chain should be essentially the same as that in its bulk, except that the constraint on the 1-chain due to the 2-chains should have a longer lifetime than that due to the 1-chains themselves. Thus, the τ_{11} is essentially the same as τ_1 but might be slightly increased with increasing w_2.

The relaxation modes of the 2-chain in the blends are more complicated. In a range of the time scale $\tau < \tau_{11}$, the constraint on the 2-chain due to the 1-chains is effective. On this time scale any 2-chains would not recognize that they are blended with shorter 1-chains. On the other hand, on the time scale $\tau > \tau_{11}$, the topological constraint on the 2-chain (imposed by the 1-chains) should be loosened because of the reptational motion of the 1-chains.

Thus, for *dilute* blends with $w_2 < w_c$ in which no entanglements among 2-chains exist, the relaxation of the 2-chain may take place in two forms: the renewal of the tubes composed of the 1-chains (the 1-tubes) and/or the reptation of the 2-chain from the 1-tubes. The characteristic time τ_{12} and intensity P_{12} of the former tube renewal process would depend on w_2, M_{w1}, and M_{w2} in the manner predicted by Klein[15] and Graessley[14] (eq 5 and 6). On the other hand, the reptation of the 2-chain in the dilute blends would be essentially the same as that in the bulk 2-chain, as long as the tubes confining the 2-chain remain as they were by the time it has escaped from the tube. Then, the characteristic time (τ_{12}') corresponding to this process should be essentially the same as that in the bulk, τ_2, or that in the *concentrated* blends τ_{22} (eq 7) except its w_2 dependence. Namely, it may be expressed as

$$\tau_{12}' \propto w_2^0 M_{w1}^0 M_{w2}^{3.5} \tag{7'}$$

The intensity P_{12}' of this process should be proportional to w_2 instead of w_2^2.

Obviously, for the *dilute* blends with a large M_{w2}/M_{w1} ratio (say, more than 10) discussed in the previous paper,[6]

the tube renewal process overwhelms the reptation, because τ_{12} is far shorter than τ_2 (or τ_{12}'). Such blends may be modeled as a dilute solution of the 2-chain in the range of time scale $\tau > \tau_{11}$, where a Rouse-wedge-type spectrum emerges.

Although eq 5 for τ_{12} was confirmed only for blends with a large M_{w2}/M_{w1} ratio and would not hold for blends with a small ratio, we estimated τ_{12} for the latter by eq 5 as a *virtual* characteristic time. Then, for the blends with increasing M_{w1}, τ_{12} approaches to and finally exceeds τ_2 or τ_{12}' (cf. the M_{w1} dependence of τ_{12}' and τ_{12} in eq 7' and 5). Thus, in the blends with a relatively small M_{w2}/M_{w1} ratio and with τ_{12} being not sufficiently shorter than τ_2, the 2-chains may relax by their own reptation before the tube renewal process completes. Under such a situation, the entanglements (due to the 1-chains) for the 2-chain remain essentially unchanged even at this long-time end. Then, the intensity (P_{12}') and the characteristic time (τ_{12}') would become proportional to w_2 and independent of w_2, respectively (cf. Figures 9 and 10). Thus, such blends should behave as a pseudo-single-component system (with broad MWD) rather than a dilute solution of the 2-chain, giving rise to a broad box-type spectrum.

For *concentrated* blends with $w_2 > w_c$, an additional process emerges for the relaxation of the 2-chain. Namely, the 2-chains now entangle not only with the 1-chains but also with themselves. Therefore, even in the blends with a large M_{w2}/M_{w1} ratio, the 2-chain would not relax completely even after the renewal of the 1-tubes, but only after the subsequent reptation from the remaining 2-tubes. (The renewal of the 2-tubes would be much slower than the reptation of the 2-chain.)[6,14,15] In other words, after the renewal of the 1-tubes the constraint due to the 1-chains becomes ineffective, and the blend behaves as a *concentrated* solution of the 2-chain. Since only a portion of the constraint imposed on the 2-chain could be released during the renewal of the 1-tubes, the intensity P_{12} for the tube renewal process in the blend with $w_2 > w_c$ becomes a weak function of w_2 (cf. Figure 10).

An essential point is that the blends behave as a solution of 2-chains only on the time scale $\tau > \tau_{12}$, where the constraint due to the 1-chains has become ineffective. Then, the effective entanglement spacing (due to the 1- and other 2-chains) for the 2-chain increases to the value ($\propto w_2^{-1}$) predicted for a concentrated solution. For such blends,

we obtained[6] eq 7 and 8 by employing Doi theory,[13] which has incorporated the contour length fluctuation of the reptating 2-chain, and by assuming that the molecular weight between the entanglements due only to the 2-chains is inversely proportional to w_2.

However, for the *concentrated* blends with a small M_{w2}/M_{w1} ratio (<8), the tube renewal processes (of both 1- and 2-tubes) are relatively slower than the reptation of the 2-chain. Then, the tube renewal processes would not contribute much to the relaxation of the 2-chain. Thus, we cannot regard such blends as a solution of the 2-chain even at the longest time end of the spectrum. The situation is essentially the same as in the *dilute* blends with a small M_{w2}/M_{w1} ratio discussed above.

For binary blends with a large M_{w2}/M_{w1} ratio, we already proposed a blending law for the relaxation spectrum H_B.[6] For the *dilute* blends with $w_2 < w_c$, the proposed blending law reads

$$H_B(\tau) \cong w_1 H_1(\tau/\lambda_{11}) + w_2 H_2(\tau)|_{\tau < \tau_{11}} +$$
$$w_2 H_{12}{}^w(\tau)|_{\tau_{11} < \tau < \tau_{12}} \qquad (w_2 < w_c, M_{w1} \ll M_{w2}) \quad (10)$$

and for the *concentrated* blends

$$H_B(\tau) \cong w_1 H_1(\tau/\lambda_{11}) + w_2 H_2(\tau)|_{\tau < \tau_{11}} +$$
$$f(w_2) H_{12}{}^w(\tau)|_{\tau_{11} < \tau < \tau_{12}} + w_2{}^2 H_2(\tau/\lambda_{22})|_{\tau_{11} < \tau < \tau_{22}}$$
$$(w_2 > w_c, M_{w1} \ll M_{w2}; \lambda_{22} \cong w_2{}^{1.5}) \quad (11)$$

Here, H_1 and H_2 represent the spectra of the 1- and 2-chains in their bulk, respectively; the shift factors λ_{11} and λ_{22} represent the difference between τ_1 and τ_{11}, and that between τ_2 and τ_{22} (cf. Figure 9), respectively; and $f(w_2)$ represents the intensity of the tube renewal process (12 mode) in concentrated blends with $w_2 > w_c$.

Figure 12 shows examples of splitting H_B of 40 wt % blends of L294/L36, L294/L83, and L294/L161 into their components. To do this, we assumed a blending law, eq 11′, formally similar to eq 11 for these concentrated blends:

$$H_B(\tau) \cong w_1 H_1(\tau/\lambda_{11}) + w_2 H_2(\tau)|_{\tau < \tau_{11}} +$$
$$\bar{P}_{22} H_2(\tau/\lambda_{22})|_{\tau_{11} < \tau < \tau_{22}} + \text{remaining cross term} \quad (11')$$

The shift factor λ_{22} and intensity factor $\bar{P}_{22}$ were determined empirically to achieve a good fitting at the terminal zone of the H_B. On the other hand, the λ_{11} ($=\tau_{11}/\tau_1$) were calculated from the empirically determined characteristic times of the 1-chain in the blend (τ_{11}) and its bulk (τ_1). We summed up the first three terms in eq 11′, which are represented by the thin broken curves in Figure 12. Then, we subtracted this sum from the H_B to see whether a cross term would remain or not.

For 40 wt % blend of L294/L36 blend with a large M_{w2}/M_{w1} ratio ($\cong 8$), the cross term on the intermediate time scale is quite significant, as represented by circles and the thick curve. As reported previously,[6] it looks like a Rouse wedge. Furthermore, $\bar{P}_{22}$ is equal to $w_2{}^2$. Namely, eq 11 holds for this blend.

For the L294/L83 blend with $M_{w2}/M_{w1} \cong 3.6$, the blending law changes its form. The empirically determined intensity and the shift factors are $\bar{P}_{22} \cong w_2{}^{1.5}$ (=0.25) and $\lambda_{22} \cong w_2{}^{1.0}$ (=0.4), respectively (instead of $w_2{}^2 = 0.16$ and $w_2{}^{1.5} = 0.25$ in eq 11). However, these factors no longer obey these power forms of w_2 in the entire range of w_2 (>w_c), but become weaker functions of w_2 as w_2 approaches w_c (cf. Figures 9 and 10). Correspondingly, the cross term (represented by the difference between the thick solid curve and the thin broken curve) becomes less significant and is within possible errors involved in the calculation of H's. Similar results were reported by Prest[21] for binary
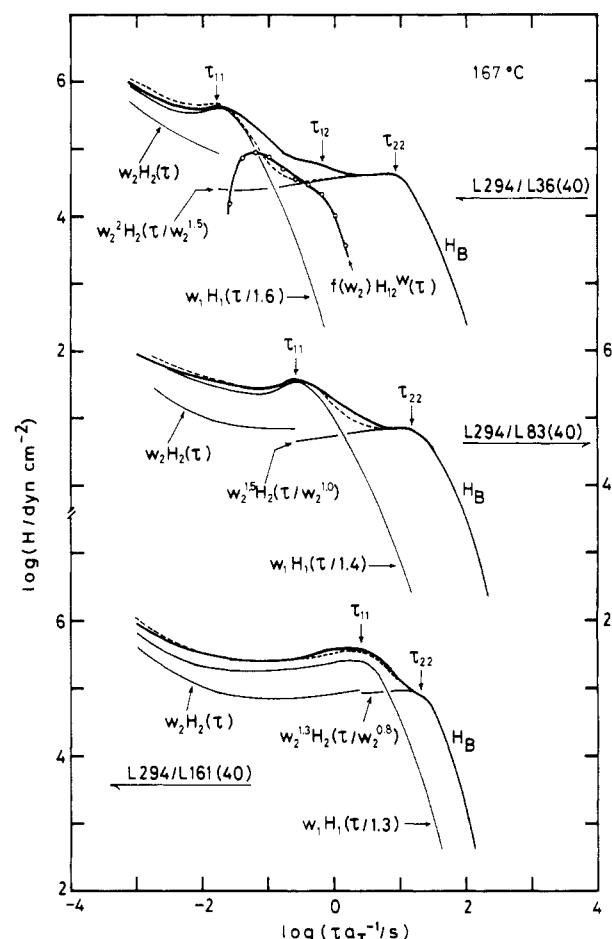

Figure 12. Examples of dividing the relaxation spectra H_B for 40 wt % L294/L36, L294/L83, and L294/L161 blends at 167 °C into the portions corresponding to eq 11′. The solid curves represent H_B, and the thin broken curves the sum of the first three terms in eq 11′.

blends of narrow MWD polystyrenes with $M_{w2}/M_{w1} \cong 4$.

Finally, the L294/L161 blend with $M_{w2}/M_{w1} \cong 1.8$ exhibits the intensity factor P_{22} (0.30 $\cong w_2{}^{1.3}$) and shift factor λ_{22} (0.5 $\cong w_2{}^{0.8}$) of much weaker functions of w_2. At the same time, the cross term disappears almost completely. These results correspond to the fact that the contribution of the tube renewal process becomes less significant and finally disappears, as M_{w1} becomes closer to M_{w2}.

For *dilute* as well as *concentrated* blends having a small M_{w2}/M_{w1} ratio, we speculate that the asymptotic form of the blending law may be given as

$$H_B(\tau) \cong w_1 H_1(\tau) + w_2 H_2(\tau) \qquad (M_{w2}/M_{w1} \to 1) \quad (12)$$

Namely, the blending law may change from eq 10 and 11 to eq 12 with decreasing M_{w2}/M_{w1} ratio, although there might exist a relatively large crossover region for this change.

Equation 12 is based on an assumption that the topological constraint for the 1- and 2-chains in the blends (with a small M_{w2}/M_{w1} ratio) is the same as that in their respective bulk states on any time scale. In other words, we assumed that the tube renewal process due to the reptation of the 1-chain hardly contributes to the relaxation of the 2-chain, and vice versa.[22] Hence, we estimate the shift factors to be unity. Otherwise, eq 12 is equivalent to the blending law of Ninomiya and Ferry.[23]

Formally, eq 12 coincides also with a blending law derived from the Doi–Edwards theory.[3,4,9] However, the empirically determined H_1 and H_2 of the monodisperse PS samples have much broader distribution of the relaxation

modes than the theoretical spectra expected from the Doi-Edwards theory.

Here, we should comment on the limitation of the blending law in its present form. The present law and presumably any other single function of a simple form cannot describe the behavior of binary blends covering whole ranges of the w_2 and M_{w2}/M_{w1} by the spectra of the components. As shown in our previous paper,[6] eq 10 for dilute blends and eq 11 for concentrated blends are valid only for the H, η_0, and J_e^0 of those with sufficiently large M_{w2}/M_{w1} ratios (presumably ≥8), while eq 12 seems to hold only for those with M_{w2}/M_{w1} ratios very close to unity (presumably <1.8, which is the value for the L294/L161 blend).

At present, we do not have a blending law of a definite form covering these two extremes of eq 10 and 11 and eq 12. This is due to the fact that entanglements for a chain in a blend may depend on w_2, M_{w2}, and M_{w2}/M_{w1} ratio, and differ from those in its bulk. To obtain a blending law covering whole ranges of these quantities, we must at first determine the relaxation spectrum of a chain placed in such a particular entanglement state.[24] Recently, such an attempt has been made but is unfortunately not yet successful.[25]

If we rely on the tube model, we must consider complicated processes, in which the reptation of a chain with fluctuating contour length, the tube renewal process, and other possible molecular motions take place cooperatively in a complicated fashion. A study on ternary blends and polydisperse polymers having a broad and continuous MWD has been undertaken. Such a study will clarify this problem to some extent, although an analysis of such complicated processes would be very difficult.

References and Notes

(1) Ferry, J. D. "Viscoelastic Properties of Polymers", 3rd ed.; Wiley: New York, 1980.
(2) Graessley, W. W. *Adv. Polym. Sci.* **1974**, *16*.
(3) Graessley, W. W. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 27.
(4) Kurata, M. *Macromolecules* **1984**, *17*, 895.
(5) Masuda, T.; Yoshimatsu, S.; Takahashi, M.; Onogi, S. *Polym. Prepr. Jpn.* **1983**, *32*, 2365.
(6) Watanabe, H.; Kotaka, T. *Macromolecules* **1984**, *17*, 2316.
(7) de Gennes, P. G. *J. Chem. Phys.* **1971**, *55*, 572.
(8) de Gennes, P. G. "Scaling Concepts in Polymer Physics"; Cornell University Press: Ithaca, NY, 1979.
(9) Doi, M.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1789, 1802, 1818; **1979**, *75*, 38.
(10) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1005, 1981.
(11) Evans, K. E.; Edwards, S. F. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 1891, 1913, 1929.
(12) Some of the recent studies on this problem are not necessarily based on the tube model. See, for example: Soong, D. S.; Shen, M.; Hong, S. D. *J. Rheol.* **1979**, *23*, 301. Soong, D. S.; Shyu, S. S.; Shen, M.; Hong, S. D.; Moacanin, J. *J. Appl. Phys.* **1979**, *50*, 6007. Soong, D. S.; Shyu, S. S.; Shen, M. *J. Macromol. Sci., Phys.* **1981**, *B19*, 49. Liu, T. Y.; Soong, D. S.; Williams, M. C. *J. Rheol.* **1983**, *27*, 7.
(13) Doi, M. *J. Polym. Sci., Polym. Phys. Ed.* **1983**, *21*, 667.
(14) Graessley, W. W. *Adv. Polym. Sci.* **1982**, *47*.
(15) Klein, J. *Macromolecules* **1978**, *11*, 852.
(16) Markovitz, H. *J. Appl. Phys.* **1952**, *23*, 1070.
(17) Mills, N. J. *Nature (London)* **1968**, *219*, 1249.
(18) Agarwal, P. K. *Macromolecules* **1979**, *12*, 343.
(19) Tschoegl, N. W. *Rheol. Acta* **1971**, *10*, 582.
(20) Although we did not examine the M_{w1} and M_{w2} dependence of τ_{22} and P_{22} for the blends with large M_{w2}/M_{w1} ratios in the present study, we already showed that eq 7 and 8 are satisfied for the blends having various M_{w1} and M_{w2} ($\gg M_{w1}$).
(21) Prest, W. M.; Porter, R. S. *Polym. J.* **1973**, *4*, 154. Prest, W. M. *Ibid.* **1973**, *4*, 163.
(22) Strictly speaking, this statement is not precise because the tube renewal process might contribute to some extent even in the monodisperse polymers having large but finite molecular weights.
(23) Ninomiya, K. *J. Colloid Sci.* **1959**, *14*, 49. Ninomiya, K.; Ferry, J. D. *Ibid.* **1963**, *18*, 421.
(24) Since by rheological measurements alone we cannot resolve the stress (or modulus) into the contributions from each component in the blend, some rheooptical methods would be a powerful tool for determining the relaxation spectrum of the component in a particular entanglement state.
(25) Fujita, H.; Einaga, Y. *Nihon Reoroji Gakkaishi* **1984**, *12*, 147.

Synthesis and Viscosity Studies of Some Novel Ionene Polymers

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ABSTRACT: To probe polyelectrolyte–polysoap transitions, three series of N,N-disubstituted ionenes have been prepared differing in their charge separation by having three, four, or six methylenes between the charged quaternary nitrogens. In each series, one N-substituent is methyl, while the other is methyl, ethyl, n-butyl, n-hexyl, or n-octyl. Ultrafiltration studies were performed to establish that all polymers range in molecular weight between 10 000 and 40 000. Viscosities were obtained in salt and salt-free solutions of water and ethanol–water mixtures. For smaller alkyl groups, the shapes of the curves were typical for polyelectrolytes. As the length of the N-alkyl increases, both the overall reduced viscosities and the steepness of the curves decreased, indicating polysoap behavior. The order of viscosities in several aqueous ethanol mixtures showed analogous changes. The charge density of the polyelectrolyte seems less important than the length of the pendant alkyl group in the onset of this transition.

Introduction

Polysoaps[1] are an interesting and useful subclass of polyelectrolytes. In general, a polysoap can be defined as a polymer in which soap molecules are part of the covalent structure.

In the course of work on counterion diffusion utilizing a series of ionene structures,[2] it became of interest to develop a new class of ionenes called ionene polysoaps[3] (**1**). These ionenes, polyelectrolytes in which the charges in the backbone are well-defined, would incorporate aliphatic,