Entanglement in Blends of Monodisperse Star and Linear Polystyrenes. 2. Concentrated Blends

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ABSTRACT: The viscoelastic behavior of blends composed of 4-arm star (4S) and linear (L) polystyrenes (PS) was compared with that of binary blends of linear PS to study the effect of the chain architecture on the relaxation dynamics. In most of the blends, the concentrations of the components were chosen to be large enough to form entanglements among each component as well as with the other component. For such a *concentrated* blend, the effect of blending is generally two-sided: The relaxation of the short chains is retarded by the long chains, and that of the long chains is accelerated by the short chains. This two-sided effect was expected to be different from 4S and L chains in the blend. For very long 4S or L chains blended with much shorter L chains, no difference due to the architecture of the long chains was observed. Both 4S and L chains behaved at long times as in concentrated solutions. Also for rather short 4S or L chains blended with much longer L chains, the relaxation behavior was not very different: The magnitude of retardation due to the much longer L chains was nearly the same for the short 4S and L chains. On the other hand, long 4S or L chains blended with still longer L chains exhibited different behavior, reflecting the difference in the chain architecture. In such blends, the relaxation of the long 4S chains was retarded more strongly than that of the long L chains. The longer the 4S chains were, the more prominent this retardation was. This behavior suggests that the constraint release mechanism becomes more significant for longer 4S chains in monodisperse systems and is suppressed more strongly in blends.

Introduction

The chain architecture, such as linear,[1,2] branched, star,[3-7] H-shaped,[8] comb,[9,10] and ring,[11,12] is one of the most important factors that determine the dynamics of condensed polymer systems. In addition to a huge number of studies on linear polymers, extensive experiments have also been done on *monodisperse* star polymers, and the following features have been found.[3-7]

For a low molecular weight (MW) star polymer, the zero-shear viscosity, η_0, is approximately equal to that of a linear polymer having the same radius of gyration. On the other hand, for the stars with high MW, η_0 increases exponentially with the arm molecular weight, M_a. This differs from the behavior of high-MW linear polymers,[1] which exhibit a power law relation $\eta_0 \propto M^{3.5}$.

The steady-state compliance, $J_e°$, for both nonentangled and entangled star chains was found to be described by the Rouse–Ham theory,[13,14] which is essentially a theory for an *isolated* and *nonentangled* chain. However, this result does not necessarily mean that the Rouse–Ham mechanism is prevailing in the entangled star systems: In fact, the terminal relaxation spectrum for entangled star polymers is quite different from that predicted by the Rouse–Ham theory and is much broader than that for the linear polymers.

The molecular weight distribution (MWD) is another important factor determining the dynamics of entangled polymers. Binary blends of narrow MWD polymers including systems composed of linear chains trapped in a network (thus having one component of high MW $\rightarrow \infty$) are simple and important model systems, because we can rather easily control the life time of the entanglement network in such blends.[15-32] In fact, such blends often exhibit relaxation modes unobservable in monodisperse systems. For example, particular modes due to entanglements between the high-MW and low-MW components became significant, besides those due to the entanglements among themselves. To amplify such an effect of entanglements between different components in a binary blend, we should keep the content of the test component dilute enough to entangle only with the other component (the matrix component). We called such blends *dilute* blends.[17-23]

For such a dilute blend of a small amount of star chains in a large excess of linear chains, we have found the following features: Dilute star chains entangled only with *much shorter* linear chains with molecular weight M_1 exhibit the Rouse–Ham-like relaxation modes with the characteristic time proportional to $M_1{}^3$.[23] In the framework of the generalized tube model, this relaxation behavior is attributable to the constraint release mechanism,[33,34] through which the star chain relaxes as the shorter matrix chains diffuse away, thereby diminishing the constraint on the star chains.

For a star chain entangled with much *longer* linear chains or trapped in a network, its mechanical relaxation time is much longer and the diffusion coefficient is much smaller than those in the bulk star state.[15,16] On the basis of the generalized tube model, we may interpret these results as due to a large contribution of both constraint release and path breathing mechanisms[33-35] in a monodisperse system, and strong suppression of the former mechanism in blends. However, a possible change in the relative contribution of these competing mechanisms with increasing arm length M_a of monodisperse star chains has not been clarified yet.

In dilute blends, the behavior of the major component is essentially identical with that in the monodisperse system, and their behavior is practically controlling the relaxation modes of the minor (test) component. Thus, the effect of blending two components to make a dilute blend is one-sided: from the major component to the minor component. On the other hand, in so-called *concentrated* blends, the amount of each component, in particular, that of the high MW component, is large enough to form entanglements not only with the other component but also among themselves. Then, we may expect a two-sided effect of blending: In general, the relaxation of the short-chain component is retarded by the longer chains, and, at the same time, the relaxation of the longer chains is accelerated by the shorter chains. This effect of blending

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Table I
Characteristics of 4-Arm Star and Linear Polystyrene Samples

code[a]	$10^{-3}M_w$	M_w/M_n	f[b]	log η_0,[c] P	log $J_e°$,[c] dyn^{-1} cm^2
		4-Arm Star			
4S77	307	1.08	4.2	5.48	−5.42
4S184	736	1.05	4.0	7.23	−5.07
4S310	1240	1.06	4.1	8.49	−4.78
		Linear			
L46[d]	46.0	1.05		3.80	−5.96
L71[d]	71.4	1.06		4.29	−5.63
L172[d]	172	1.07		5.50	−5.50
L503	503	1.06		7.16	−5.26
L1810	1810	1.10		9.01[e]	

[a] The code number indicates the rounded number of the arm molecular weight, $M_a = M_w/4$, and weight-average molecular weight, M_w, for 4-arm star and linear samples, respectively, in units of 1000. [b] $(M_w)_{star}/(M_w)_{precursor}$. [c] Zero-shear viscosity and compliance of concentrated solutions with ϕ_p = 60 vol % at the iso-free-volume state with f_r = 0.0644 (T_r = 54, 71 °C for DBP, DOP systems, respectively). [d] From Tosoh Co. [e] Extrapolated from the values of seven samples in the M_w range from 88.5 × 10^3 to 775 × 10^3.

would possibly be different for star and linear chains in blends, because the change in the relaxation mechanism induced by blending should be different for star and linear chains. Thus, a study on the behavior of star chains in a *concentrated* blend is an interesting and important task that would complement the knowledge on the behavior in a dilute blend. In this paper, we present dynamic data on concentrated 4S/L and L/4S blends and discuss the relaxation behavior of 4-arm star chains in these blends in relation to the behavior of linear chains in L/L blends.

Experimental Section

Materials. Anionically polymerized narrow molecular weight distribution (MWD) 4-arm star and linear polystyrenes (PS) were used as the samples. Details of the synthesis and characterization were described elsewhere.[23] The characteristics of these samples are summarized in Table I together with their η_0 and $J_e°$ data. The linear PS samples are coded, for example, as L1810 with the number representing M_w, and the 4-arm star samples, as 4S with the number representing the arm molecular weight, $M_a = M_w/4$, both in the unit of 1000.

The MWD of all the samples used are sufficiently narrow, as can be seen from the heterogeneity index data, M_w/M_n, given in Table I. In the following, we designate all the 4-arm star (4S) and linear (L) narrow MWD PS samples as *monodisperse* and do not distinguish the weight- and number-average molecular weights.

We examined several series of binary blends: blends composed of high-MW 4S (4S310) and low-MW L (L71) samples (designated as 4S310/L71), and those of a high-MW L (L1810) and two low-MW 4S (4S184 or 4S77) samples (designated as L1810/4S184 and L1810/4S77). We also examined two L/L blends (L1810/L503 and L1810/L172) for comparison. The low-MW L503 and L172 samples have η_0 very close to those of 4S184 and 4S77, respectively, as can be seen in Table I. For convenience, we designate the low-MW component as "1-chain" and the high MW one as "2-chain". Hereafter, the subscripts 1 and 2, respectively, refer to the quantities of 1- and 2-chains.

Measurements. Dynamic measurements were carried out on the blends described above with a laboratory rheometer (Model IR-200, Iwamoto Seisakusho, Ltd., Kyoto) of a cone and plate type, similar to the one described previously.[17-19] The high MW 4S and L samples in the melt did not relax in the temperature and frequency ranges accessible to the present rheometer.[23] In fact, high-MW 4S samples degraded within 2 h at temperatures above 200 °C. Thus, we added to the systems dibutyl phthalate (DBP) as a plasticizer.[20,21,23] For some systems containing a much higher MW component, we used dioctyl phthalate (DOP) as a less volatile plasticizer.[23] The blends were prepared as described previously.[20]

The volume fraction, ϕ_p, of the total polymer component (1 + 2 chains) was 60 vol %, except for two DBP solutions of 4S310 with ϕ_p = 40 and 20 vol %. The characteristic molecular weight, M_c, and the entanglement spacing, M_e, for the systems with ϕ_p = 60 vol % were 51 × 10^3 and 30 × 10^3, respectively.[1]

The measurements were carried out in the temperature ranges of 18–106, 10–74, and 10–58 °C for the DBP systems with ϕ_p = 60, 40, and 20 vol %, respectively, and in the range from 42 to 151 °C for the DOP systems. The time–temperature superposition principle[1] was applied to obtain master curves of the storage, G', and loss, G'', moduli. All the data for the systems with ϕ_p = 60 vol % were reduced to an isofriction state with the free volume fraction, f_r = 0.0644. Although the result is not shown here, the shift factor, a_T, was well described by the previously reported WLF equation: $\log a_T = -6.74\,(T - T_r)/(133.6 + T - T_r)$.[19,20] The reference temperatures T_r were 54 and 71 °C, respectively, for the DBP and DOP systems.

We have already demonstrated that the viscoelastic behavior was the same for the DBP and DOP systems, with ϕ_p = 60 vol % at their respective T_r.[23] In the following, we always compare the data at T_r and do not distinguish the two plasticizers used.

Data Analysis. From the data for the blend and monodisperse 1-chains with the same ϕ_p (=60 vol %), the viscosity, $\eta_{2,bB}$, the elastic coefficient, $A_{2,bB}$, and the compliance, $J_{2,bB}$, of the 2-chain *placed in a blend* were evaluated by[19-23]

$$\eta_{2,bB} = \eta_{bB} - (\phi_1 \eta_{1,m}/\phi_p) \tag{1a}$$

$$A_{2,bB} = A_{bB} - (\phi_1 A_{1,m}/\phi_p) \tag{1b}$$

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

Here, the subscripts bB and 1,m stand for the experimentally determined quantities of the blend as a whole and the monodisperse 1-chain, respectively.

We have to point out that eqs 1a–c are the relations for a dilute blend in which the relaxation of the 1-chain is identical with that in the monodisperse system.[20,21,23] For a concentrated blend, we need to consider, in principle, retardation of the relaxation due to the 2-chains.[18,21] However, the correction for this retardation[36] was negligibly small for all the blends examined in this paper. Thus, we use $\eta_{2,bB}$, $A_{2,bB}$, and $J_{2,bB}$ values evaluated from eqs 1a–c in this paper.

Results

High-MW 4S/Low-MW L Blends. Figure 1 shows master curves of the storage, G', and loss, G'', moduli of the 4S310/L71 blends reduced to T_r (with f_r = 0.0644). For these blends, ϕ_p ($\equiv \phi_1 + \phi_2$ = 60 vol %) was kept constant, and ϕ_2 was varied from 0 to 60 vol %, as indicated in the figure.

As can be clearly seen in Figure 1, the terminal relaxation modes of the 1- and 2-chains are observed separately at high and low frequencies, respectively. The relaxation time of the linear 1-chain (L71) in the blend with ϕ_2 = 40% was 0.15 ± 0.02 s, that is, about 3 times longer than that (=0.05 ± 0.01 s) in the monodisperse state (ϕ_2 = 0%).[37] Similar behavior was already seen also for blends consisting of linear PS's (L/L blends) with large M_2/M_1 ratios.[18]

Figure 2 shows the ϕ_2 dependence of the viscosity $\eta_{2,bB}$ of the star 2-chain in the blends examined in Figure 1. The filled circle indicates the viscosity for the monodisperse 4S310 sample with ϕ_p = 60 vol %. We clearly see a linear relationship, $\eta_{2,bB} \propto \phi_2$, for small ϕ_2 and a stronger dependence for large ϕ_2.

As described in the previous paper,[23] the critical volume fraction, $(\phi_2)_c$, for the onset of the entanglement among the star 2-chain (4S310) may be estimated in two different ways:[4,31] $(\phi_2)_c = M_c°/(g_1 M_2) \simeq 4.0$ vol % and $(\phi_2)_c' = M_e°/M_a \simeq 5.8$ vol %, respectively, from the characteristic molecular weight $M_c°$ (=31 × 10^3) and the entanglement

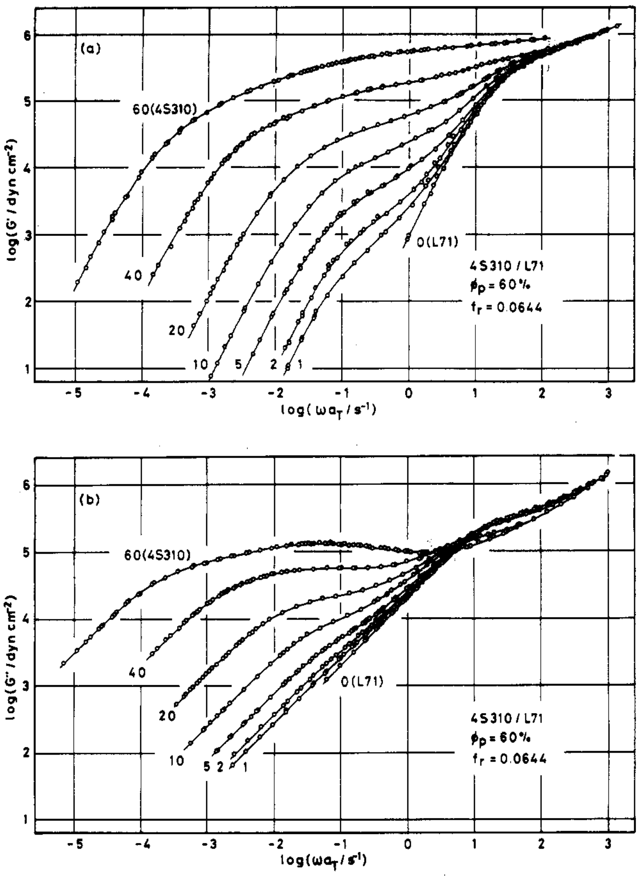

Figure 1. Master curves of (a) storage, G', and (b) loss, G'', moduli for 4S310/L71 blends with ϕ_p = 60 vol % at the iso-free-volume state with f_r = 0.0644 (T_r = 54, 71 °C for DBP, DOP systems, respectively). The number represents the volume fraction ϕ_2 of 4S310 in volume percent.

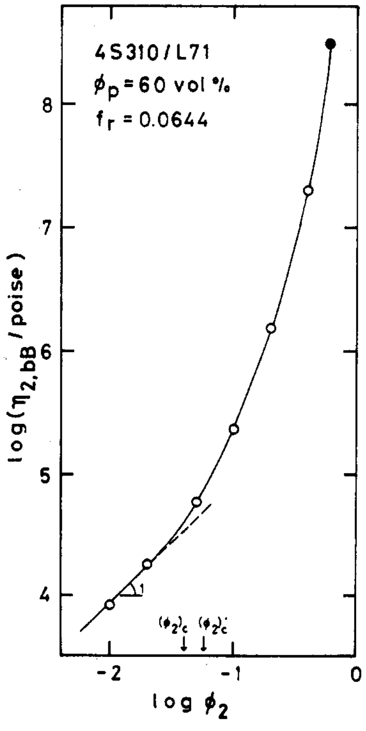

Figure 2. ϕ_2 dependence of the viscosity, $\eta_{2,bB}$, of the star 2-chain in 4S310/L71 blends at the iso-free-volume state with f_r = 0.0644 (open circles). The filled circle represents the datum for the monodisperse 4S310 system with $\phi_p = \phi_2$ = 60 vol %.

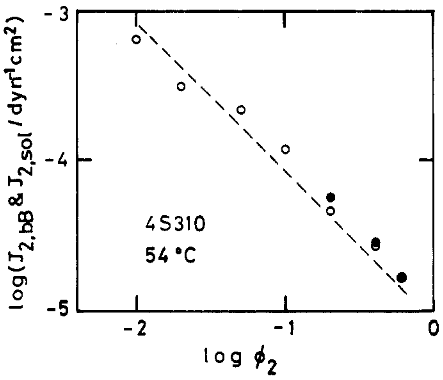

Figure 3. ϕ_2 dependence of the compliance, $J_{2,bB}$ (open circles), of the star 2-chain in 4S310/L71 blends with ϕ_p = 60 vol % and of the compliance, $J_{2,sol}$ (filled circles), for 4S310/DBP solutions at 54 °C. The broken line indicates the compliance predicted by the Rouse–Ham theory (eq 3).

spacing $M_e°$ (=18 × 10^3) for bulk PS.[1,2] The factor g_1 is defined by[13,14]

$$g_1 = (3f-2)/f^2 \text{ } (\simeq 0.625 \text{ for the 4-arm star chain}) \quad (2)$$

with f being the number of arms. This factor represents the difference in the statistical dimension for f-arm star and linear chains of the same MW. The arrows in Figure 2 indicate $(\phi_2)_c$ and $(\phi_2)_c'$.

As is clear from Figure 2, the linear relationship $\eta_{2,bB} \propto \phi_2$ for *dilute* blends is observed for ϕ_2 smaller than the critical values $(\phi_2)_c$ and/or $(\phi_2)_c'$. On the other hand, we note $\eta_{2,bB}$ to depend on ϕ_2 more strongly for $\phi_2 > (\phi_2)_c$ and/or $(\phi_2)_c'$. This is indicative of the 2–2 entanglements, and these blends should be classified as *concentrated* blends: The ϕ_2 dependence of $\eta_{2,bB}$ for these 4S/L concentrated blends cannot be described by any power law relationship and is stronger than the relation, $\eta_{2,bB} \propto \phi_2^{3.5}$, for linear 2-chains in L/L blends with $M_2 \gg M_1$ and $\phi_2 \gg (\phi_2)_c$.[22]

Figure 3 shows the ϕ_2 dependence of the compliance $J_{2,bB}$ (open circles) of the star 2-chain for the 4S310/L71 blends examined in Figure 1. The compliance, $J_{2,sol}$, for the concentrated solutions of 4S310 in DBP at 54 °C is also indicated by the filled circles for comparison. The broken line in the figure indicates the compliance, J, predicted for an f-arm star chain by the Rouse–Ham theory[13,14]

$$J = 2g_2M_2/(5\rho\phi_2RT); \quad g_2 = (15f-14)/(3f-2)^2 \quad (3)$$

where ρ is the bulk density of the polymer and RT has the usual meaning. For convenience, the viscoelastic data for 4S310/L71 blends are summarized in Table II.

In Figure 3, we note that $J_{2,bB}$ and $J_{2,sol}$ are roughly proportional to ϕ_2^{-1} in the entire range of ϕ_2 examined and close to the prediction of the Rouse–Ham theory, as reported previously by Graessley.[4-6] For the blends and solutions with $\phi_2 > (\phi_2)_c$, however, the agreement between the observed and theoretical values of J_2 does not necessarily mean that the star chain relaxes through the Rouse–Ham mechanism. In fact, for those blends and solutions, the shape of the G' and G'' curves in the terminal to (second-step) plateau region is different from the shape predicted by the Rouse–Ham theory, which predicts G' to be always smaller than G''.[1]

Figure 4 compares the master curves of G' and G'' for the 4S310/L71 blend and 4S310/DBP solution both with ϕ_2 = 40 vol %. The curves for the 4S310/DBP solution are shifted along the ω axis so that the low ω ends of these curves are superposed on those of 4S310/L71. We clearly see that the two sets of the curves are very close to each

Table II
Zero-Shear Viscosity, η_0 (P), and Recoverable Compliance, J_e° (dyn^{-1} cm^2), of the 4S310/L71 Blends and the Monodisperse 4S310 and L71 Samples

ϕ_1	ϕ_2	log η_0	log J_e°
	Blends with ϕ_p = 60 vol %[a]		
60	0	4.29	−5.63
59	1	4.44	−4.22
58	2	4.57	−4.13
55	5	4.89	−3.89
50	10	5.40	−3.99
40	20	6.19	−4.34
20	40	7.30	−4.57
0	60	8.49	−4.78
	DBP Solutions[b]		
0	40	6.78	−4.55
0	20	5.08	−4.25

[a] The data at the iso-free-volume state with f_r = 0.0644 (T_r = 54, 71 °C for DBP, DOP systems, respectively). The plasticizer was DOP for ϕ_2 = 60 vol % and DBP for the others. [b] The data are at 54 °C.

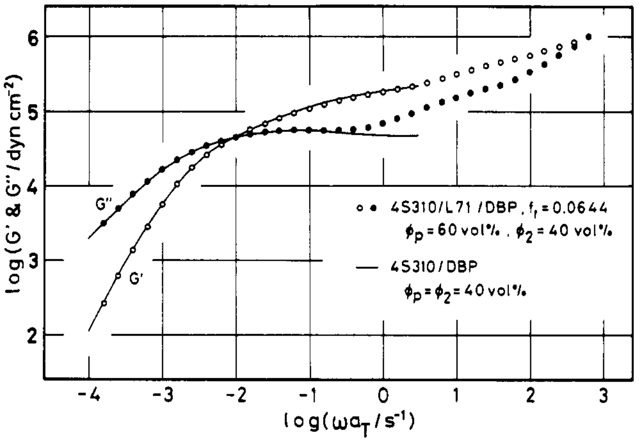

Figure 4. Comparison of G' and G'' curves for the 4S310/L71 blend with ϕ_2 = 40 vol % and ϕ_p = 60 vol % at f_r = 0.0644 (open and filled circles) and those for the 4S310/DBP solution with the same ϕ_2 (solid curves). The curves for the 4S310/DBP solution are shifted to superpose on those for the 4S310/L71 blend at low frequencies.

other at low ω. This suggests that the terminal relaxation modes of the star chains in the blends with $M_2 \gg M_1$ and $\phi_2 \gg (\phi_2)_c$ are the same as those in concentrated solutions, and correspond to the disengagement from the 2–2 entanglements. A similar result was found also for blends and solutions of linear chains.[17-19,21]

High-MW L/Low-MW 4S Blends. Figure 5 shows the master curves of G' and G'' for the L1810/4S77 and L1810/L172 blends with $\phi_1 = \phi_2$ = 30 vol %. The L1810 linear sample is the high-MW component (2-chain), and the 4S77 star and L172 linear samples are the low-MW components (1-chain). The thin solid and dotted curves, respectively, indicate the behavior of 4S77 and L172 samples at their monodisperse states (with ϕ_p = 60 vol %). For comparison, the G' and G'' curves for a L1810/L46 blend with $\phi_1 = \phi_2$ = 30 vol % and M_2/M_1 = 39 are shown in Figure 5 by thick solid curves.

For a concentrated blend with $M_2 \gg M_1$, the longer 2-chain behaves at low frequencies as if it is in a concentrated *solution*.[17-19,21] The terminal relaxation intensity of the 2-chain is then smaller by a factor of $(\phi_2/\phi_p)^2$ and the relaxation time by $(\phi_2/\phi_p)^{1.5}$ than those in the monodisperse state with $\phi_2 = \phi_p$. The L1810/L46 blend should be an example of such an *extreme* case: a concentrated solution limit, in which the entanglement between the 2-chain determines the slow behavior of blends.

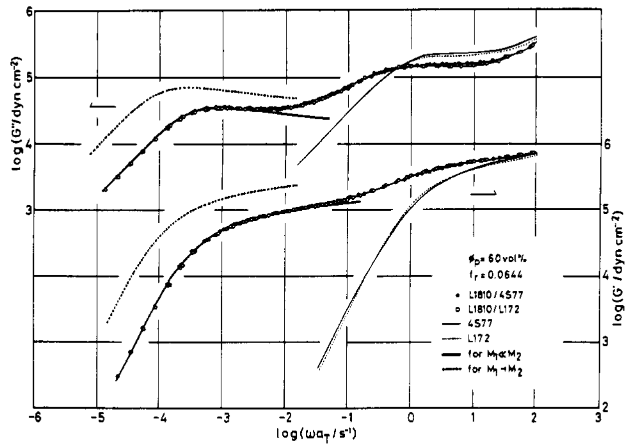

Figure 5. Master curves of G' and G'' for the L1810/4S77 and L1810/L172 blends with $\phi_1 = \phi_2$ = 30 vol % at the iso-free-volume state with f_r = 0.0644 (T_r = 54, 71 °C for DBP, DOP systems, respectively). The thin solid and dotted curves, respectively, indicate the behavior of the 4S77 and L172 samples at their monodisperse states. The thick solid and dotted curves, respectively, indicate the behavior expected for the L1810 (longer) chains in blends with $M_1 \ll M_2$ and $M_1 \to M_2$; for the details, see the text.

On the other hand, if the 1-chains are long enough, the entanglements due to the 1-chains are still effective even in the terminal relaxation zone of the 2-chain. In such a blend the 2-chain behaves as if in its monodisperse state:[18,21] The terminal relaxation intensity of the 2-chain in the blend is smaller by a factor of ϕ_2/ϕ_p than that in the monodisperse state with ϕ_p but the relaxation time remains the same. Such a system is another extreme case, for which the thick dotted curves in Figure 5 represent the G' and G'' curves.[38]

In Figure 5, we note that the behaviors of the 4S77 and L172 chains in their respective monodisperse states (the thin curves) are very close to each other and that the G' and G'' curves of the two blends are almost indistinguishable. Namely, in these blends the effect of the much longer linear 2-chain (L1810) appears to be the same for the rather short star and linear 1-chains. The relaxation of these 1-chains is retarded to the same extent due to the longer 2-chains.

In Figure 5, we also note that the low-frequency behavior of the blends, or more precisely, that of the 2-chains is very close to that of the L1810/L46 blend, the extreme case expected for concentrated solution of the 2-chains (thick solid curves). This indicates that the effects of the short star and linear 1-chains are the same for the terminal relaxation behavior of the 2-chains. The entanglements due to these 1-chains are ineffective at the terminal relaxation zone of the 2-chain. Thus, for the blends examined in Figure 5, the difference in the architecture of the 1-chains does not lead to any significant difference in the dynamic behavior of the blends.

Figure 6 compares the G' and G'' curves for L1810/4S184 and L1810/L503 with $\phi_1 = \phi_2$ = 30 vol %. In these blends the 4S184 star and L503 linear chains are the low-MW components (1-chain), for which the thin solid and dotted curves, respectively, show the behavior in the monodisperse states. The meaning of the thick solid and dotted curves is the same as that for Figure 5. Note that the 1-chains examined in Figure 6 are considerably longer than those examined in Figure 5.

In Figure 6, we first note that the behavior of the star and linear 1-chains in the respective monodisperse states (the thin curves) is not very different. In particular, the viscosities of the 1-chains, 4S184 and L503, differ only by

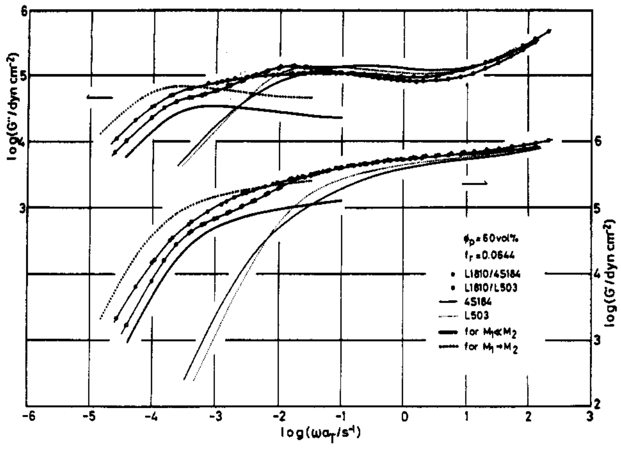

Figure 6. Master curves of G' and G'' for the L1810/4S184 and L1810/L503 blends with $\phi_1 = \phi_2 = 30$ vol % at the iso-free-volume state with $f_r = 0.0644$ (T_r = 54, 71 °C for DBP, DOP systems, respectively). The thin solid and dotted curves, respectively, indicate the behavior of the 4S184 and L503 samples at their monodisperse states. The meaning of the thick curves is the same as that in Figure 5.

a factor of 17%, as can be seen from Table I. Nevertheless, the behavior of the blends having these 1-chains appears to be considerably different.

As can be clearly seen in Figure 6, the L1810/L503 blend exhibits a two-step relaxation, while the L1810/4S184 blend relaxes monotonously, not via a two-step manner. We also note that the terminal relaxation intensity is larger and the relaxation time is longer for the latter blend than for the former. These results suggest that the contribution of the 4S184 chains to the terminal relaxation of the blend is larger than that of the L503 chains. In other words, the relaxation *in the blend* seems to be slower for the 4S184 chain than for the L503 chain, despite the fact that their behavior in the monodisperse system is nearly the same. Thus, the retardation effect of the L1810 chain appears to be larger for the 4S184 star chains than for the linear L503 chains.

Discussion

In Figures 1–4, we have seen that the effect of the shorter L chains on the behavior of the much longer 4S chains in concentrated 4S/L blends is the same as that on the longer L chains in L/L blends: In such blends (with $M_2 \gg M_1$), the short L chains simply behave as a *solvent* for the much longer chains at long times, irrespective of the topological architecture of the long chains.

For the star (4S77) and linear (L172) 1-chains in the blends with the long L chains (L1810), we still see no effect of the architecture. As explained for Figure 5, the relaxation of those shorter 1-chains is retarded due to the much longer 2-chains (L1810) by the same factor, while the relaxation of the latter is accelerated to the same extent by those shorter 4S and L chains.

On the other hand, for the L1810/4S184 and L1810/L503 blends in which M_1 is considerably large, we have observed a significant difference due to the chain architecture (cf. Figure 6). The relaxation of the 4S184 star chains appears to be more strongly retarded by the 2-chain (L1810) than that of the linear L503 chains, despite the fact that the behavior in their monodisperse systems is nearly the same. Correspondingly, the acceleration effect of 4S184 on the L1810 chains appears to be less significant than that of L503. This leads to the terminal relaxation of the L1810 chains (and hence that of the blend as a whole) being slower in the L1810/4S184 blend than in the L1810/L503 blend, as observed in Figure 6. As mentioned earlier, we observed the two-sided effect: The acceleration of 2-chains by 1-chains and the retardation of 1-chains by 2-chains differ for the L/4S and L/L blends.

The generalized tube model provides a possible interpretation for the strongly retarded relaxation of star chains due to surrounding longer linear chains, as explained below. The tube model concept suggests two competing mechanisms: path breathing and constraint release for entangled star chains; reptation and constraint release (or tube renewal) for entangled linear chains. The stronger retardation for the star chains (4S184) induced by the longer linear chains in the blend, observed in Figure 6, can be a result of suppression of the constraint release mechanism, which, in turn, seems to contribute significantly in a monodisperse star system. In earlier work on linear chains,[17-19] we suggested that the constraint release mechanism is important when the molecular weights are well separated (i.e., $M_2 \gg M_1$) in the L/L blends and is also important for monodisperse systems when the molecular weight is not very large. Comparison of the retarded relaxation behavior of the star (4S184) and linear (L503) chains in the blends (Figure 6) suggests that, in high-MW monodisperse systems, this mechanism is more important for star chains rather than for linear chains.

Comparing Figures 5 and 6, we also note that the constraint release mechanism appears to be more important for a monodisperse star system with a *larger* M_a, because of a very strong retardation of the path breathing mode with increasing M_a. In fact, a large contribution of the constraint release mechanism to the dynamic behavior of monodisperse star chains was already found in previous studies on the diffusion coefficient and relaxation modulus.[15,16] Thus, the situation for star chains appears to be entirely different from that for monodisperse linear chains: For linear chains, the constraint release mechanism becomes less significant and reptation dominates with increasing MW.[19,33]

The above speculation is qualitatively consistent with the generalized tube model proposed by Graessley, who considered both path breathing and constraint release mechanisms for star chains.[34] Further investigation on the dynamic behavior of star chains with various MW is necessary to examine this speculation: For example, birefringence and/or infrared dichroism measurement on optically labeled stars in blends may provide a clue to solve this problem.

References and Notes

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(36) We can make this correction by comparing the relaxation spectra $H_{1,\mathrm{bB}}$ and $H_{1,\mathrm{m}}$ of the 1-chain in the blend and the monodisperse system:[21] We evaluate the shift λ of the longest relaxation time of the 1-chain due to the 2-chain in the blend. Then, the viscosity, $\eta_{1,\mathrm{bB}}$, and elastic coefficient, $A_{1,\mathrm{bB}}$, of the 1-chain in the blend are estimated from those in the monodisperse system, $\eta_{1,\mathrm{m}}$ and $A_{1,\mathrm{m}}$, and the shift λ. $\eta_{1,\mathrm{bB}}$ and $A_{1,\mathrm{bB}}$ are used in eqs 1a and 1b, instead of $\eta_{1,\mathrm{m}}$ and $A_{1,\mathrm{m}}$, to obtain $\eta_{2,\mathrm{bB}}$ and $A_{2,\mathrm{bB}}$ for the 2-chain in the blend.
$\eta_{2,\mathrm{bB}}$ and $A_{2,\mathrm{bB}}$ for concentrated blends are insensitive to fast relaxation modes due to 1–2 entanglements. Thus, $\eta_{2,\mathrm{bB}}$ and $A_{2,\mathrm{bB}}$ evaluated as explained above are in general close to those evaluated from eqs 1a and 1b with $\eta_{1,\mathrm{m}}$ and $A_{1,\mathrm{m}}$, unless M_1 is very close to M_2.[22] This was the case also for the blends examined in this study.
(37) These relaxation times were estimated from the peak location of the relaxation spectrum calculated from the G' and G'' data.
(38) The data for the monodisperse L1810 sample (2-chain) could not be obtained because of an experimental difficulty to shear this sample without slippage to measure the stress. Thus, we estimated the thick dotted curves for the L1810 chains given in Figures 5 and 6 by shifting the curves for the L1810/L46 blend with $\phi_1 = \phi_2 = 30$ vol % by the factors ϕ_{p}/ϕ_2 and $(\phi_2/\phi_{\mathrm{p}})^{1.5}$, respectively, along the G^* and ω axes. Since the L1810 chains in the L1810/L46 blend behave as in a concentrated solution, the above shifts give the G^* curves expected for the L1810 chains in blends with $M_1 \rightarrow M_2$.

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