

Viscoelastic Relaxation of a Linear Chain in Star Matrices: Examination of the Constraint Release Mechanism in Star Matrices

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ABSTRACT: The viscoelastic relaxation behavior of blends of high molecular weight (M) linear (L) and low- M 4-arm star (4S) polystyrenes was examined. In those blends, the high- M L chains were a dilute component and entangled only with low- M 4S matrix chains. The results obtained for the high- M L/low- M 4S blends were qualitatively the same as the previous results on high- M L/low- M L blends: The constraint release (CR) dominated the terminal relaxation of the high- M L chain in *much shorter* matrices, and competition of CR and other mechanisms such as reptation took place in matrices of large M . Quantitatively, however, a difference was found for the 4S and L matrices. For 4S and L matrices having the same relaxation time and/or viscosity, the relaxation of the high- M L chain was faster in the former than in the latter. This difference was discussed in relation to the differences in the relaxation mode distribution in the terminal to rubbery region for 4S and L matrices. The results for the present high- M L/low- M 4S blends and those for the previously examined high- M L/low- M L and high- M 4S/low- M L blends were used to evaluate the CR time τ_{CR} for *monodisperse* systems of 4S and L chains. The τ_{CR} was found to be in the vicinity of the actual relaxation time τ_{obs} for monodisperse 4S systems even in a well-entangled regime, while τ_{CR} was considerably longer than τ_{obs} for well-entangled L chains. These results demonstrated the importance of the CR mechanism for relaxation of star chains and also the importance of topological architecture on entanglement dynamics.

I. Introduction

Binary blends of monodisperse polymer chains of low and high molecular weights (M) often exhibit relaxation modes not clearly observable in monodisperse systems. Thus such blends are a very important model system for investigating entanglement dynamics, and their viscoelastic behavior has been extensively studied.¹⁻¹⁵ In so-called *dilute* blends that contain only a small amount of high- M chains being entangled *only* with low- M matrix chains, the slow (terminal) relaxation of the high- M chains reflects the motion of the matrix chains. In this regard, we may consider such high- M chains as a *probe* for examining the behavior of the matrix.

For dilute blends of *linear* and/or 4-arm *star* probe chains with *much shorter linear* matrix chains, we found that the slow viscoelastic relaxation of the probe chain proceeds via a Rouse-Ham-like mode with a characteristic time $\tau \propto M_1^3 M_2^2$, with M_1 and M_2 ($\gg M_1$) being the molecular weights of the matrix and probe chains, respectively.^{2-5,8,10,11} However, as M_1 approaches M_2 , the M_1 and M_2 dependences of τ become weaker and stronger, respectively, and the relaxation mode distribution becomes narrower as compared to those found for the cases of $M_2 \gg M_1$.^{3,8,10,11} Within a framework of the generalized tube model,^{1,16,17} these results can be attributed to competition of constraint release (CR)¹⁷⁻²⁰ and reptation¹⁶ (for linear probes) or path-breathing^{16,17,21-23} (for star probes) mechanisms: For $M_2 \gg M_1$, the matrix motion is so rapid that the CR mechanism (leading to the above-mentioned Rouse-Ham-like behavior of the probe chain) overwhelms reptation and/or path-breathing mechanisms, while for $M_2 \rightarrow M_1$ the matrix motion is not rapid enough and the CR dominance no longer holds.

As can be seen from the above argument, the relaxation behavior of the probe chain can provide us information on the matrix motion that induces *local jump*¹⁷ (local CR relaxation) of the probe. Thus, through the behavior of long linear probe chains in matrices of star chains, we can examine the motion of the star matrices and further

estimate the CR relaxation time for *monodisperse* star chain systems (that are blends of the star matrices and star probes of the same molecular weight). From these points of view, we made viscoelastic studies on dilute blends of linear probe and star matrix chains. This paper presents the results.

II. Experimental Section

II-1. Measurements. Anionically polymerized 4-arm star (designated as 4S) and linear (L) polystyrenes were used as the matrix and probe, respectively. Details for the synthesis and characterization were described elsewhere.⁸ Table I summarizes the molecular characteristics of the 4S and L samples used in this study. The sample code number indicates the molecular weight of the arm M_a for the 4S samples, and the (total) molecular weight for the L sample, both in units of 1000. As seen in Table I, all samples have a narrow molecular weight distribution ($M_w/M_n < 1.1$).

Linear viscoelastic measurements were made with a laboratory rheometer (IR-200; Iwamoto Seisakusho) on blends of L (probe) and 4S (matrix) samples cited in Table I. All blends contained 40 vol % of dioctyl phthalate (DOP) or dibutyl phthalate (DBP) as a plasticizer. The total content ϕ_p of the polymeric components (=probe plus matrix) was always 60 vol %, and the content ϕ_2 of the probe chains was 1 vol %. For this small ϕ_2 , the L2810 probe chains entangle only with the matrix chains.^{3,4} The characteristic molecular weight for entanglements, M_e , is 51×10^3 for $\phi_p = 60$ vol %. All 4S samples have the span molecular weight $2M_a > M_e$ so that they entangle with the probe L2810 chain.

The measurements were made at temperatures $T = 26-105^\circ\text{C}$ for the DBP systems and at $T = 50-149^\circ\text{C}$ for the DOP systems. The time-temperature superposition principle was applied to the data to obtain master curves of storage (G') and loss (G'') moduli. The shift factors, a_T , were well described by the previously reported WLF equation^{3,4,8} $\log a_T = -6.74(T - T_r)/(133.6 + T - T_r)$, with T_r ($=54$ and 71°C for the DBP and DOP systems with $\phi_p = 60$ vol %) being the reference temperature for an isofriction (iso- ζ) state with the free-volume fraction $f_r = 0.0644$. All the data were reduced and compared at T_r . As shown in the previous paper,⁸ the viscoelastic behavior was the same for the DBP and DOP systems at their respective T_r .

II-2. Data Analysis. In dilute blends with the matrix content ϕ_1 being much larger than the probe chain content ϕ_2 , the vis-

Table I
Characteristics of Polystyrene Samples

code	$10^{-3}M_w$	M_w/M_n
4-Arm Star		
4S34	135	1.07
4S77	307	1.08
4S171	684	1.06
Linear		
L2810	2810	1.09

coelastic behavior of the matrix chains is hardly affected by the probe chains. Then, the dynamic moduli $G^*_{2,B} (= G'_{2,B} + iG''_{2,B})$ at angular frequency ω , viscosity $\eta_{2,B}$, elastic coefficient $A_{2,B}$, and compliance $J_{2,B}$ of the probe chain in the blends are evaluated as^{2,8}

$$G^*_{2,B}(\omega) = G^*_B(\omega) - (\phi_1/\phi_p)G^*_{1,m}(\omega) \quad (1)$$

$$\eta_{2,B} = \eta_B - (\phi_1/\phi_p)\eta_{1,m} (= G''_{2,B}(\omega)/\omega|_{\omega \rightarrow 0}) \quad (2)$$

$$A_{2,B} = A_B - (\phi_1/\phi_p)A_{1,m} (= G'_{2,B}(\omega)/\omega^2|_{\omega \rightarrow 0}) \quad (3)$$

$$J_{2,B} = A_{2,B}/[\eta_{2,B}]^2 \quad (4)$$

Here, the subscript 1,m stands for the experimentally determined quantities of the monodisperse system of the matrix chains, and B, for those of the blend as a whole, with ϕ_p (=60 vol % in this study) being the same for both systems. The product $J_{2,B}\eta_{2,B}$ represents a weight-average relaxation time of the probe chain in the blend. (In some of our recent papers,^{10,11} we used subscripts S and L to represent the short matrix and long probe chains. In this paper, instead of S and L, we use 1 and 2 as we did in our earlier papers²⁻⁹ so that the symbols used for linear and star chains (L and 4S) are not confused.)

III. Results

Figures 1 and 2 respectively show the G'_B and G''_B master curves (circles) for the three L/4S dilute blends at the iso- ζ state with $f_r = 0.0644$. The dashed curves indicate the behavior of the matrix 4S chains in their monodisperse state (with $\phi_p = \phi_1 = 60$ vol %). For the blends, fast and slow relaxation processes are observed at high and low ω , respectively. The former is very close to the relaxation of the monodisperse matrix and is mainly due to the matrix chains in the blend, while the latter is attributed to the long probe chains.

The shape of $G^*_{2,B}$ curves reflects the relaxation mode distribution, as most clearly seen from a representation for $G^*_{2,B}$ in terms of the relaxation spectrum $H_{2,B}$ of the probe chain in the blend:⁸

$$G'_{2,B}(\omega) = \phi_2 \int_{-\infty}^{\infty} H_{2,B}(\tau) \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} d \ln \tau \quad (5a)$$

$$G''_{2,B}(\omega) = \phi_2 \int_{-\infty}^{\infty} H_{2,B}(\tau) \frac{\omega \tau}{1 + \omega^2 \tau^2} d \ln \tau \quad (5b)$$

(Here, $H_{2,B}$ is the spectrum reduced to $\phi_2 = 1$.) Because of the difference in the weighing factors $\omega^2 \tau^2/(1 + \omega^2 \tau^2)$ and $\omega \tau/(1 + \omega^2 \tau^2)$ for $G'_{2,B}$ (eq 5a) and $G''_{2,B}$ (eq 5b), slow relaxation modes ($H_{2,B}$ for large τ) are much more clearly observed through $G'_{2,B}$ at low ω than through $G''_{2,B}$ when the terminal relaxation intensity is not large. In fact, the low ω relaxation is more prominent in Figure 1 than in Figure 2. We also note in Figure 1 that $G'_{1,m}$ is much smaller than G'_B and thus than $G'_{2,B}$ at intermediate to low ω , enabling us to accurately evaluate $G'_{2,B}$ by eq 1 in wide ω ranges. Thus we can best examine the slow relaxation mode distribution of the probe chain in blends through the $G'_{2,B}$ curves. The narrower (or broader) the

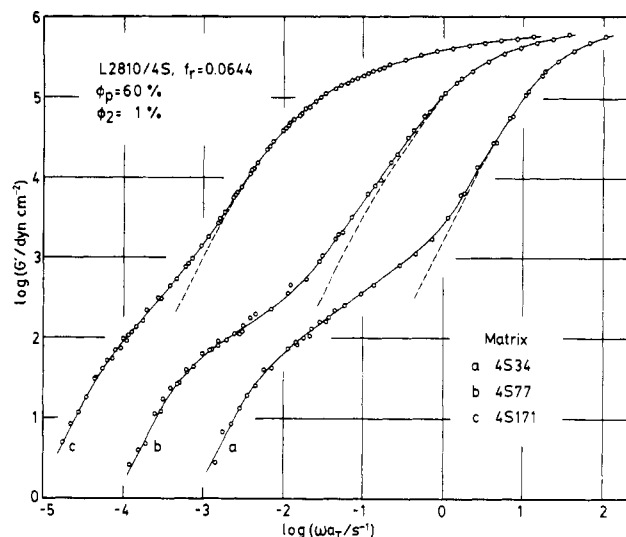


Figure 1. Master curves of storage moduli for the blends of probe L2810 and matrix 4S chains at an iso- ζ state with $f_r = 0.0644$. For the blends, $\phi_p = 60$ vol % and $\phi_2 = 1$ vol %. The dashed curves indicate the behavior of the 4S matrices in their monodisperse systems ($\phi_p = \phi_1 = 60$ vol %).

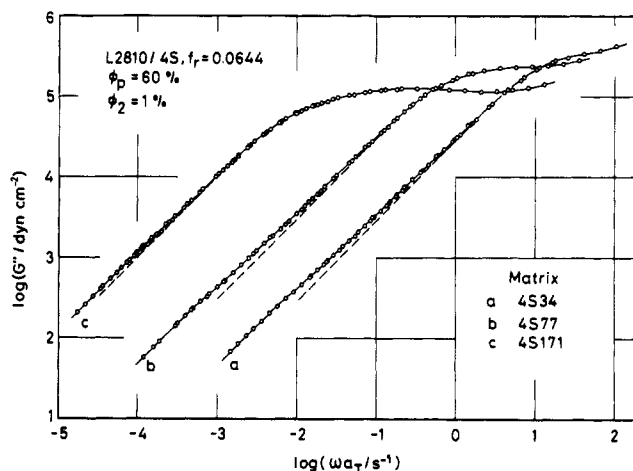


Figure 2. Master curves of loss moduli for the blends examined in Figure 1. The dashed curves indicate the behavior of the 4S matrices in their monodisperse systems ($\phi_p = \phi_1 = 60$ vol %).

mode distribution, the steeper (or broader) the $G'_{2,B}$ curve at low ω (cf. eq 5a).

Figure 3 shows the $G'_{2,B}$ curves of the L2810 probe chain ($\phi_2 = 1$ vol %) in three 4S matrices as indicated. For comparison, some of the curves of this probe chain in previously examined^{4,8} L matrices are shown in Figure 4. For the clearest comparison of the shape of $G'_{2,B}$ curves, we shifted in Figures 3 and 4 the curves along the ω axis by adequate factors λ so that their low- ω tails (where $G'_{2,B} \propto \omega^2$) are superposed, as we did in our previous work.^{8,10,11}

In Figure 3, we note that the matrix molecular weight (M_1) strongly affects the relaxation behavior of the L2810 probe chain. In the 4S34 and 4S77 star matrices with $M_1 \ll M_2$ (probe molecular weight), the L2810 probe chain has the $G'_{2,B}$ curves of almost identical shape and thus almost identical relaxation mode distribution in the terminal region (cf. eq 5a). This M_1 -independence of the shape of the $G'_{2,B}$ curves is seen also in linear matrices with $M_1 \ll M_2$ (see unfilled circles in Figure 4).^{8,10,11} The shape of such $G'_{2,B}$ curves in L matrices is indicated in Figure 3 with the solid curve. Comparing the curves for 4S and L matrices in Figure 3, we note that the L2810 probe chain in much shorter matrices has the universal relaxation mode distribution dependent on neither the

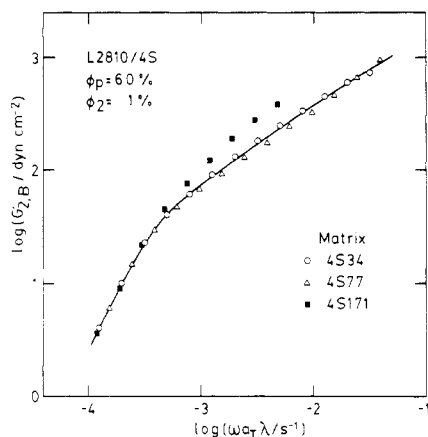


Figure 3. Comparison of the shape of the $G'_{2,B}$ curves for the probe L2810 chain in 4S matrices ($\phi_p = 60$ vol %, $\phi_2 = 1$ vol %, $f_r = 0.0644$). For the easiest comparison, the curves are shifted along the ω axis by adequate factors λ so that their low- ω tails are superposed. The $\log \lambda$ values used are -0.99 for the 4S34 matrix, 0 for 4S77, and $+0.99$ for 4S171. The solid curve indicates the shape of the $G'_{2,B}$ curves for the probe L2810 chain in much shorter L matrices shown in Figure 4.

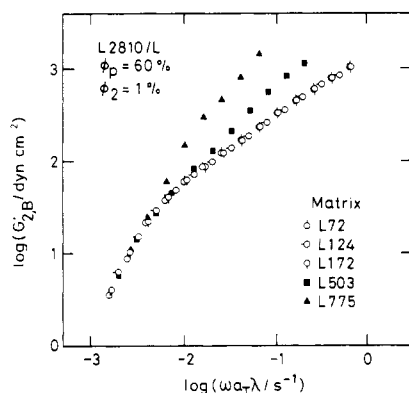


Figure 4. Comparison of the shape of the $G'_{2,B}$ curves for the L2810 chain in L matrices ($\phi_p = 60$ vol %, $\phi_2 = 1$ vol %, $f_r = 0.0644$) obtained in our previous work.^{4,8,11} The curves are shifted along the ω axis by adequate factors λ so that their low- ω tails are superposed. The $\log \lambda$ values used are 0 for the L72 matrix, 0.74 for L124, 1.12 for L172, 2.11 for L503, and 2.26 for L775. The sample code numbers for the L matrices indicate their M_1 in units of 1000.

matrix molecular weight nor the matrix architecture (star or linear).

In Figures 3 and 4, we also note that the shape of the $G'_{2,B}$ curves changes with M_1 if M_1 is not much smaller than M_2 (see filled symbols). With increasing M_1 ($\rightarrow M_2$), the curve becomes steeper and thus the relaxation mode distribution of the probe L2810 chain becomes narrower in the terminal region.

Figure 5 compares the weight-average relaxation time $J_{2,B}\eta_{2,B}$ of the probe L2810 chain in the present 4S (circles) and previously examined^{4,8,11} L (triangles) matrices. The $J_{2,B}\eta_{2,B}$ is plotted against the matrix molecular weight M_1 . We note that $J_{2,B}\eta_{2,B}$ increases with M_1 first rapidly for small M_1 ($\ll M_2$) and then rather gradually for large M_1 . We also note that $J_{2,B}\eta_{2,B}$ is smaller in the 4S matrix than in the L matrix having the same M_1 . Thus, the matrix molecular weight is not the fundamental quantity that uniquely describes the effects of both star and linear matrix chains on the slow relaxation of the probe linear chain.

Figure 6 shows another type of comparison of $J_{2,B}\eta_{2,B}$ of the probe L2810 chain in the 4S (circles) and L (triangles) matrices examined in Figure 5. In part a of Figure 6, $J_{2,B}\eta_{2,B}$ is plotted against the weight-average relaxation time of the matrix $J_{1,m}\eta_{1,m}$ and, in part b, against the matrix

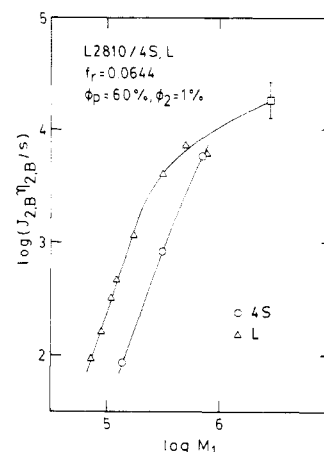


Figure 5. Dependence of weight-average relaxation time $J_{2,B}\eta_{2,B}$ of the L2810 probe chain in dilute blends ($\phi_p = 60$ vol %, $\phi_2 = 1$ vol %, $f_r = 0.0644$) on matrix molecular weight M_1 . The circles are for L2810/4S blends, and the triangles, for L2810/L blends examined in our previous work.^{4,8,11} The square represents the relaxation time of the monodisperse L2810 system ($\phi_p = 60$ vol %).

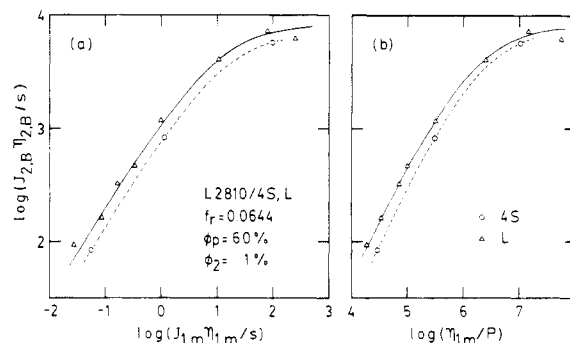


Figure 6. Plots of weight-average relaxation time $J_{2,B}\eta_{2,B}$ of the probe L2810 chain in dilute blends ($\phi_p = 60$ vol %, $\phi_2 = 1$ vol %, $f_r = 0.0644$) against (a) the matrix relaxation time $J_{1,m}\eta_{1,m}$ and (b) the matrix viscosity $\eta_{1,m}$. The circles are for L2810/4S blends, and the triangles, for L2810/L blends examined in our previous work.^{4,8,11}

viscosity $\eta_{1,m}$. (These quantities were obtained for the monodisperse systems of the matrix chains with $\phi_p = 60$ vol %.)

As seen in Figure 6, $J_{2,B}\eta_{2,B}$ increases first rapidly and then rather gradually with increasing $J_{1,m}\eta_{1,m}$ and/or $\eta_{1,m}$ for both 4S and L matrices. This behavior of $J_{2,B}\eta_{2,B}$ corresponds to the M_1 dependence of $J_{2,B}\eta_{2,B}$ seen in Figure 5. More importantly, we note in Figure 6 that $J_{2,B}\eta_{2,B}$ is not the same in the 4S and L matrices having the same $J_{1,m}\eta_{1,m}$ and/or $\eta_{1,m}$. This result means that the effects of star and linear matrices on the slow relaxation of the probe chain are not uniquely described even by the quantities $J_{1,m}\eta_{1,m}$ and $\eta_{1,m}$ that characterize the terminal relaxation of the matrix chains.

IV. Discussion

L/4S and L/L Blends. As seen in Figure 5, for the cases of $M_2 \gg M_1$ the relaxation time of the probe L2810 chain in linear matrices increases very rapidly with M_1 ($J_{2,B}\eta_{2,B} \propto M_1^3$).^{4,8,11} For such cases the terminal relaxation mode distribution of the probe chain is independent of M_1 (cf. Figure 4) and is close to the Rouse mode distribution as demonstrated in our previous work.^{8,10,11} These results suggest the constraint release (CR) dominance for the terminal relaxation of the probe chain in much shorter L matrices. On the other hand, as $M_1 \rightarrow M_2$, the M_1 dependence of the relaxation time becomes weaker (Figure 5) and the relaxation mode distribution becomes narrower

(Figure 4) for the probe chain in L matrices. This behavior can be attributed to competition of CR and other possible mechanisms like reptation for the relaxation of the probe L chain.^{10,11,20} (The relaxation mode distribution of the probe is much broader for the CR mechanism than for the reptation mechanism, so that the distribution becomes narrower as M_1 increases and the latter mechanism contributes more largely to the probe relaxation.^{10,11,20})

The results for the L2810/4S blends shown in Figures 3 and 5 indicate that the effects of the 4S matrices on the probe L2810 relaxation are qualitatively the same as those of the L matrices. Thus, the probe chain relaxes mainly by the CR mechanism in the short 4S matrices (4S34 and 4S77), and the above-mentioned competition takes place in the long 4S matrix (4S171). However, quantitatively, we found in Figure 6 that the CR relaxation rate is not exactly the same even in the 4S and L matrices having the same viscoelastic character of terminal relaxation ($J_{1,m}\eta_{1,m}$ and/or $\eta_{1,m}$). The L2810 probe chain relaxes more rapidly in the former than in the latter (by a factor $\sim 50\%$ for the shortest 4S34 matrix). This difference may be related to the difference in the relaxation mode distribution of the 4S and L matrix chains as we discuss below.

To induce a CR relaxation of the probe chain, the matrix chains should move and make some space that allows a local jump (or local relaxation) for the probe chain.¹⁷⁻¹⁹ Thus, fundamental quantity for the CR relaxation is a segment displacement¹⁶ of the matrix chains that is not identical but related to their viscoelastic relaxation reflecting the decay of segment orientation anisotropy.¹⁶ To make the space for the local jump, the matrix segments would need to move, on average, not by the end-to-end distance (or radius of gyration) of the matrix chains but by some fraction of that distance, because the probability for the entanglement with the probe chain would be the same throughout the contour of the matrix chain. In other words, it would not be the *longest* relaxation time τ_1 for the segment displacement of matrices but some fraction of τ_1 that is necessary for the local jump of the probe chain to take place. For entangled monodisperse systems, the viscoelastic relaxation mode distribution in the terminal to rubbery region is broader for star chains than for linear chains,¹ and this would be possibly the case also for the segment displacement. In other words, if the star and linear matrices have the same viscoelastic character of the terminal relaxation ($J_{1,m}\eta_{1,m}$ and/or $\eta_{1,m}$), the former would have more modes for segment displacement at an intermediate time scale (in the terminal to rubbery region) than the latter does. The star matrix would use those modes to create the space for the local jump of the probe more rapidly than the linear matrix, meaning that the ratio of the time necessary for the local jump to τ_1 is smaller for the star matrix. This is one possible idea for explaining the results found in Figure 6, and further examination of this idea is considered as future work.

Monodisperse 4S and L Systems. The results obtained for dilute blends can be used for evaluation of (hypothetical) constraint release time τ_{CR} in monodisperse 4S and L systems, and comparison of τ_{CR} and actual relaxation time enables us to examine the contribution of the CR mechanism in monodisperse systems.

In CR relaxation processes, a local jump of the probe chain is induced by matrix motion, and an accumulation of such jumps leads to the global relaxation of the probe chain (with the characteristic time τ_{CR}).¹⁷ Viscoelastic studies revealed that the features of such CR processes of long L and 4S probe chains (in much shorter L matrices) at long time scales are reasonably well described by the Rouse-Ham dynamics.^{2-4,8,10,11} In other words, the probe chain can be regarded at long time scales as a Rouse-Ham

chain with its local friction being determined by the matrix motion. Thus, for long probe chains, we can write the CR time as²⁴

$$\tau_{CR} = C_{\text{probe}} M_{\text{probe}}^2 \tau_w(\text{matrix}) \quad (6)$$

Here, C_{probe} is a constant dependent only on the topological architecture of the probe chain, and τ_w is a mean waiting time for a local jump of the probe chain (that is equivalent to the local friction for the probe). As we explained for Figure 6, the matrix motion at intermediate time scales (in the terminal to rubbery region) depends on the matrix architecture and would play an important role for the frequency of the local jump. Thus, τ_w should be determined by both molecular weight and architecture (linear, star, etc.) of the matrix. To explicitly indicate this, we have written τ_w in eq 6 as the $\tau_w(\text{matrix})$.

For various linear (L) probe chains in much shorter L matrices, previous work led to an empirical equation:^{3,4,8,11}

$$J_{2,B}\eta_{2,B} \approx 10^{-25.3} M_{L\text{-probe}}^2 M_{L\text{-matrix}}^3 \quad (\text{for } L/L_p = 60 \text{ vol } \%, f_r = 0.0644) \quad (7)$$

We may regard this viscoelastic relaxation time as the (weight-average) CR time of the probe L chains in L matrices. Thus, as we did in our previous work,^{3,11} we can evaluate the CR time of monodisperse L chain systems by eq 7 with $M_{L\text{-probe}} = M_{L\text{-matrix}}$.

No empirical equation similar to eq 7 is available for τ_{CR} of monodisperse systems of a 4-arm star (4S) chain. However, we can still estimate their τ_{CR} in the following way. First, for a 4S probe in a 4S matrix, we modify eq 6 as

$$\tau_{CR} = [C_{4S\text{-probe}} M_{4S\text{-probe}}^2 \tau_w(L\text{-matrix})] \left[\frac{\tau_w(4S\text{-matrix})}{\tau_w(L\text{-matrix})} \right] \quad (\text{for } 4S/4S) \quad (8)$$

where $\tau_w(L\text{-matrix})$ is a τ_w for an arbitrarily chosen linear matrix. The first term in eq 8 represents a CR time for the 4S probe in that L matrix and is evaluated from an empirical equation for the previous data⁸ on 4S/L dilute blends as

$$\begin{aligned} C_{4S\text{-probe}} M_{4S\text{-probe}}^2 \tau_w(L\text{-matrix}) &\approx J_{2,B}\eta_{2,B} \quad (\text{for } M_{4S\text{-probe}} \gg M_{L\text{-matrix}}) \\ &\approx 10^{-26.3} M_{4S\text{-probe}}^2 M_{L\text{-matrix}}^3 \quad (\text{for } 4S/L, \phi_p = 60 \text{ vol } \%, f_r = 0.0644) \quad (9) \end{aligned}$$

Thus, if the L-matrix chosen and the 4S matrix have the same τ_w , the second term in eq 8 becomes unity and eq 9 gives the CR time for the 4S probe in the 4S matrix. To find out such an L matrix for each of the 4S matrices examined in this study, we can use the experimental results on L2810/4S and L2810/L blends shown in Figure 5.

The probe L2810 chain relaxes via CR and other possible mechanisms like reptation, and the matrix motion only affects the CR contribution. This strongly suggests that τ_w is the same for a particular pair of 4S and L matrices if the probe relaxation time ($J_{2,B}\eta_{2,B}$) is the same in these two matrices. (In a CR-dominant regime where $J_{2,B}\eta_{2,B} \approx \tau_{CR}$, this conclusion is directly obtained from eq 6.) For each 4S matrix examined in this study, we can find in Figure 5 an L matrix in which $J_{2,B}\eta_{2,B}$ is the same as that in the 4S matrix. Thus we evaluated the $M_{L\text{-matrix}}$ of such L matrices. The results were $10^3 M_{L\text{-matrix}} = 70.8, 151, \text{ and } 427$ for the 4S34, 4S77, and 4S171 matrices, respectively. Using these $M_{L\text{-matrix}}$ values in eq 9 and equating $M_{4S\text{-probe}}$ and $M_{4S\text{-matrix}}$ in eqs 8 and 9, we can finally estimate τ_{CR} for the monodisperse 4S systems.

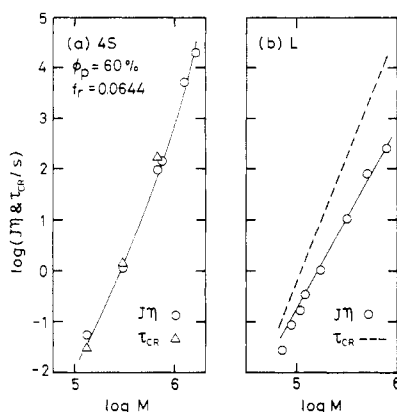


Figure 7. Comparison of constraint release time τ_{CR} evaluated from the blend data and actual relaxation time $J\eta$ for monodisperse systems ($\phi_p = 60$ vol %, $f_r = 0.0644$) of (a) a 4-arm star and (b) previously examined^{4,8,11} linear polystyrenes.

Figure 7 compares the CR time evaluated in the above-mentioned way and the actual relaxation time $J\eta$ for the entangled monodisperse systems ($\phi_p = 60$ vol %) of (a) 4S and (b) L chains at the iso- ζ state with $f_r = 0.0644$. In part b, we can clearly see that $J\eta < \tau_{CR}$ and the difference between $J\eta$ and τ_{CR} increases with increasing molecular weight M for the linear chains, as found in our previous work.^{3,5,11} This means that the actual terminal relaxation of linear chains in well-entangled monodisperse systems is considerably faster than the CR relaxation and suggests a rather minor CR contribution to terminal relaxation of such systems. On the other hand, the results obtained for the star chains are entirely different. As seen in part a of Figure 7, τ_{CR} is in the vicinity of $J\eta$ even for the 4S177 system with $M = 684 \times 10^3$ ($M/M_e \approx 13.4$). Thus, the CR mechanism quite possibly has a significant contribution to relaxation of monodisperse star chains even in a well-entangled regime.²⁴ This conclusion is consistent with the previous observation^{9,25,26} that mechanical relaxation and diffusion of long star chains are strongly retarded in high- M matrices (including networks) and is also consistent with the recent result²⁷ suggesting the importance of the CR mechanism for diffusion of linear probes in star matrices.

Finally, we add a few comments on the tube models^{1,21-23} for monodisperse star chains. The Doi-Kuzuu (DK)²¹ and Pearson-Helfand (PH)²² models assume a path-breathing motion of a star arm in a *fixed* tube and do not incorporate a CR mechanism. On the other hand, the Ball-McLeish (BM)²³ model assumes the path breathing of the arm in a *dilating* tube and incorporates the effect of CR only as the tube dilation that is induced by *path breathing* of other arms. Namely, the CR mechanism for monodisperse stars may lead to both tube dilation and the Rouse-Ham-like motion⁸ of the stars themselves, but the latter is not incorporated in the three models. Therefore, although good agreements with experimental data were obtained for the PH²² and BM²³ models, the results of this and previous work^{2-4,8,10,11,25-27} suggest a necessity of incorporation of the Rouse-Ham-like CR process (in addition to path breathing) in further refinement of the tube models for monodisperse stars.

V. Conclusion

We found that the behavior of probe linear (L) chains in 4-arm star (4S) and linear (L) matrices is qualitatively the same. In much shorter matrices the probe L chain relaxes mainly by the constraint release (CR) mechanism, while competition of CR and other mechanisms like reptation takes place in longer matrices. We also found,

however, a quantitative difference between the 4S and L matrices. For the 4S and L matrices having the same relaxation time and/or viscosity, the relaxation of the probe chain was faster in the former than in the latter. This difference may be related to the difference in the relaxation mode distribution in the terminal to rubbery region for the 4S and L chains.

Using the data obtained for L/4S as well as L/L and 4S/L blends, we evaluated the CR time for *monodisperse* 4S and L systems. The CR time was in the vicinity of the actual relaxation time for the 4S systems even in a well-entangled regime, as entirely different from the results on the L systems. This indicates the importance of the CR mechanism for the relaxation of star chains and also the importance of the topological architecture on entanglement dynamics.

References and Notes

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- (24) For L and/or 4S probe chains with a small M/M_e and/or $2M_e/M_e$ ratio, the CR relaxation completes after an accumulation of a rather small number of random local jumps for entanglement segments. For the CR processes of such short chains, the Rouse-Ham dynamics and resulting eq 6 are not necessarily a good approximation. Thus, in Figure 7, we should not expect too much accuracy of τ_{CR} estimated on the basis of eq 6 for short chains, i.e., for the L chains with $M < 10^5$ ($M/M_e \leq 4$) and for the 4S34 chain (with $2M_e/M_e \approx 3$). (Here, $M_e = 24 \times 10^3$ is an entanglement spacing evaluated from the Doi-Edwards expression¹⁸ for the plateau modulus of PS systems with $\phi_p = 60$ vol %.) However, for the longer L (with $M/M_e > 5$), 4S77 ($2M_e/M_e \approx 6.4$), and 4S171 ($2M_e/M_e \approx 14$) chains, we can evaluate τ_{CR} by eq 6 with small uncertainty. Thus, the results of Figure 7 enable us to conclude the minor and important CR contributions for high- M L and high- M 4S monodisperse systems, respectively.
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