iterations. The CPU time required on the VAX 11/780 for such a computation was about 11 h and approximately 5 min on the Cray 1.

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Tube Renewal in the Relaxation of 4-Arm-Star Polybutadienes in Linear Polybutadienes†

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ABSTRACT: The terminal relaxation of a series of high molecular weight star polybutadienes (M) dissolved at low concentration ($c < 2.5\%$) in low molecular weight linear polybutadienes (P) has been studied. The experimental conditions are favorable for the observation of relaxation by tube renewal of the stars. The longest relaxation time (τ_1) of stars with $f = 4$ and $f = 18$ can be superimposed on the values of τ_1 of linear polymers plotted against $2M_w/f$. It is found that $\tau_1 \propto M_w^{2.2}P_w^{2.6}$. The $M^{2.2}$ dependence indicates that the tube around the test chain is a Rouse tube. The $P_w^{2.6}$ dependence deviates considerably from the prediction of the reptation theory (P^3). It is suggested that contour-length fluctuations are ineffective in tube renewal.

Introduction

Reptation was originally devised as a model for diffusion and relaxation of linear polymers in the fixed surroundings of a network of entanglements.[1] Experiments that relate directly to this situation have been performed.[2] However, in linear polymer melts or concentrated solutions the entangling neighbors of a chain are not necessarily fixed on the time scale of the reptation of that chain. Neighboring chains reptate and abandon the entanglement. The imaginary tube around each polymer molecule is thereby locally and temporarily destroyed, and relaxation by lateral hopping becomes possible. This process is called tube renewal or constraint release.[1]

The relation between the primary reptation time τ_{rep} and the longest tube renewal time τ_{R} for a linear n-mer is given by[3,4]

$$\tau_{\mathrm{rep}}(n) \propto \tau_0 n^3/n_{\mathrm{e}} \tag{1}$$

and

$$\tau_{\mathrm{R}}(n) \propto N^2\tau_{\mathrm{rep}}(p) \tag{2}$$

where n and p are degrees of polymerization, n_{e} is the number of monomers between two consecutive entanglements along the chain, and τ_0 is the time between jumps of the size of one monomer unit along the (curvilinear) tube. Equation 2 indicates that the relaxation by tube renewal is a Rouse type process, its longest time depending on the square of the number of entanglements per chain: $N = n/n_{\mathrm{e}}$.[1,5] For homopolymer $p = n$ and eq 2 becomes

$$\tau_{\mathrm{R}}(n) \propto N^2\tau_{\mathrm{rep}}(n) \propto n^5 \tag{3}$$

The numerical coefficient in eq 2 and 3 has been estimated.[3,5] Tube renewal is expected to be less important than reptation for homopolymers. In the overall relaxation process other shorter Rouse relaxation times down to $\tau_{\mathrm{R}}(n)/N^2$ will also contribute, so that tube renewal modifies the longest relaxation time of a homopolymer.[5,6]

Tube renewal can be studied by observing the relaxation of an isolated long n-mer in a matrix of entangling low molecular weight p-mers.[7] It is required that no entanglements exist between the n-mers. Moreover, for a linear test chain, eq 1 and 2 require that $nn_{\mathrm{e}}^2/p^3 > 1$, a condition that is not easily satisfied in practice.[7] Others have studied tube renewal in more concentrated mixtures of a large test chain in smaller chains.[6,8] Under these conditions both processes coexist, and there is a rather delicate interaction between tube renewal of n–p entanglements and reptation along n–n entanglements.[6]

The importance of tube renewal has been demonstrated very convincingly in the study of the diffusion of linear

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Table I
Characteristics of Polybutadienes

sample	$M_w \times 10^{-5}$	N^a or N_a	$[\eta]^{35°}_{Tol}$	η_0,[b] P	log τ_{max},[c] s
linear matrices[19]					
PBD 10	0.111	5.6	0.26_9	2.25×10^2	−4.4
PBD 20	0.236	12.0	0.44	2.82×10^3	−3.3
PBD 40	0.394	20.0	0.64_7	1.81×10^4	-2.4_5
PBD 65	0.59	30.0	0.89_2	6.8×10^4	−1.9
PBD 120	1.14	57.9	1.40	6.5×10^5	-0.9_5
test chains					
linear[19]					
PBD 120	1.14	57.9	1.40	6.5×10^5	-0.9_5
PBD 400	3.61	183	3.2_3	2.9×10^7	0.6_5
4-arm star					
4SB4[20]	1.43	18.1	1.18	5.4×10^6	0.9_5
PBD 4S400B2[14]	3.75	47.6	2.45		(7.7)
PBD 4S800B3	8.26	105	4.2		(20)
PBD 4S1600B3	13.67	173	6.4		(35)
18-arm star[15]					
PBD 3718B3	7.6_2	21.5	1.26	1.4×10^7	1.35
PBD 9918B3	19.0	53.6	2.5		(9.0)

[a] N is the number of entanglements per chain = $M_w/1970$. N_a is the number of entanglements per arm for stars. [b] Melt viscosity at 27 °C. [c] $\tau_{max} = 1/\omega_{max}$ for linear; $\tau_{max} = 4/\omega_{G''=G'}$ for stars.[12] Values in parentheses calculated with $\ln(\tau_{max}/N_a^{3/2}) = -11.28 + 0.487N_a$.[14,15]

polysytrenes in various matrices of polystyrene.[9]

In the case of entangled regular star polymers relaxation occurs predominantly by an arm retraction mechanism.[10-12] According to the best founded model, the longest relaxation time of a star, T_a, is given by[12]

$$T_a \propto n_a N_a^{1/2} \exp(\alpha N_a) \tag{4}$$

with n_a and N_a the number of monomers and entanglements per arm, respectively, and $\alpha \approx 0.6$ from the theoretical model[13] and between 0.5 and 0.6 from measurements on stars with f = 4–18 arms.[12,14,15] Other theories for T_a differ only in the preexponential factor.[10,11] For $N_a \gg 1$, T_a of a star is much larger than the reptation time of the linear polymer with the same molecular weight. On the other hand, when embedded in a linear p-mer, the tube around the star will be renewed according to[16]

$$\tau_R \propto (2N_a)^2 \tau_{rep}(p) \tag{5}$$

where the effective tube for the star is two arms long. This is deduced from the Rouse relaxation time for a star, $\tau_{star} = \tau_{lin}(2/f)^2$.[17] The relation between the longest time for tube renewal of a star in a linear matrix and the arm retraction time has been explored theoretically by Klein.[16] Approximately, tube renewal will dominate when $N_a > (1/\alpha) \ln P^3$, the exact form depending slightly on the preexponential term in eq 4.[16] The conditions for observing tube renewal are easily accessible in the case of stars in linear matrices. The molecular weight dependence of diffusion coefficients of large 3-arm polyethylenes in a linear matrix is consistent with dominant tube renewal.[18]

In this work the longest relaxation times for isolated long 4-arm-star polybutadienes in various matrices of entangling linear polybutadienes have been measured. For comparison, two linear and two 18-arm stars have also been studied. The results should check the validity of eq 2 and 5. A comparison of the relaxation times of polymers with different architecture should verify the assumptions underlying eq 5.

Experimental Section

The synthesis and dilute solution properties of the polymers have been described in detail previously.[14,15,19] The melt properties have also been given. The important properties are listed in Table I. All samples have a narrow molecular weight distribution.

Sample mixtures were prepared by dissolving the low molecular weight component into a solution of the high molecular weight polymer in benzene and freeze-drying to constant weight. Shear moduli were measured with a Rheometrics mechanical spectrometer (RMS 605) in the dynamic mode. Loss (G'') and storage (G') moduli were collected at five frequencies per decade between ω = 0.01 and 100 rad/s. The temperature was varied from 106 to −76 °C. Temperature–frequency superposition is used to construct $G''(\omega)$ and $G'(\omega)$ master curves at 27 °C. The temperature shift factors are identical with those for linear polybutadienes.[19] An example of the moduli–frequency master curves is shown in Figure 1. The large range of frequencies covered should be noted. The low-frequency shoulders in G'' and particularly in G' are due to the presence of the high molecular weight test chain. In the high-frequency part of the plateau the relaxation of the matrix polymer is observed. The magnitudes of $G''(\omega)$ and $G'(\omega)$ at high frequencies are practically unchanged from those in the bulk.[6,7]

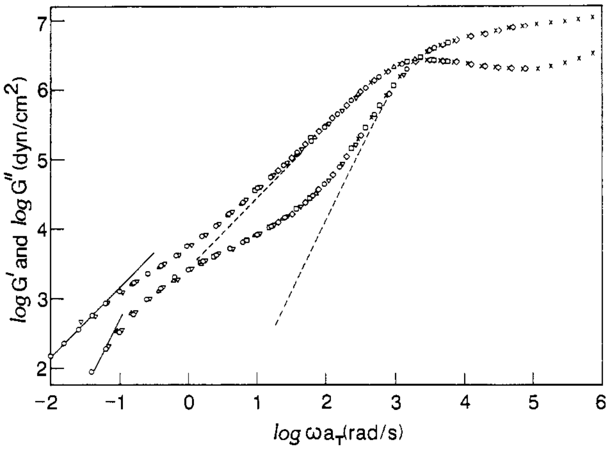

Figure 1. Moduli–frequency master curves at 27 °C for PBD 20 with 2.5% PBD 4S1600. The dotted lines are $G'(\omega)$ and $G''(\omega)$ for bulk PBD 20.[19]

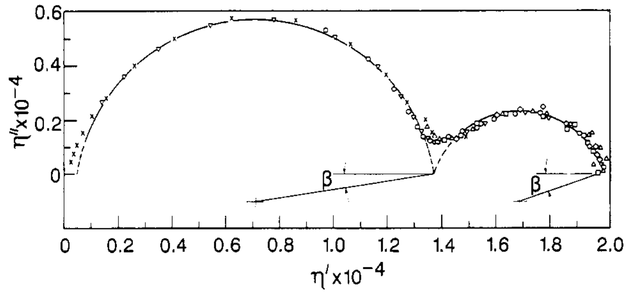

Figure 2. MMM plot for PBD 10 containing 1.25% PBD 4S400. Reference temperature −10 °C.

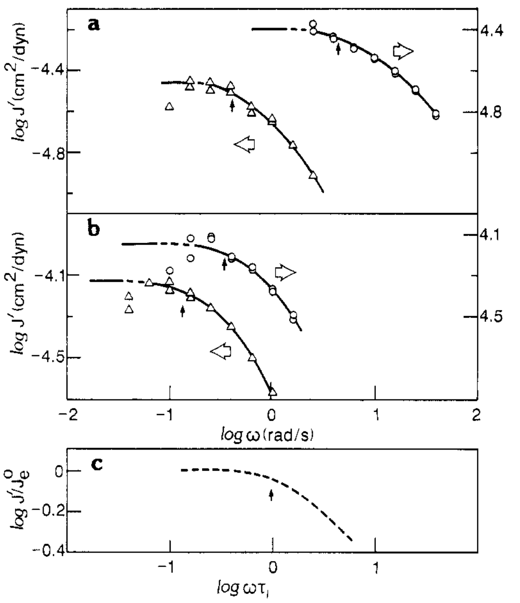

Figure 3. Double-logarithmic plot of $J'(\omega)$ vs. ω at low frequencies used in the determination of τ_1. The vertical arrows indicate the frequency at which $J'(\omega) = 0.9J_e^0$: (a) PBD 9918, 2.5% in PBD 10 at 27 and -20 °C; (b) PBD 4S800, 2.5% in PBD 20 at 27 and -10 °C; (c) log J'/J_e^0 for the Rouse spectrum of a linear polymer plotted against log $\omega\tau_1$.

An extensive discussion of methods to derive an average relaxation time of the test chain in a polymer matrix has been given.[7] The method retained by these authors consists in plotting $G'/\omega = \eta''$ against $G''/\omega = \eta'$ as shown in Figure 2. The reciprocal of the frequency at $\eta''_{\max}$ is taken as the *average* relaxation time, $\bar{\tau}$. The maximum on the right provides the relaxation time of the test chain, the maximum on the left the relaxation time of the matrix. The results are referred to as obtained by the MMM method.

In order to compare the experimental results with theory it is desirable to measure the *longest* relaxation time of the test chain (τ_1). In order to estimate τ_1, a time is arbitrarily defined as the reciprocal of the frequency at which $J'(\omega) = 0.9J_e^0$, where

$$J'(\omega) = G'(\omega)/[G'(\omega)^2 + G''(\omega)^2] \qquad (6)$$

and $J_e^0 = \lim_{\omega\to 0} J'(\omega)$, the zero-shear recoverable compliance. Examples of the procedure are shown in Figure 3. The evaluation of J_e^0 and the extraction of τ_1 from the experimental data on mixtures are more difficult than for monodisperse samples because the frequency-independent region is only reached for very small moduli. The measured signals were sometimes increased by increasing the strain from 0.3 to 0.9 and extrapolating back to 0.3 strain. The error in τ_1 is estimated to be 0.1 log units.

Results and Discussion

Evaluation of $\bar{\tau}$ and τ_1. The MMM method is well suited to derive an average relaxation time for narrow molecular weight distribution samples. For the linear polybutadienes we observe that $\bar{\tau} = \bar{\tau}_w$, where $\bar{\tau}_w = \eta_0 J_e^0$. For polystyrene melts $\bar{\tau} = 0.7\bar{\tau}_w$ has been found, indicating a broader terminal spectrum.[7] The small polydispersity of the linear polybutadienes is also revealed by the small subscribed angle tan $\beta < 0.1$ (Figure 2). However, η'' vs. η' plots for 4- and 18-arm stars are less successfully assimilated to a semicircle. The reason for this is that the terminal relaxation spectrum of stars is much broader[12] than that of linear polymers, which is dominated by the longest relaxation time.[21]

In our application of the MMM method to mixtures of stars in linear p-mers, it became apparent that the terminal relaxation time spectrum as measured by tan β increases as the size of the test chain increases. On the other hand, tan β appears to be independent of the concentration of the test chain. The dependence of tan β on the matrix MW is unclear, as it is either unaffected or decreases slightly with increasing MW. In view of these observations it can be argued that the dependence of $\bar{\tau}$ on N and P may be influenced by the width of the relaxation time spectrum. In any case the relation between $\bar{\tau}$ and $\bar{\tau}_w$ or the longest relaxation time remains ill-defined.

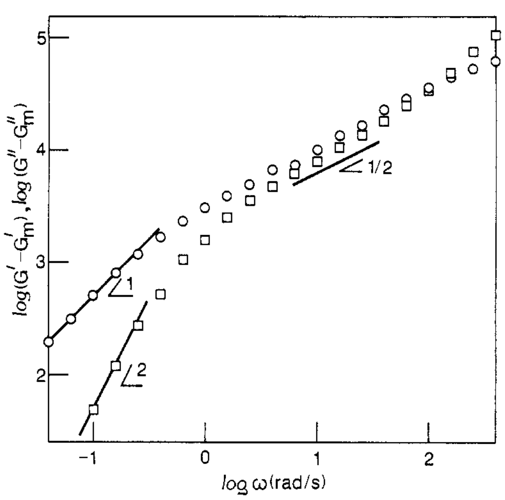

Figure 4. Double-logarithmic plot of storage and loss moduli of test chain against frequency. The slopes are for the Rouse model. 2.5% PBD 4S800 in PBD 20.

The terminal relaxation spectrum of the mixtures is expected to be of the Rouse type if the relaxation of the test chains is dominated by tube renewal.[1] This can be checked qualitatively by subtracting the matrix contribution from the low-frequency moduli in Figure 1. This is a delicate operation which assumes that the presence of a few percent high MW test chain does not affect the properties of the matrix. This is roughly indicated by the unchanged frequency in the maximum of G'' (Figure 1 and Figure 14 in ref 6). The subtraction is expected to be less accurate when the longest relaxation time of the test chain is close to that of the matrix. Also, at high frequencies the test-chain moduli are obtained as small differences between large values. An example of the moduli–frequency response of the test chain is shown in Figure 4. At low frequencies $G'' \propto \omega$ and $G' \propto \omega^2$ and at high frequencies $G' \approx G'' \propto \omega^{1/2}$ are indicative of a Rouse type relaxation process.[21] However, in more detail, the transition from low- to high-frequency behavior is somewhat more gradual than in the theoretical model for either linear or star polymers. In general, the Rouse type frequency response cannot be represented satisfactorily by a semicircle in the η''–η' plane.

Since J_e^0 and values $J'(\omega)$ at low frequencies are heavily weighted by the longest relaxation time, the latter should be extracted from storage moduli data however imprecise they may be. The choice for taking $\tau_1 = 1/\omega$ at $J'(\omega) = 0.9J_e^0$ is arbitrary but is supported by the fact that for a pure Rouse spectrum of a linear polymer $J'(\omega) = 0.905J_e^0$ at $\omega\tau_1 = 1$ (0.939 for a 4-arm star). The experimental dependence of J' on ω compares reasonably well with the Rouse dependence at low frequencies (see Figure 3). Furthermore, it is found that the frequency differences between either $J'(\omega) = 0.95J_e^0$ or $J'(\omega) = 0.8J_e^0$ and $J'(\omega) = 0.9J_e^0$ are rather constant for all mixtures.

Effect of Concentration of Test Chain. It is a prerequisite of the method that each test chain be isolated from other test chains. Different criteria for this situation have been advanced. The test-chain concentration should be less than c^* (g/mL), where

$$c^* < M/N_A R^3 \qquad (7)$$

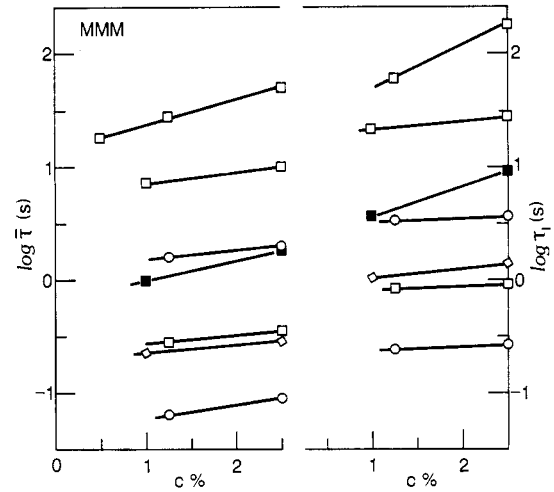

Figure 5. Effect of test-chain concentration on $\bar{\tau}$ (MMM) and τ_1 for various mixtures at -10 °C in PBD 10: (○) linear polybutadienes; (□) 4-arm stars (top two in PBD 20); (◇) 18-arm star; (■) PBD 4S1600 in PBD 40 at 66 °C.

N_A is Avogadro's number and $R = \langle s^2\rangle_\theta^{1/2}$, the static radius, or $R = R_S = [3[\eta]_\theta M/10\pi N_A]^{1/3}$, the hydrodynamic radius from intrinsic viscosity. The molecular constants have been published.[14,15,19]

Alternatively, it may suffice that there be less than one entanglement on each arm of the test chains. In that case, the volume fraction of the test chain must satisfy

$$\phi_n < 1/N_a \tag{8}$$

where N_a is the number of entanglements per arm in the bulk. The demarcation between entangled and nonentangled regimes is not sharp.[23]

Most experiments have been performed at $\phi_n = 0.025$. In order to ascertain that the observed $\bar{\tau}$ and τ_1 are indeed concentration-independent, mixtures with lower test-chain concentrations have been investigated. The concentration dependence of $\bar{\tau}$ and τ_1 is summarized in Figure 5. For most samples $\bar{\tau}$ and τ_1 vary little with concentration up to 2.5%. Only samples 4S800 and 4S1600 show clearly increasing $\bar{\tau}$ and τ_1 with concentration. This is in agreement with the conditions outlined by eq 7 and 8. No extrapolation to zero concentration has been attempted for $\bar{\tau}$ or τ_1 of the high molecular weight 4-arm stars because of the large possible errors involved in the individual measurements. The data at the lowest available concentration are used in the subsequent discussion. The difference between the experimental $\bar{\tau}$ and τ_1 can be read from Figure 5. On average, $\tau_1 \approx 2\bar{\tau}$–$6\bar{\tau}$.

Chain Architecture. The relaxation times of linear chains and 4-arm and 18-arm stars in the PBD 10 matrix at 27 °C are given in Table II and compared in Figure 6. Superposition is achieved for the three types of polymers when log τ_1 is plotted against log $(2M_a)$ for the stars and against log M for the linear polymers. At constant molecular weight τ_1 of a star is shorter than τ_1 of a linear polymer in accordance with eq 5, which is based on the Rouse model.

Molecular Weight Dependences. The dependence of τ_1 (see Table II) on the molecular weight of the 4-arm star test chains is shown in Figure 6 for different linear matrices. The slope of the line indicates that

$$\tau_1 \propto n^{2.2\pm0.1} \tag{9}$$

as expected for a Rouse tube and given in eq 2. This agrees with the results on polystyrene.[7] Three observations confirm that the tube surrounding the test chain relaxes by a Rouse mechanism: (a) the Rouse-like moduli–frequency behavior of the test chain (Figure 4), (b) the dependence of τ_1 on $(2M_a)^2$ for different stars, and (c) the $\tau_1 \propto n^2$ dependence. Zimm-type non-free-draining relaxation of the tube for which $\tau_1 \propto n^{3/2}$ can be rejected under the experimental conditions used. Zimm relaxation is expected at higher n/p ratios.[16]

Table II
log Longest Relaxation Times (τ_1) for Isolated Polybutadienes in Linear Polybutadiene Matrices at 27 °C

	matrix				
test chain	PBD 10	PBD 20	PBD 40	PBD 65	PBD 120
linear					
PBD 120	-1.7				
PBD 400	-0.5				
4-arm star					
4SB4	-2.1	-1.4			
PBD 4S400B2	-1.0	-0.3_5	0.2	0.6	
PBD 4S800B3		0.3	0.2		
PBD 4S1600B3		0.8_5	1.3	1.6	2.5
18-arm star					
PBD 3718B3	-1.9				
PBD 9918B3	-1.0				

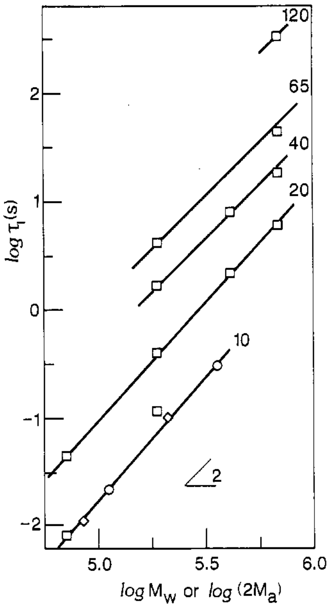

Figure 6. Dependence of τ_1 on molecular weight of test chain: (○) linear; (□) 4-arm stars; (◇) 18-arm stars. The numbers refer to the matrix polymer.

The dependence of τ_1 (see Table II) on the matrix molecular weight at constant test-chain MW is shown in Figure 7. Two sets of data are available. It is observed that

$$\tau_1 \propto p^{2.6\pm0.2} \tag{10}$$

The dependence of $\bar{\tau}$ on n and p is 2.1 and 2.4, respectively. The 2.6 power dependence on matrix molecular weight is almost as low as that found for polystyrene (2.3)[7] and reveals an important discrepancy with eq 2. It should be pointed out that a p^{-3} dependence has been deduced from tracer diffusion measurement on linear polystyrenes,[9] although higher powers ($p^{-2.4}$–$p^{-2.6}$) have also been suggested.[9b,c]

It seems necessary to divide the problem into two parts. In general it is expected that tube renewal scales as the longest relaxation time of the matrix. For a matrix composed of linear polymers, i.e., $\tau_1 \propto p^{3.4}$. This differs from

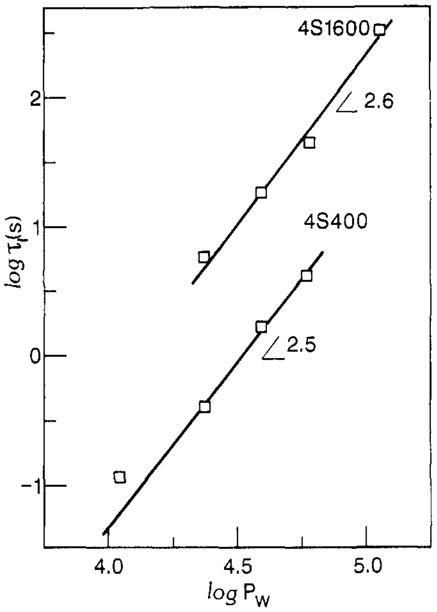

Figure 7. Dependence of τ_1 on the matrix molecular weight. The codes refer to the test chains.

the p^3 dependence of the reptation theory given in eq 1 and 2. The stronger dependence has been traced to contour-length fluctuations.[19,24,25] The characteristic time for contour-length fluctuations is of the order[26]

$$\tau_B \propto \frac{\zeta_0 b^2}{kT} n^2 \tag{11}$$

and is much longer than the lateral hopping time

$$\tau_A \propto \frac{\zeta_0 b^2}{kT} n_e^2 \tag{12}$$

Many reversible lateral jumps are expected over the period that an entanglement is formed by a fluctuating chain end. However, the effect of the lateral jumps becomes permanent only when the entanglement is completely abandoned and a new entanglement is formed by reptating neighboring chains. Contour-length fluctuation does not accelerate tube renewal and $\tau_1 \propto p^3$ is expected.

At this point one is left with the discrepancy between the observed 2.6 and the theoretical third power dependence on the matrix molecular weight. It has been suggested that entanglements along a tube are not necessarily independent[7] and that this may lower the dependence of the tube renewal time to $p^{2.5}$.[16] Note that diffusion experiments do not exclude a possible $p^{2.5}$ dependence.[9b,c]

The experimental data can be summarized by

$$\tau_1 = 4 \times 10^{-24} M_w^{2.2} P_w^{2.6} \tag{13}$$

where for stars $M_w = 2M_a$. The longest tube renewal time for a linear melt, $P_w = M_w$ in eq 13, can be compared with the experimental $\tau_{max} = 7.15 \times 10^{-19} M_w^{3.38}$.[19] In the range $M_w > 2M_e$, $\tau_{max} < \tau_1$.

In order to make any further comparison between tube renewal and reptation, the tube renewal data are *forced* to comply with the theoretical exponents and are cast in the form of eq 2 as

$$\tau_1' = 2.4 \times 10^{-18} M_w^2 P_w^3 / M_e^2 \tag{14}$$

Reptation times without contour-length fluctuation have been estimated for linear polybutadienes as T_d^∞ [19]

$$T_d^\infty = 1.95 \times 10^{-16} M_w^3 \tag{15}$$

Comparison of τ_1' and T_d^∞ indicates that tube renewal will dominate when $M_e^2 M/P^3 > 0.012$. In view of the uncertainties in both τ_1' and T_d^∞, this is in reasonable agreement with 0.08 found from diffusion.[9] Klein estimates $M_e^2 M/P^3 > 0.006$,[3] and Graessley finds 0.037 for $z = 3$ and 0.023 for $z = 4$.[5]

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