Estimation of the contribution of tube renewal in the terminal relaxation of linear polybutadiene

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A set of low-molecular-weight (low-*MW*) entangled linear polybutadienes with molecular weights between 1.1×10^4 and 2.5×10^5 have been dilutedly embedded in a high-molecular-weight linear polybutadiene ($M_w = 7.6 \times 10^5$) matrix. The viscoelastic properties of these blends with 9.1% low-*MW* polymer have been measured. The loss moduli–frequency master curves, $G''(\omega)$, contain contributions from both polymers. The contribution of the low-*MW* polymer is obtained by subtracting the contribution of the matrix. The maximum in G'', G''_m, due to the low-*MW* polymer occurs at a lower frequency (0.3 to 0.5 log units) than in the homopolymer. This result indicates that the longest relaxation time of the entangled linear polymer embedded in a high-molecular-weight matrix is increased by a factor of 2.0 to 3.0 because tube renewal normally operating in the homopolymer is almost completely absent in the matrix. The longest relaxation time of the polymers in the matrix depends on $M^{3.3_0}$. This is only slightly less than the dependence found in linear polymer melts ($M^{3.3_7}$). This indicates that reptation and chain-end fluctuation together contribute to the relaxation of linear polymers in permanent networks.

(Keywords: viscoelasticity; tube renewal; blend; linear polybutadiene)

INTRODUCTION

The original reptation model considers the diffusion and relaxation of a linear polymer in a network of permanent entanglements[1]. The model is also applied to melts and concentrated solutions of linear polymers, although the entanglements are formed by neighbouring reptating chains and are therefore not completely permanent on the timescale of the reptation process. Relaxation of a chain due to the disappearance of entanglement is called tube renewal or constraint release[2]. The effect of the non-permanence of entanglements on the relaxation of linear polymers is rather subtle. Since the longest relaxation time is:

$$\tau_{\text{rep}} \propto \tau_0 (n^3/n_e) \tag{1}$$

where τ_0 is the monomeric jump time, n the degree of polymerization and n_e the number of monomers between entanglements, it can be shown[3,4] that the tube renewal time is:

$$\tau_{\text{ren}} \propto \tau_0 (n^5/n_e^3) = \tau_{\text{rep}} (n^2/n_e^2) \tag{2}$$

For all but the smallest entangled linear polymers, $\tau_{\text{ren}} \gg \tau_{\text{rep}}$, and reptation will dominate chain relaxation processes.

Nevertheless, Graessley has shown how τ_{rep} itself is affected by the ongoing tube renewal process[2]. In general, tube renewal will narrow the relaxation-time spectrum because it affects more strongly the longest-time processes in the relaxation-time spectrum.

The effect of tube renewal on the relaxation of narrow-molecular-weight-distribution linear polymers is best assessed by comparing the relaxation of a linear homopolymer melt and the relaxation of the same polymer in a permanent network. Three questions can be asked. How much longer is the longest relaxation time in the absence of tube renewal? How does the longest relaxation time depend on molecular weight? How do the relaxation-time spectra in the two cases compare?

In an impressive series of publications Ferry and his coworkers have addressed these questions[5–11]. They observed that the relaxation of unattached polymers in networks was either identical[5,6] or three[7], ten[8] or more[9,10] times slower than in the undiluted polymer. The molecular-weight dependence of the relaxation times of the unattached chains in the network is given by M^3 (refs. 5, 7) or $M^{3.4}$ (refs. 8, 11). This difference is important because the third-power dependence agrees exactly with the reptation theory (equation (1)). The latter dependence is identical to the one observed experimentally in polymer melts. The time spectrum of the relaxation due to the unattached chains was either found to be the same as[5,7,8] or much more gradual than[9,10] in the homopolymer.

Similar work was reported by Kraus and Rollmann[12] for a series of polybutadienes embedded in a radial poly(styrene-*b*-butadiene) copolymer. They observed a 3.1 power dependence on molecular weight for the longest relaxation time of the added polybutadiene[12]. Recently, Kotaka and coworkers[13] studied polyisoprene in vulcanized natural rubber. They observed that the relaxation time depends on $M^{3.3}$. Their dielectric relaxation experiments on the same samples provided a much enhanced contribution of the unattached chains to the signal. From these measurements a 2.5-fold increase of the relaxation time in the network was found[14].

The problems associated with the correct extraction of the small contribution of the unattached chains from the total modulus of the system (network + unattached chains) have been discussed[5–11,13]. The interaction

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between the network and the unattached chains should be thermodynamically neutral. There are usually small differences in the chemical composition of the matrix and free polymer. These are particularly prominent in end-linked polymer networks[8–10]. The spectrum of the relaxation in the network and in the bulk changes unless the molecular-weight distribution of the unattached chains is narrow[9,10] and comparison of the longest relaxation times cannot be made unless this condition is satisfied. Finally, the relaxation time of the unattached chain may depend on the molecular weight between crosslinks (M_x). When $M_x \geqslant M_e$ (the molecular weight between entanglements) the relaxation is expected to be independent of M_x. When $M_x < M_e$, strangulation[13,15] may occur and the relaxation time is expected to increase with decreasing M_x according to[16]:

$$\tau_{rep} = \tau_{rep}(M_e)(M_e/M_x)$$

In this paper we describe the viscoelastic properties of blends containing 9.1% linear entangled polybutadiene in a high-molecular-weight linear polybutadiene matrix. No chemical crosslinks have been introduced. In this system, most of the problems enumerated for the network systems are avoided. For most of the polybutadienes the high-molecular-weight matrix acts as a permanent network. Furthermore, the longest relaxation times of the added polymers are derived from the dynamic viscoelastic measurements, which provide improved accuracy. The longest relaxation times observed in the matrix are compared with those reported for the melts of the same polymers[17]. The linear viscoelastic properties of the homopolymers have been described in detail previously[17]. The general shape of $G''(\omega)$ of the added polymer is compared to $G''(\omega)$ of the homopolymer because it is related to the relaxation-time spectrum.

EXPERIMENTAL

The synthesis and characterization of the linear polybutadienes have been given in full previously[17]. The linear matrix polymer was made by the same method as the other polymers. Its light scattering molecular weight is 7.6×10^5. The melt viscosity at 86.3°C is 3.75×10^7 P and is estimated to be 3×10^8 P at 26.3°C[18]. Blends of the matrix polymer with the linear polybutadienes are made by mixing weighed benzene solutions containing about 5% of each polymer. The mixtures were freeze dried and further dried under vacuum to constant weight. The viscoelastic data were obtained with a Rheometrics 605M mechanical spectrometer in the dynamic mode[17,19]. Measurements were made between 0.01 and 100 rad s^{-1} at five frequencies per decade at seven temperatures between 86.3 and −76.2°C. Master curves at the reference temperature ($T_r = 26.3$°C) were constructed from measurements at the other temperatures by appropriately shifting along the frequency and moduli axes. First, the horizontal shift factor along the frequency axis, a_T, was determined from $\tan \Delta = G''(\omega)/G'(\omega)$ against $\log \omega$ plots:

$$\tan \Delta(\omega_{T_r}) = \tan \Delta(a_T \omega_T)$$

Secondly, the vertical shift factor, b_T, is determined by superimposing the loss moduli G'' according to:

$$G''(\omega_{T_r}) = b_T G''(a_T \omega_T)$$

Table 1 Temperature shift factors for linear polybutadiene melt viscoelastic properties

Temperature	$\log a_T$	$\log b_T$
86.3	-0.93_5	−0.05
26.3[a]	–	–
−10.2	1.00	0.04
−30.2	1.81	0.06
−50.2	2.92	0.09
−66.0	4.16	0.11_5
−76.2	5.30	0.13

[a] Reference temperature T_r

This two-step method of superimposing data avoids the use of $\log G''(\omega)$ and $\log G'(\omega)$ values and simultaneous shifting along both axes. In the superposition most weight was put on data in the frequency regions where $\tan \Delta$ changes rapidly. Similarly, in order to determine b_T most weight was put on data around maxima and minima in $G''(\omega)$. The occurrence of multiple maxima and minima in $\tan \Delta(\omega)$ and $G''(\omega)$ of the blends was of great help in this regard. Values of $\log a_T$ and $\log b_T$ are given in *Table 1*. The standard deviations in $\log a_T$ and $\log b_T$ are 0.02 and 0.01 respectively.

Although this procedure is considered a refinement of the older procedure, the a_T shift factors fit $\log a_T = 740/(T - T_\infty)$, with $T_\infty = T_g - 60 = -156$°C. This is not significantly different from the temperature dependence previously observed for linear polybutadienes[17]. As can be seen from *Table 2*, the seven temperatures were chosen so that $\log a_T \approx 1$ between consecutive temperatures and experimental data overlap over a three-decade frequency range.

RESULTS AND DISCUSSION

Typical loss moduli–log frequency master curves for the matrix linear polybutadiene and the same polymer diluted with 9.1% of a non-entangling linear polybutadiene (PBD1800)[19] are shown in *Figure 1*. The viscoelastic data are collected in *Table 2* (top three lines). The zero-shear viscosity is determined from:

$$\eta_0 = \lim_{\omega \to 0} G''(\omega)/\omega$$

The plateau modulus is calculated from:

$$G_N^0 = (2/\pi) \int_{-\infty}^{+\infty} [G''(\omega) - G''_S(\omega)] \, d \ln \omega$$

where $G''_S(\omega)$ is the contribution of the transition zone to the loss modulus. $G''_S(\omega)$ is shown as a dotted curve in *Figure 1*[7,19]. The maximum value of $G''(\omega)$, $(G''_m)_M$, and the frequency at which the terminal maximum occurs, $(\omega_m)_M$, are also given in *Table 2*.

Dilution with a small amount of a very low-molecular-weight non-entangling linear polybutadiene is not expected to have a thermodynamic effect on the conformation of the matrix polymer. Since the glass transition is unchanged on dilution, the monomeric friction coefficient is not affected. This is confirmed by the unchanged shift factors for the blends. The following relations for the terminal properties hold for the matrix diluted with very low-*MW* linear polybutadiene ($M_n = 1800$)[19]:

$$(\eta_0)_{DM} = v_2^{3.37}(\eta_0)_M \qquad (\omega_m)_{DM} = v_2^{3.37}(\omega_m)_M$$

$$(G''_m)_{DM} = v_2^2(G''_m)_M \qquad (G_N^0)_{DM} = v_2^2(G''_m)_M$$

where the subscripts DM and M indicate the property of the diluted and undiluted matrix, respectively, and v_2 is the volume fraction of the matrix polymer.

The calculated values of $(\eta_0)_{DM}$ are 2.63×10^7 and 2.72×10^7 P for the matrix diluted with 10 and 9.1% low-*MW* polybutadiene respectively. The calculated values of $(G''_m)_{DM}$ are 2.62×10^6 and 2.86×10^6 dyn cm^{-2} respectively. These calculated values agree with the experimental values of *Table 2* within experimental error. Similar agreement is found for $(\omega_m)_{DM}$ and $(G_N^0)_{DM}$. It has been suggested[20,21] that G''_m and G_N^0 depend on $v_2^{2.25}$ rather than on the theoretically supported[22] square dependence used here. However, it would be difficult to distinguish between the two exponents at $v_2 = 0.9$.

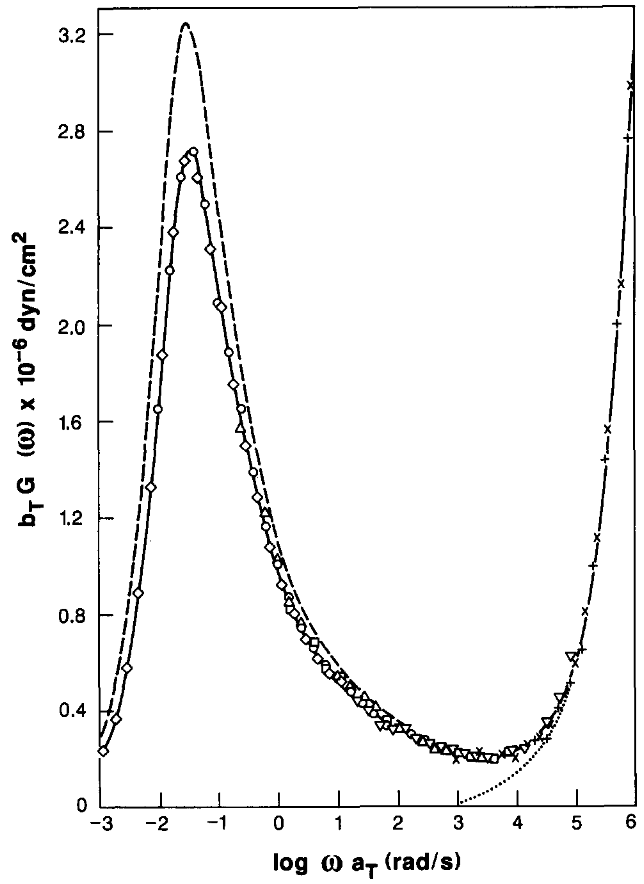

Figure 1 Loss moduli–log frequency master curves at 26.3°C for the linear polybutadiene matrix, PBD800 (broken curve), and the matrix diluted with 9% PBD1800 (full curve). For clarity, a fraction of the experimental data are shown only for the blend. Also shown is $G_S''(\omega)$ (dotted curve)

In *Figure 2* the loss modulus–log frequency master curve of a blend containing 9.1% PBD40 is shown. The contribution due to PBD40 produces a new maximum in $G''(\omega)$, G''_m, centred at log $\omega a_T = 2.2$. Of course, the position of G''_m due to the added polymer moves to higher frequency as the *MW* decreases. This will be discussed in detail later. The blend containing PBD10 shows only a shoulder at log $\omega a_T > 4$. Blends with PBD170 and PBD300 exhibit a shoulder on the high-frequency side of the terminal peak in $G''(\omega)$.

We discuss first the properties of the terminal region, which is dominated by contributions of the matrix. Inspection of *Table 2* suggests that the terminal properties of the matrix with linear entangling polybutadienes resemble more the terminal properties of the diluted matrix than the properties of the bulk matrix. Only when the ratio of the matrix to added polymer molecular weight, *R*, drops below 7 do the values of $\log(\omega_m)_M$ approach the bulk matrix values. Struglinski and Graessley[21] found $\log(\omega_m)_{DM}$ unchanged for polybutadiene blends with $R < 10.7$.

It is worth noting that values of G_N^0 (*Table 2*) of all the blends with entangled linear polymers are equal to the bulk matrix value.

We now turn our attention to the contribution of the added polymer to the moduli–frequency master curves. The experimental values of the frequency of the maximum G''_m, ω_m, are given in column 2 of *Table 3*. In order to evaluate correctly the contribution of the added polymer to the overall master curve, the contribution of the matrix in the blend has to be subtracted. Theory and experiments on binary blends have shown that moduli–frequency master curves are not the weighted sums of the contributions of the two components[21,23–26]. Even the most sophisticated models for binary blends are not sufficiently accurate in describing the master curves of a

Table 2 Terminal properties of matrix PBD800 and its blends with low-*MW* linear polybutadiene[a]

Sample	$MW^b \times 10^{-3}$	$v_2{}^c$	$\eta_0^{86.3°C} \times 10^{-7}$ (P)	$\log(\omega_m)_M$ (rad s^{-1})	$(G''_m)_M \times 10^{-6}$ (dyn cm^{-2})	$G_N^0 \times 10^{-7}$ (dyn cm^{-2})
PBD800	760	1.000	3.7_5	-1.5_5	3.2_4	1.10
+PBD1800	1.8	0.909	2.7	-1.4_7	2.7_4	0.93
+PBD1800	1.8	0.900	2.6_5	-1.4_0	2.6_7	0.92
+PBD10	11.1	0.909	2.8	-1.4_6	2.7_4	1.08
+PBD22	23.6	0.909	2.8_5	-1.4_8	2.7_0	
+PBD40	39.4	0.909	2.8	-1.4_8	2.7_3	1.09
+PBD65	59.0	0.909	2.8_5	-1.4_8	2.7_5	1.10
+PBD120	114	0.909	2.9	-1.4_8	2.6_8	1.09
+PBD170	164	0.909	2.9	-1.5_2	2.7_9	1.10
+PBD300	256	0.909	$\geqslant 3.1_5$	-1.5_2	2.7_9	1.09

[a] Values at $T_r = 26.3$°C
[b] *MW* of added linear polybutadiene[17] except for the matrix PBD800
[c] v_2 is the volume fraction of matrix

blend[24]. Therefore a practical approach is used here to subtract the contribution of the matrix. As will be shown, in most cases the subtraction is not critical for a correct determination of ω_m of the added polymer.

Two methods were adopted. In the first method we subtract from the total modulus of the blend, $[G''(\omega)]_t$, the modulus of the diluted matrix $[G(\omega)]_{DM}$:

$$G''(\omega)=[G''(\omega)]_t-[G''(\omega)]_{DM} \qquad (3)$$

This is equivalent to saying that all entanglements with the added polymer are ineffective for the relaxation of the matrix. The second method represents the other extreme. The weighted contribution of the matrix is subtracted according to:

$$G''(\omega)=[G''(\omega)]_t-v_2^2[G''(\omega)]_M \qquad (4)$$

This is equivalent to assuming that the timescale of the relaxation of the matrix is unchanged from the bulk in the presence of the added lower-*MW* polymer. The first method is expected to be better when the molecular weight of the added polymer is low. The second method should be more suitable when the molecular weight of the added polymer is comparable to that of the matrix.

The contributions of the added polymer obtained with equation (3) are shown in *Figure 3*. The values of ω_m are given in *Table 3*. Except for the two extremes in the sample *MWs*, they agree well with the directly observed values. The moduli–frequency curves of the added polymers are all very similar. This is remarkable because the subtracted contributions of the matrix vary considerably over the six decades of frequency covered by the seven different added polymers. At low frequencies $G''(\omega)\propto\omega$. At high frequencies two regimes are observed. For frequencies slightly higher than ω_m, $G''(\omega)\propto\omega^{\frac{1}{2}}$; and

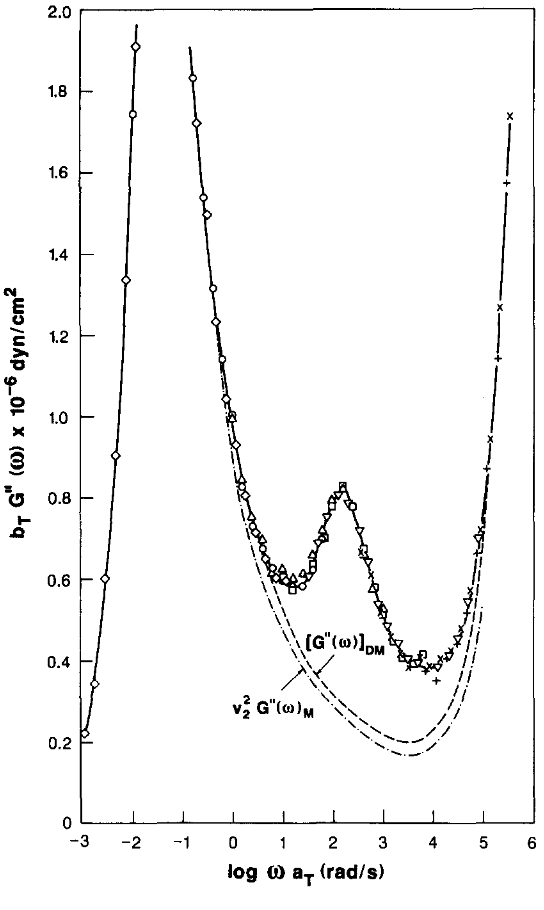

Figure 2 Loss moduli–log frequency master curves at 26.3°C for a blend of 9.1% linear PBD40 in the linear matrix PBD800 (full curve). $[G''(\omega)]_{DM}$ and $v_2^2[G''(\omega)]_M$ curves used to evaluate the contribution of PBD40 are also shown

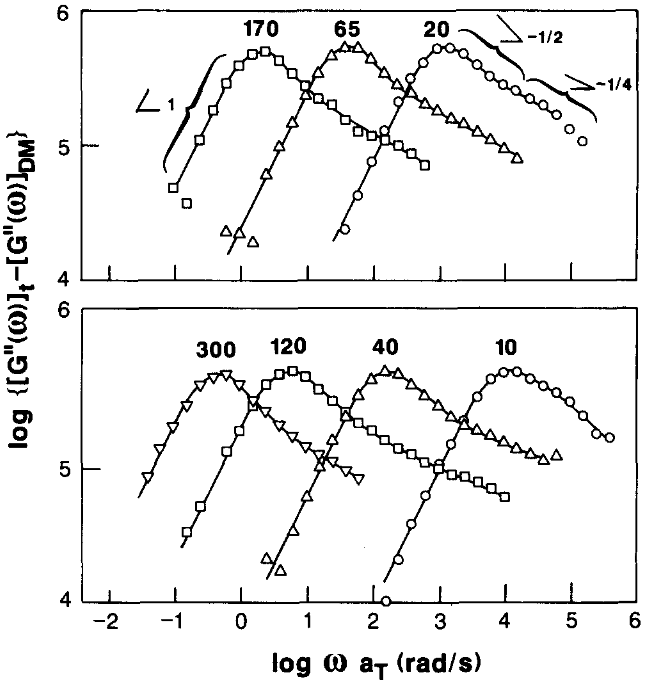

Figure 3 Contributions to the modulus of the low-molecular-weight fraction in the matrix obtained by equation (3) against frequency. The code number identifies each polymer

Table 3 Properties of the low-*MW* linear polybutadiene in the polybutadiene matrix[a]

	Log ω_m			
Sample matrix	Experimental	Equation (3)	Equation (4)	Homopolymer melt[b]
+PBD10	4.3 (sh)	4.10	4.1_5	4.60
+PBD22	3.1	3.10	3.10	3.48
+PBD40	2.2	2.20	2.24	2.60
+PBD65	1.6	1.6_5	1.66	2.04
+PBD120	0.6	0.75	0.80	1.06
+PBD170	(sh)	0.3_5	0.26	0.60
+PBD300	(sh)	−0.3	−0.40	−0.10

[a] All values at T_r = 26.3°C
[b] Data from ref. 17

at still higher frequencies, $G''(\omega) \propto \omega^{\frac{1}{4}}$ over two decades. This shape of $G''(\omega)$ is in good agreement with that obtained for the homopolymers[17] and is characteristic of a combined reptation and chain-end fluctuation mechanism[27] for the relaxation of the embedded polymer. This strong similarity between the $G''(\omega)$ curves of the added polymer and the $G''(\omega)$ curves of the homopolymer melt suggests clearly that the relaxation-time spectrum of the added polymer has changed little on embedding in the high-molecular-weight matrix.

The value of G''_{m} varies between 5.0×10^5 and 5.25×10^5 dyn cm^{-2}. If multiplied by $(1 - v_2^2)^{-1}$ values of $(2.87 - 3.02) \times 10^6$ dyn cm^{-2} are obtained, which are in good agreement with the values of $G''_{\mathrm{m}}(\omega)$ for homopolymer polybutadienes[17]. No dependence of G''_{m} on molecular weight is discernible as is found in the homopolymer.

The values of ω_{m} obtained with equation (4) are given in the third column of *Table 3*. When using equation (4) much poorer $G''(\omega)$ curves for the added polymer are obtained. In particular $\log G''(\omega)/\log \omega < 1$ at low frequencies and $\log G''(\omega)/\log \omega < 0.25$ at very high frequencies. The values of G''_{m} varied between 5.5×10^5 and 6.0×10^5 dyn cm^{-2}, which yields on multiplication by $(1 - v_2^2)^{-1}$ values of $G''_{\mathrm{m}} = (3.17 - 3.45) \times 10^6$ dyn cm^{-2}, slightly higher than values for the homopolymer. It should be noted that values of ω_{m}, obtained by both methods and given in columns 3 and 4 of *Table 3*, are little affected by the choice of method except for PBD170 and PBD300. As explained the values of ω_{m} of method II (equation (4)) are preferred for these polymers.

Comparison of the frequencies of the maxima in the blend with the frequencies in the homopolymer (taken from ref. 17 and given in the last column of *Table 3*) indicates that the polymers in the matrix relax 0.5 to 0.3 log units slower than in the homopolymer. It is to be expected that the difference decreases as the molecular weight of the added polymer increases to the molecular weight of the matrix since tube renewal may not be completely inhibited for the highest-*MW* added polymers. For this reason it seems appropriate to conclude that the experiments indicate a slowing of relaxation by a factor of 2.0 to 3.0 with a preference for a true value nearer 3, when the polymer is embedded in a high-*MW* matrix. This value is in good agreement with the factor of 3 for butadiene in SBS block copolymers with spherical styrene domains[7]. Struglinski and Graessley[21] give values of 3.7 to 4.8 for blends of polybutadienes with $R = 2.5$ and 10.7[21]. Their measurement with the ERD technique does not extend to very high frequencies and no correction for matrix contribution is included. The 2.0- to 3.0-fold increase is also in good agreement with the recent work of Kotaka on polyisoprene in natural rubber networks[14].

In *Figure 4* the molecular-weight dependence of $\tau_1 = 1/\omega_{\mathrm{m}}$ is shown. In the homopolymer $\tau_1 \propto M^{3.3_7}$ (ref. 17). In the blend $\tau_1 \propto M^{3.3_0}$. The 3.3_0 exponent in the blend may be due to increasing tube renewal for the highest-*MW* added polymers. The exponents are therefore considered identical within experimental error. Both are larger than the third power expected for pure reptation. An exponent larger than 3 has been ascribed to the participation of chain-end fluctuation in the relaxation by reptation[17,27]. Both processes occur also simultaneously in the medium with fixed entanglements.

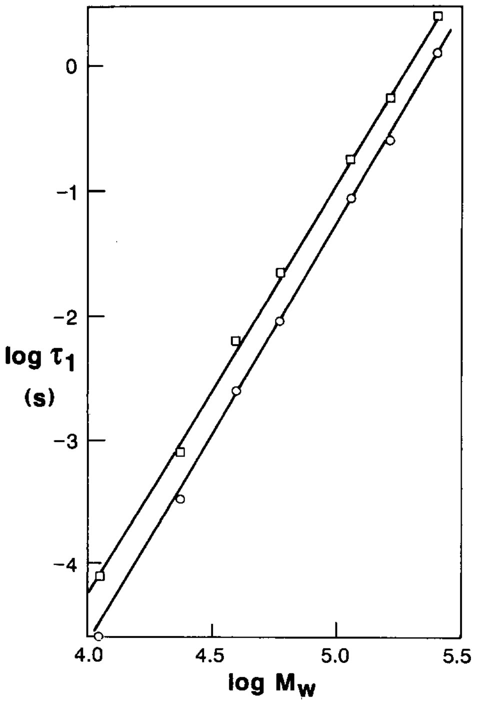

Figure 4 Log τ_1 *versus* log (molecular weight) of the linear polybutadiene. Circles: data obtained for bulk samples[17]. Squares: data obtained in the high-molecular-weight linear matrix

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REFERENCES

1 de Gennes, P. G. *J. Chem. Phys.* 1971, **55**, 572
2 Graessley, W. W. *Adv. Polym. Sci.* 1982, **47**, 67
3 Klein, J. *Macromolecules* 1978, **11**, 852
4 Daoud, M. and de Gennes, P. G. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 1971
5 Kramer, O., Greco, R., Neira, R. A. and Ferry, J. D. *J. Polym. Sci., Polym. Phys. Edn.* 1974, **12**, 2361
6 Berglund, C. A., Carriere, C. J. and Ferry, J. D. *J. Rheol.* 1981, **25**, 251
7 Kan, H.-C., Ferry, J. D. and Fetters, L. J. *Macromolecules* 1980, **13**, 1571
8 Nelb, G. W., Pedersen, S., Taylor, C. R. and Ferry, J. D. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 645
9 Taylor, C. R. Kan, H.-C., Nelb, G. W. and Ferry, J. D. *J. Rheol.* 1981, **25**, 507
10 Granick, S., Pedersen, S., Nelb, G. W., Ferry, J. D. and Macosko, C. W. *J. Polym. Sci., Polym. Phys. Edn.* 1981, **19**, 1745
11 Kramer, O., Greco, R., Ferry, J. D. and McDonel, E. T. *J. Polym. Sci., Polym. Phys. Edn.* 1975, **13**, 1675
12 Kraus, G. and Rollmann, K. W. *J. Polym. Sci., Polym. Phys. Edn.* 1977, **15**, 385
13 Poh, B. T., Adachi, K. and Kotaka, T. *Macromolecules* 1987, **20**, 2569
14 Poh, B. T., Adachi, K. and Kotaka, T. *Macromolecules* 1987, **20**, 2574
15 Antonietti, M. and Sillescu, H. *Macromolecules* 1985, **18**, 1162
16 de Gennes, P.-G. *Macromolecules* 1986, **19**, 1245
17 Roovers, J. *Polym. J.* 1986, **18**, 153
18 Colby, R. H., Fetters, L. J. and Graessley, W. W. *Macromolecules* 1987, **20**, 2226
19 Hadjichristidis, N. and Roovers, J. *Polymer* 1985, **26**, 1087
20 Raju, V. R., Menezes, E. V., Marin, G., Graessley, W. W. and Fetters, L. J. *Macromolecules* 1981, **14**, 1668

21 Struglinski, M. J. and Graessley, W. W. *Macromolecules* 1985, **18**, 2630
22 Rubinstein, M. and Helfand, E. *J. Chem. Phys.* 1985, **82**, 2477
23 Rubinstein, M., Helfand, E. and Pearson, D. S. *Macromolecules* 1987, **20**, 822
24 Rubinstein, M. and Colby, R. C. *J. Chem. Phys.* 1988, **89**, 5927
25 Doi, M., Graessley, W. W., Helfand, E. and Pearson, D. S. *Macromolecules* 1987, **20**, 1900
26 des Cloizeaux, J. *Europhys. Lett.* 1988, **5**, 437
27 Doi, M. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 667