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Rheological Study of Miscible Blends of 1,4-Polybutadiene and 1,2-Polybutadiene (63% 1,2)†

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ABSTRACT: Blends of 1,4-polybutadiene (7% 1,2) and 1,2-polybutadiene (63% 1,2) have been studied. The molecular weights are sufficiently high that the polymers are in the entanglement regime (5–20 entanglements per chain). DSC studies confirm that the blends are miscible. A single glass transition is observed, intermediate between the glass transition temperatures of the homopolymers. The T_g of the blends is however 2–3 times wider than that in the homopolymers. The viscoelastic properties of the blends have been studied over a wide range of temperatures and frequencies. The blends appear to be thermorheologically complex. This is a consequence of different temperature dependences of the relaxation times of the components of the blends. Analysis of these temperature dependences suggests that each component experiences its own T_g, slightly different from the average DSC T_g. These different T_g's suggest that each polymer is preferentially surrounded by its own chains. Other consequences of thermorheological complexity are also described.

Introduction

In order to study in detail the viscoelastic properties of miscible blends of two polymers, certain experimental conditions have to be met. First, it is desirable that the two polymers have a narrow molecular weight distribution.[1] Narrow molecular weight distribution samples have played a crucial role in the elucidation of the relaxation of polymers and their homopolymer blends because discrete relaxation phenomena are observable only with these samples.[2,3]

Second, the samples must have molecular weights sufficiently high that they are entangled. The phenomena occurring in the relaxation of entangled polymers are specific to polymers and quite different from those found in low molecular weight liquids. As will be shown later, certain molecular weight ratios have to be satisfied so that the relaxation times of the components of the blend are separated by at least 1 but less than 3 orders of magnitude. These conditions depend on the glass transition temperature (T_g) and on the molecular weight between entanglements (M_e) of the individual polymers.

Third, the samples must be thermodynamically miscible over a wide range of temperature and blend composition. In this study we describe blends made with anionically prepared 1,4-polybutadiene (7% 1,2) and 1,2-polybutadiene containing 63% 1,2 units. The thermodynamic miscibility of 1,4- and 1,2-polybutadiene (>99%) has been studied extensively. Cohen and Wilfong used block copolymers and found that the interaction parameter $\chi_c = 9 \times 10^{-3}$ at room temperature.[4] This value was confirmed by Bates et al.[5] He also derived $\chi = 8.2 \times 10^{-3}$ at 108 °C and a preliminary $\chi = 4.7 \times 10^{-3} + 1.35/T$.[6] From SANS study on 50/50 diblocks that contained deuterated 1,4-polybutadiene the temperature dependence of χ is given by $\chi = 6.79 \times 10^{-3} + 0.561/T$.[7] A differential scanning calorimetry study of blends of homopolymers yields $\chi > 4.3 \times 10^{-3}$ presumably for blends at room temperature.[8]

Recently, Sakurai and co-workers have studied blends of 1,4-polybutadiene and deuterated 1,2-polybutadiene (63% 1,2) by SANS.[9] For this pair they obtained

$$\chi = -5.64 \times 10^{-4} + 0.825/T \qquad (1)$$

From a set of three equations obtained on blends of polymers with different 1,4 and 1,2 fractions they were able to derive the interaction parameter between pure hydrogenous 1,4-polybutadiene and 1,2-polybutadiene

$$\chi_{1,2\text{-}1,4} = 2.69 \times 10^{-3} + 1.87/T \qquad (2)$$

Values of χ in eq 2 allow the calculation of the interaction parameter for any pair of polybutadiene copolymers composed of 1,4 and 1,2 units, according[10] to

$$\chi_{\text{blend}} = (x - y)^2 \chi_{1,2\text{-}1,4} \qquad (3)$$

For the case of anionically prepared 1,4-polybutadiene ($x = 0.07$) and 1,2-polybutadiene (63%) ($y = 0.63$) one obtains from eq 3

$$\chi = 8.447 \times 10^{-4} + 0.586/T \qquad (4)$$

Values of χ calculated with eq 4 are not very different from those calculated with eq 1, indicating that the deuterium substitution is a minor perturbation on the interaction between 1,4- and 1,2-polybutadiene units. Although eq 2 is specific for a blend composition with $\phi = 0.48$, no dependence of χ on blend composition has been found and this assumption has been used in this work. In the preceding analysis, 1,4-cis and 1,4-trans units have been considered thermodynamically equal. It is worthwhile to recall that SANS data yield the interaction parameter for the spinodal. For a system with a UCST as is the case for 1,4-polybutadiene and 1,2-polybutadiene the spinodal decomposition temperature is below the binodal curve.

The spinodal temperature is calculated from[9]

$$\chi_s = \frac{\nu_0}{2}\left[\frac{1}{\nu_1 \phi_1 \langle Z_1 \rangle_w} + \frac{1}{\nu_2 \phi_2 \langle Z_2 \rangle_w}\right] \qquad (5)$$

together with eq 4 where ν_1, ϕ_1, and $\langle Z_1 \rangle_w$ are the molar volume, volume fraction, and weight-average degree of polymerization of component 1 in the blend, etc. The mean molar volume of the two components is ν_0. In the case of 1,4- and 1,2-polybutadiene $\nu_1 \approx \nu_2 \approx \nu_0$.

In Figure 1 the spinodal temperature of a 50/50 blend of all-hydrogenous 1,4-polybutadiene (7% 1,2) and 1,2-polybutadiene (63%) is shown as a function of the molecular weight of each component. It shows the molecular weight range in which a 50/50 blend is expected to be

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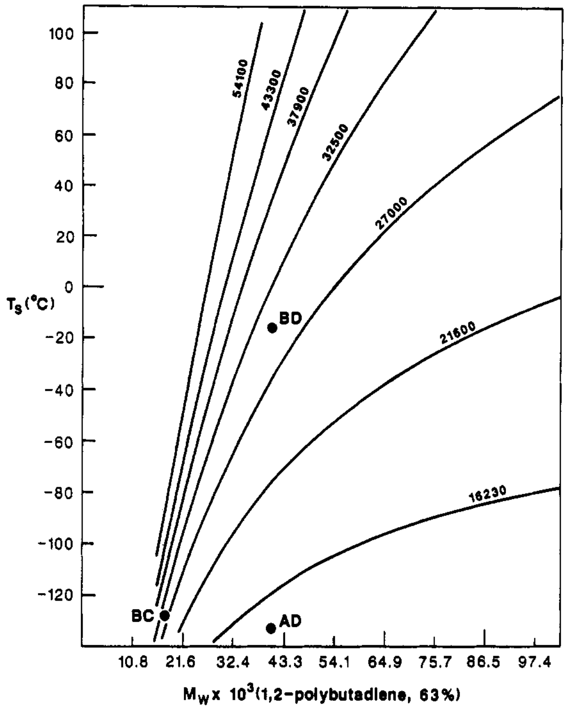

Figure 1. Spinodal decomposition temperature as a function of M_w of 1,2-polybutadiene (63%) in a 50/50 blend with 1,4-polybutadienes with indicated MW's. The loci marked AD, BC, and BD are for blends used in this study. Blend AC has $T_s <$ -140 °C.

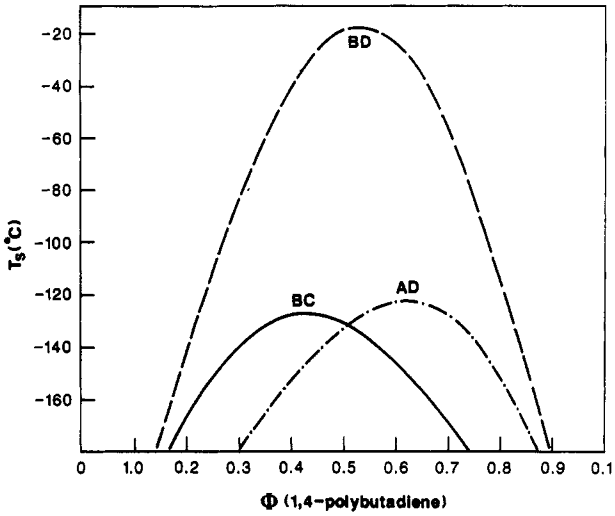

Figure 2. Composition dependence of T_s for blends of 1,4-polybutadiene and 1,2-polybutadiene (63%) studied in this work.

thermodynamically compatible. Blends of other composition have very often lower spinodal temperatures. This is shown in Figure 2 for the polymer pairs that have been studied in this work. In most cases phase separation will not occur because T_g of the blends is often higher than the spinodal temperature.

In this study we have probed blends of 1,4-polybutadiene and 1,2-polybutadiene (63%) by DSC. A rheological study of the blends has been made. The discussion of the result is in terms of the relaxation times of the individual components of the blends. The composition and the molecular weight dependence of the relaxation times are also considered. Other properties like η_0 and $J_e°$ are also described and analyzed.

Experimental Section

Samples of 1,4-polybutadiene were prepared with *sec*-BuLi in a cyclohexane/butene mixture. Samples of 1,2-polybutadiene (63% 1,2) were prepared in the presence of diglyme. The molecular weight and microstructure of each sample is given in Table I.

Table I
Sample Characterization

sample	$M_w \times 10^{-3}$ [a]	M_w/M_n [a]	microstructure[b] 1,4-cis	1,4-trans	1,2	T_g,[c] °C
A	14.6	1.05	41	53	6	-95
B	30.0	1.04	43	49	7	-94
C	17.1	1.03	12	23	65	-45
D	40.2	1.04	15	29	56	-51.8

[a] By GPC. [b] By ^{13}C NMR. [c] By DSC at 10 °C/min.

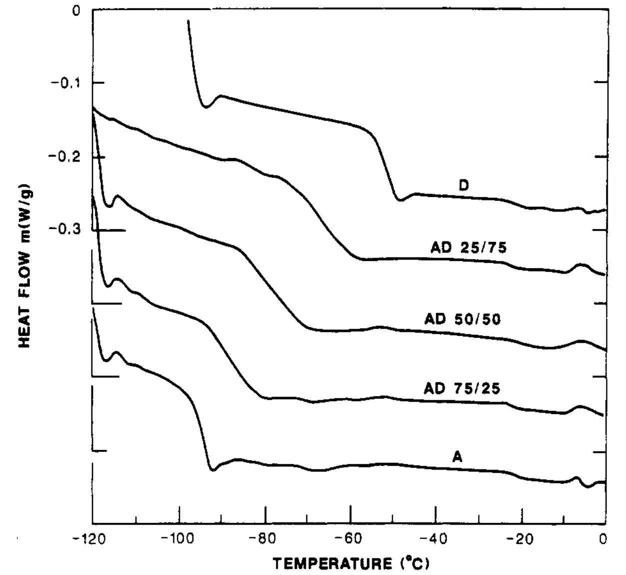

Figure 3. DSC traces for samples A and D and their blends.

Blends were prepared by weight in cyclohexane or benzene and freeze-dried to constant weight. For some samples this is achieved within 48–72 h. Samples rich in component C or D sometimes took 1 week to 10 days to reach constant weight. All blend samples are clear. A Du Pont 910 DSC coupled with a 2100 data acquisition system was used. Samples (4–7 mg) were rapidly cooled down from room temperature and scanned at 10 °C/min. Some blend samples were held for long times at 10–20 °C above their T_g and then immediately rescanned. No evidence for phase separation was found however.

Rheological measurements were made with a Rheometrics mechanical spectrometer (605 M) in the dynamic mode. The frequency range was from 1 × 10^{-2} to 1 × 10^2 rad/s. The strain was kept as small as possible (<30% and decreasing with increasing frequency) to stay within the linear regime and to obtain a sufficient output signal. The temperature of the measurements has been varied from high temperatures where the limiting properties η_0 and $J_e°$ are measured to low temperatures, usually 15–20 °C above the DSC T_g. It was observed that rheological properties were completely independent of the thermal history.

Results and Discussion

a. Glass Transition. The DSC study was undertaken to confirm qualitatively the thermodynamic miscibility of the polybutadiene samples. Examples of DSC traces are shown in Figure 3. Values of T_g of the homopolymers are given in Table I. The width of the glass transition of the homopolymers is about 6 °C. They also show a small enthalpic relaxation. Values of T_g and the width of the transitions for the blends are given in Table II. The composition dependence of T_g is slightly concave for all the blends. It appears that this dependence fits well a

Table II
Glass Transition Temperatures of Blends

blend	composition	T_g, °C	width, °C	$\Delta\alpha_2/\Delta\alpha_1$
AD	25/75	−66	15	0.67
	50/50	−77	14	0.71
	75/25	−87	10.5	0.68
BC	25/75	−60	17	0.76
	50/50	−75	18	0.63
	75/25	−87	11	0.50
AC	24.7/75.3	−61	15	0.70
	47.4/52.6	−74	17	0.65
	76.5/23.5	−85	12	0.81
BD	24.5/75.5	−66	12	0.64
	47.2/52.8	−77	15	0.60
	70.7/29.3	−85	10	0.65

Table III
Rheological Characterization of Polymers at 25.8 °C

sample	η_0, P	$J_e° \times 10^7$, cm²/dyn	$G''_{max} \times 10^{-6}$, dyn/cm²	$J_e°G_N°$ [a]	M_e [b]
A	1.1×10^3 [c]	1.66	[3.63] [d]		
B	$1.2_4 \times 10^4$ [e]	1.78	3.16	2.0	1900
C	1.93×10^4 [f]	2.47	2.27	2.0	2800
D	2.56×10^5 [g]	2.69	2.16 [h]	2.1	2860

[a] $G_N°$ calculated by $3.56 \times G''_{max}$. [b] $M_e = \rho RT/(3.56 \times G''_{max})$. [c] $M_w = 17\,600$ from $\eta_0 = 4.7 \times 10^{-12} M_w^{3.38}$.[13] [d] Value of G''_{max} contains a contribution from the glass transition. [e] $M_w = 35\,000$ from $\eta_0 = 4.7 \times 10^{-12} M_w^{3.38}$.[13] [f] $M_w = 21\,100$ from $\eta_0 = 2.8 \times 10^{-12} M_w^{3.65}$.[14] [g] $M_w = 41\,600$ from $\eta_0 = 2.8 \times 10^{-12} M_w^{3.65}$.[14] [h] From integration under $G''(\omega)$, $G_N° = 8.0 \times 10^6$ dyn/cm².

Gordon–Taylor–Wood equation

$$\frac{\Delta\alpha_2}{\Delta\alpha_1} = \frac{\phi_1(T_{g_1} - T_g)}{\phi_2(T_g - T_{g_2})} \qquad (6)$$

where subscript 1 represents the 1,4-polybutadiene and $\Delta\alpha$ the difference between the thermal expansion coefficient below and above T_g. Within experimental error $\Delta\alpha_2/\Delta\alpha_1 = 0.66$ (Table II). The width of the glass transition is about 2–3 times larger than in the homopolymers. Colby has found a glass transition width of 30 °C for his miscible blend of PEO and PMMA.[1] Blends rich in 1,4-polybutadiene show the smallest transition width, suggesting that there is some dissymmetry in blends of 1,4-polybutadiene and 1,2-polybutadiene (63%). The larger transition for blends than for homopolymers or random copolymers has been ascribed to composition fluctuations.[11] In agreement with this hypothesis we have observed that wide transitions occur also in blends in which one component has a MW equal to 2000.[12] For such blends thermodynamic miscibility would be beyond doubt. It should be noted that the width of the transition observed in this study is less than that in blends of *cis*-polyisoprene and 1,2-polybutadiene.[11,12]

b. Rheological Properties of Homopolymers. A full rheological characterization of the homopolymers has been made. Values of the low-frequency limiting properties, the zero-shear melt viscosity

$$\eta_0 = \lim_{\omega \to 0} (G''/\omega) \qquad (7)$$

and the zero-shear recoverable compliance

$$J_e° = \lim_{\omega \to 0} (G'/\omega^2) \qquad (8)$$

are given in Table III.

The molecular weight of the samples is too small to evaluate accurately the plateau modulus $G_N°$ from integration under the loss peak. $G_N°$ has been estimated from $G_N° = 3.56 G''_{max}$.[15] The product $J_e°G_N° \approx 2$ as expected for narrow molecular weight distribution samples.[13,16] In the last column of Table III are given values of the molecular weight between entanglement[17]

Table IV
WLF Parameters for Homopolymers

sample	T_g, °C	c_1^g	$c_2^g(T)$	f_0^g	$\alpha \times 10^4$
A	−95	11.66	61.9	0.037	6.0
B	−95	11.48	62.3	0.038	6.1
C	−45	11.76	52.9	0.037	7.0
D	−51.8	12.02	62.2	0.036	5.8
PBd(1,2)180 [a]	2	11.39	59.2	0.038	6.4

[a] Reference 14.

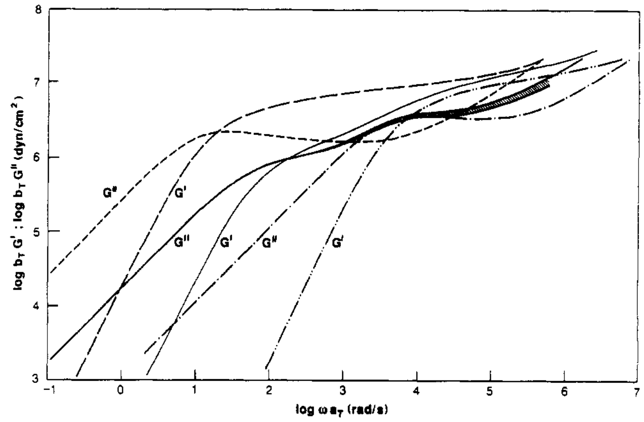

Figure 4. Double-logarithmic master curves of $G''(\omega)$ and $G'(\omega)$ for sample A and sample D and their blend AD 50/50. The latter is only an approximate master curve as indicated by the shaded area in the plateau zone (see text). T_r = 25.8 °C.

$$M_e = \rho RT/G_N° \qquad (9)$$

where ρ is the density, R the gas constant (8.3×10^7), and T the absolute temperature. These values are in good agreement with literature values.[15,17]

For the homopolymers, the rheological data obtained at different temperatures can be combined into a master curve at a reference temperature by shifting the data along the frequency axis (a_T) and by a small vertical shift (b_T). The latter has been studied in detail for 1,4-polybutadiene[13] and 1,2-polybutadiene.[14] The temperature dependence of the frequency shift factor is of the WLF form[17]

$$\log a_T = \frac{-c_1(T - T_0)}{c_2 + T - T_0} \qquad (10)$$

where T_0 is a reference temperature. When the DSC T_g is chosen as the reference temperature, c_1^g and c_2^g are obtained. These are given in Table IV. It can be seen from Table IV that c_1^g and c_2^g are independent of the microstructure of the polybutadiene as previously observed by Carella.[15] Also given in Table IV are the fractional free volume at T_g, $f_0^g = B/2.303c_1^g$, and the thermal expansion coefficient of the fractional free volume, $\alpha = B/2.303c_1^g c_2^g$, as obtained from the temperature dependence of a_T and with B set equal to unity. These values are in good agreement with values in the literature.[17]

c. Rheological Properties of Blends. Temperature Dependence. Figure 4 compares double-logarithmic master curves of $G''(\omega)$ and $G'(\omega)$ of a 50/50 blend of A and D with the master curves of the homopolymers at 25.8 °C. The plateau region of $G''(\omega)$ has been shaded to indicate that temperature–frequency superposition is not satisfactory in the case of the blend. Figure 4 is useful however because it shows that there are two relaxation processes in the blend. The terminal one is assigned to the D component, 1,2-polybutadiene (63%), and the shoulder

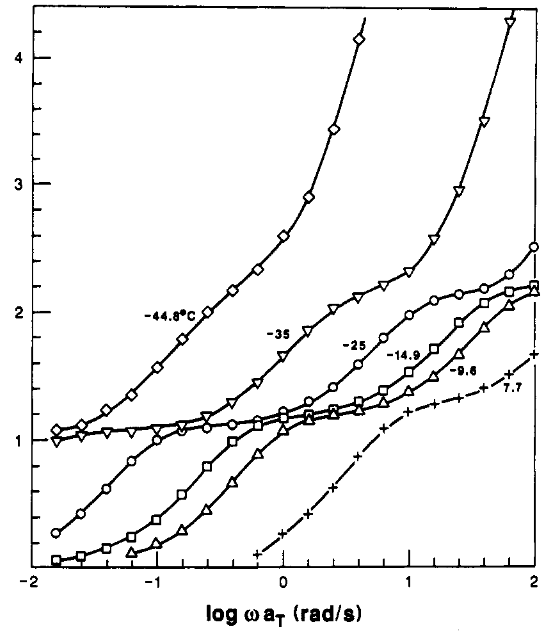

Figure 5. $G''(\omega)$ against log ω for AD 25/75 at different temperatures.

at $3 < \log \omega a_T < 4$ is due to A, 1,4-polybutadiene. This assignment is confirmed by comparison with master curves of blends AD 25/75 and AD 75/25.

Thermorheological complexity has been reported only once for a miscible blend.[1] It forces us to study the temperature dependence of the two relaxation processes separately. Figure 5 shows $G''(\omega)$ against log ω for AD 25/75 at different temperatures. For example, at −25 °C, the shoulder at $\log \omega = -0.8$ is due to the terminal relaxation of the D component and the shoulder at $\log \omega = 1.4$ is due to that of the A component. It can clearly be seen in Figure 5 that the slope and shape of $G''(\omega)$ between the two relaxation processes change with temperature. This precludes superposition. The relaxation time of the D component at each temperature is evaluated either as $1/\omega_{G''=G'}$, i.e., the inverse of the terminal crossover frequency (see Figure 4) or from matching the terminal zone with the $G''(\omega)$ and $G'(\omega)$ curves of the Rouse model for a linear polymer. In general, the temperature dependence of the relaxation time of the D component is very nearly equal to that of the zero-shear viscosity.[1] The relaxation time for the A component is more difficult to extract from the experimental results. Most satisfactory, this relaxation time is defined as the inverse of the frequency at which $(\Delta G''(\omega)/\Delta \log \omega)$ is a minimum (see Figure 5). The shift factors corresponding with the relaxation times of each component are plotted against an arbitrary $T - T_g$ in Figure 6. By horizontal and vertical shifting the experimental data can be matched with the experimental log a_T versus $T - T_g$ curve of the homopolymers (solid line). The apparent T_g of each component in the blend can then be determined. Values of these apparent T_g's are given in Table V and compared to the DSC values. We have called this a Colby analysis because he first proposed to compare the shift factors of the components of a miscible blend with those of the homopolymers.[1]

Our analysis implies that the experimentally observed difference between a_T of the components is due to different T_g's. The assumption is made that the components in the blend have the same $f_0{}^g$ and α parameters as the homopolymers. See Table IV. This further implies that the density of the blends is a weighted average of the densities of the components. An alternative proposal has been made by Colby for blends of poly(methyl methacrylate) and poly(ethylene oxide).[1] He assumed that both components have an identical T_g but maintain the different $f_0{}^g$ and α of the respective homopolymers. This seems not plausible for the 1,4- and 1,2-polybutadiene blends because their $f_0{}^g$ and α are very similar.

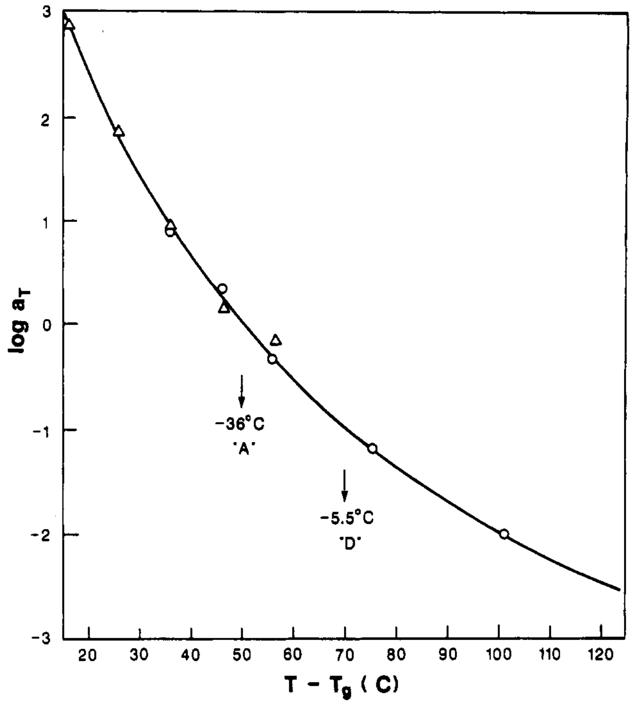

Figure 6. log a_T versus $T - T_g$. The solid curve is for both homopolymers A and D with their individual T_g. The symbols are for the individual components in AD 75/25: (○) D; (△) A. The data are shifted along the axes. For D, $-5.5 - T_g = 70$. For A, $-36 - T_g = 50$.

Table V
Apparent T_g's of Components of a Blend

	DSC			$T_g{}^a$	
samples	onset	T_g	end	A	D
AD 25/75	-75	-66	-60	-65	-61
AD 50/50	-85.7	-77	-71.7	-78	-65
AD 75/25	-93	-86.7	-82	-86	-75

[a] Colby analysis (see text).

The T_g's derived from the Colby analysis are in general higher than the T_g's of the DSC experiments and fall often outside the width of the DSC glass transition. The reason for this is not known. Nevertheless it is worth noting that the apparent T_g of the A component is always lower than that of the D component, suggesting that each component is preferentially surrounded by its own species. In other words, perfect mixing is not realized in blends of this pair of polymers.

d. Rheological Properties of Blends. Composition Dependence. If we wish to study the composition dependence of the relaxation times of the individual components in blends of 1,4-polybutadiene and 1,2-polybutadiene, we have to choose iso-free-volume conditions. In the homopolymers, this is usually achieved at a constant temperature from T_g.

Although the Colby analysis provides us with an estimate of the individual T_g's of each component, we have chosen as a rough first approximation to use the average T_g from DSC as the common reference temperature. Values of the relaxation times of components A and D at $T_g + 50$ °C are given in Table VI. At a constant temperature from T_g, the relaxation time of 1,4-polybutadiene decreases on

Table VI
Relaxation Times at T_g + 50 °C

sample	1,4-polybutadiene		1,2-polybutadiene (63% 1,2)	
(T_g + 50 °C)	log τ, s	$\langle N\rangle^a$	log τ, s	$\langle N\rangle^a$
A (−45)	−1.43	(7.7)		
AD (75/25) (−37)	−1.80	(6.8)	0.58	(18.8)
AD (50/50) (−27)	−1.84	(6.1)	0.24	(16.9)
AD (25/75) (−16)	−2.02	(5.6)	0.24	(15.3)
D (−1.8)			0.04	(14.1)

[a] Number of entanglements from eq 11.

dilution with 1,2-polybutadiene (63%). Two effects operate on dilution. First, the constraint release process of pure 1,4-polybutadiene is inhibited by the presence of the slower relaxing 1,2-polybutadiene (63%). From a study of this phenomenon in homopolymers it is known that this can cause a 3-fold increase of the relaxation time of 1,4-polybutadiene.[2,18] However, on dilution with 1,2-polybutadiene, 1,4-polybutadiene experiences on average fewer entanglements, because $M_e(1,2) > M_e(1,4)$. In the mean-field approximation the average number of entanglements of each component can be calculated[19] as

$$N_i = \frac{M_i}{\phi_i M_{ei} + \phi_j M_{ej}} \qquad (11)$$

where M_i is the molecular weight of the ith component. Values of N_i are given in Table VI. Fewer entanglements will decrease the relaxation time of 1,4-polybutadiene. It is obvious that the latter effect dominates on dilution of 1,4-polybutadiene by 1,2-polybutadiene. If the mean-field approximation is not valid, as suggested by the Colby analysis of the temperature shift factors, then values of N_i change less on dilution than given in Table VI.

The situation for the 1,2-polybutadiene (63%) component is the complete opposite of that of 1,4-polybutadiene. The presence of the faster relaxing 1,4-polybutadiene is expected to decrease the relaxation time by a more efficient constraint release process. However, this effect is not very large in homopolymers.[2] In the blends 1,2-polybutadiene experiences more entanglements. Values of a mean-field estimation are given in Table VI. The larger number of entanglements increases the relaxation times as shown in Table VI.

e. Other Blends. Three other blends were studied: AC, BC, and BD. Three compositions of each (25/75, 50/50, and 75/25) were investigated. The glass transition temperatures are given in Table II. Thermorheological complexity has been observed also in these nine blends. However, the relaxation times of the individual components are not as well separated as in the case of the AD blends and are therefore more difficult or impossible to evaluate from the experimental results. The composition dependence of the zero-shear viscosity at T_r = 25.8 °C is shown in Figure 7. Despite the thermorheological complexity of these blends, log η_0 depends linearly or slightly concavely on the composition of the blends.[20] Similarly, $J_e°$ at 25.8 °C shows the dependence typically observed when two homopolymers with different molecular weights are mixed (Figure 8). Addition of a small amount of polymer with a long relaxation time produces the largest increase in $J_e°$, because it produces the widest distribution in the terminal relaxation time spectrum.[2,3] On the other hand, the relaxation times of B and C are nearly identical in BC blends and $J_e°$ shows the smallest increase.

The patterns of $J_e°$ against composition in Figure 8 vary considerably with temperature, because the temperature dependence of $J_e°$ is different for each blend. This is shown in Figure 9. The temperature dependence of $J_e°$ of the homopolymers A and B is typical for 1,4-polybutadiene.[13] The temperature dependence of $J_e°$ of samples C and D is less pronounced. This is consistent with their mixed microstructure. It is known that the temperature dependence of $J_e°$ of pure 1,2-polybutadiene is of opposite sign.[14,15] In the blends the temperature dependence of $J_e°$ is always stronger than that in the homopolymers. This is another consequence of the thermorheological

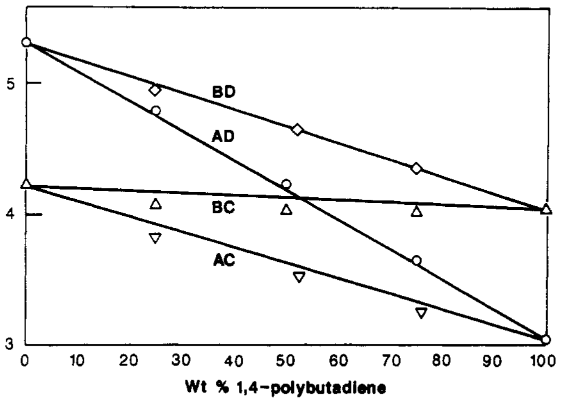

Figure 7. Dependence of log η_0 on the composition of blends of 1,4-polybutadiene with 1,2-polybutadiene (63%) at 25.8 °C.

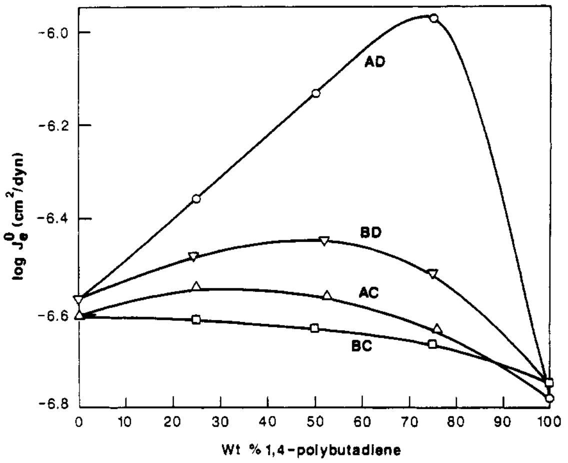

Figure 8. Dependence of log $J_e°$ on the composition of the blends at 25.8 °C. Lines are drawn as a guide to the eye.

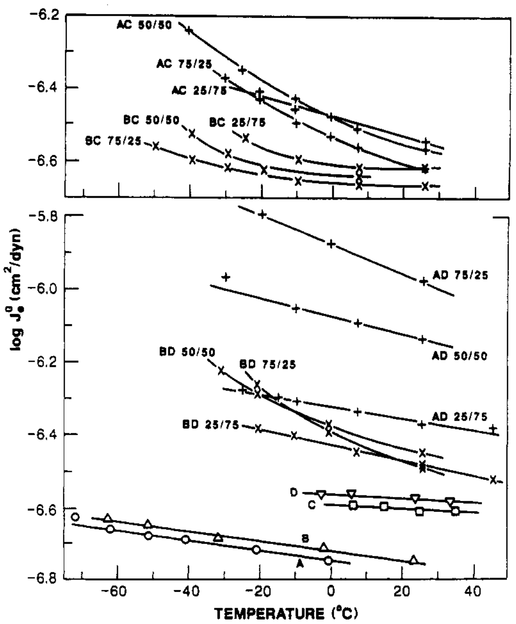

Figure 9. Temperature dependence of log $J_e°$ for different blends and homopolymers.

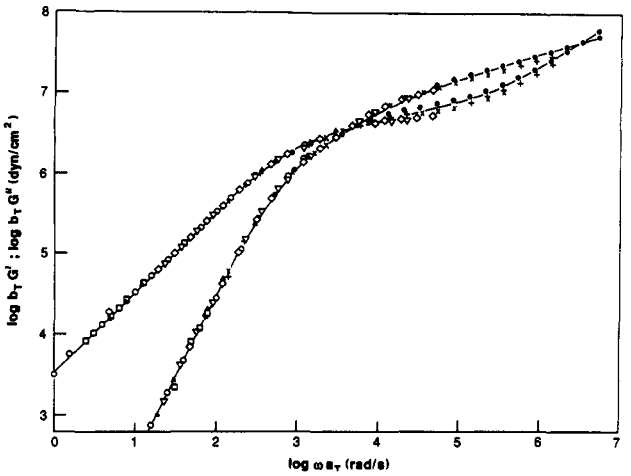

Figure 10. Attempted superposition in the terminal zone leading to large deviations in the plateau zone. Sample AC 50/50.

complexity of these blends. When the spacing of the relaxation times of the components changes with temperature, then the relaxation time distribution in the terminal zone changes. This change is strongly reflected in $J_e°$. In blends in which the relaxation times of the components are far apart, changes with temperature have a small effect on the terminal relaxation time distribution. This is the case of AD blends. Nevertheless, a somewhat stronger temperature dependence of $J_e°$ is found in AD 75/25. The small fraction of the D component in the terminal zone is relatively more affected by the large fraction of A. In BC blends, in which the two components have almost equal relaxation times, values of $J_e°$ are low and vary little with temperature. The largest dependence of $J_e°$ on temperature is observed in BD and AC blends, where the relaxation times of the components are approximately separated by 1 order of magnitude in time. Consequently, although temperature–frequency superposition in the terminal zone is possible when large values of log b_T are used, very poor superposition is observed in the plateau zone of these blends. An example is shown in Figure 10. It should be noted that thermorheological complexity is also observed in blends of the relatively low MW samples A and C far from the glass transition temperature and spinodal temperature for this pair.

f. Effect of Molecular Weight on Relaxation Times in Blends. Although there are uncertainties in the exact evaluation of the characteristic relaxation times in blends AC, BC, and BD, it is worthwhile to compare these estimated times for each component in different blends. Comparison of the relaxation times in AD and BD at constant composition gives information on the effect of the molecular weight of the 1,4-polybutadiene component in an environment that contains D. Figure 11 shows a plot of the characteristic times of each component as a function of temperature for the case of the 25/75 blends. It can be seen that the longest relaxation time of the D component is independent of the MW of the 1,4-polybutadiene. This is analogous to the situation of blends of homopolymers differing only in molecular weight.[2,18] On the contrary, the relaxation times of B are approximately 11 times longer than the times of A at constant temperature. This is consistent with the relation for entangled homopolymer blends where $\tau_B/\tau_A = (M_B/M_A)^{3.4} = 10.6$. The relaxation times of A and B in the 50/50 and 75/25 blends with D have similar ratios. Interestingly, the relaxation time of D in BD 75/25 is 1.5 times larger than that in AD 75/25. This shows that the large fraction of 1,4-polybutadiene affects the relaxation time of the slower relaxing polymer. Some constraint release assists in the relaxation of D in AD.

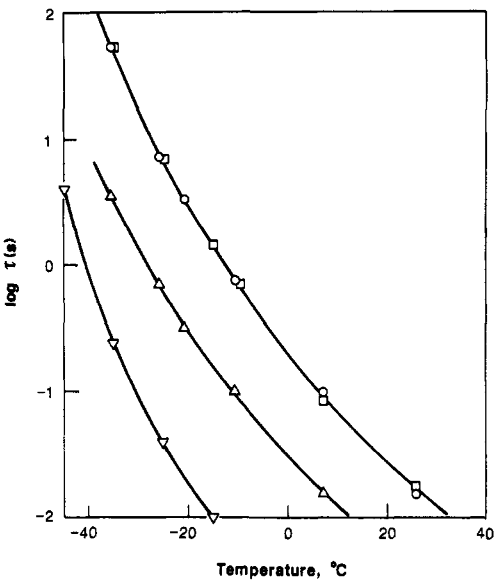

Figure 11. Temperature dependence of relaxation times: (○) D in BD 25/75; (□) D in AD 25/75; (△) B in BD 25/75; (▽) A in AD 25/75.

A similar comparison of AC and AD blends is used to determine the effect of MW on the relaxation times of the slower relaxing component (C or D) of the blends. It is observed that at constant temperature τ_D/τ_C = 13–17 for the blends at equal compositions. This is in good agreement with the behavior of linear polymers for which $\tau_D/\tau_C = (M_D/M_C)^{3.4} = 18$.

Conclusions

It has been shown that blends of narrow molecular weight linear miscible polymer pairs show the individual relaxation of each component. The behavior of such blends has much in common with entangled homopolymer blends. However, in contrast with homopolymer blends thermorheological complexity is observed in 1,4-polybutadiene–1,2-polybutadiene (63% 1,2). Analysis of the temperature shift factor of the individual components suggests that different T_g's are experienced by each component in the blend. This is in qualitative agreement with the wide glass transition observed in DSC experiments. The different T_g's for each component of the blend suggest that each component experiences an environment that is different from the average blend composition. It would be interesting to relate this to the composition fluctuations expected from the random-phase approximation. The connectivity of the segments of the chain and the absence of strong heterocontacts has been shown theoretically to lead to nonrandom segment distributions in polymer blends.[21,22] It must be concluded then that we are observing the rheological consequences of this microheterogeneity.

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