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Microheterogeneity in Miscible Blends of 1,2-Polybutadiene and 1,4-Polyisoprene†

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ABSTRACT: Blends of anionically prepared narrow molecular weight distribution 1,2-polybutadiene (>99% 1,2; 1,2-PBd) and polyisoprene (93% 1,4; PI) have been studied. The molecular weights are sufficiently high that the polymers are entangled in the melt (11-50 entanglements per chain). DSC studies confirm that the polymers are miscible but the glass transition region is very broad for blends with high 1,2-PBd content. The viscoelastic properties of the blends have been studied over a wide temperature range. Individual relaxations of the components are observed. The blends are thermorheologically complex because the temperature dependence of the 1,2-PBd relaxation is stronger than that of PI. Analysis of the temperature dependence of the relaxation times suggests that each component in the blend experiences its own T_g. Isothermal relaxation times are very dependent on composition. However, iso-free volume relaxation times are not very dependent on composition, in agreement with rather small changes in the entanglement state when one polymer is diluted by the other.

Introduction

The study of the viscoelastic properties of polymer melts is of great industrial importance. As a bonus to the scientist, the viscoelastic properties reveal the underlying molecular relaxation processes that occur in polymer melts. The relaxation processes are characterized by one or more relaxation times. For example, after deformation of a narrow molecular weight distribution (MWD) linear polymer that is strongly entangled, the evolution of the modulus with time can be described as the sum of exponential relaxation functions whose time constants increase to a longest relaxation time (T_d). This is the essential conclusion of the reptation model as elaborated by Doi and Edwards and is described by[1]

$$G(t) = \frac{8}{\pi^2} G_N{}^0 \sum_{p=\mathrm{odd}} \frac{1}{p^2} \exp\left(\frac{-p^2 t}{T_d}\right) \qquad (1)$$

where $G_N{}^0$ is the initial modulus. Equation 1 is a fair description of experimental results.[2,3] It appears that $G_N{}^0$ depends on the chemical nature of the polymer but is further independent of the molecular weight and little dependent on temperature.

The large variations that are observed experimentally in the relaxation rates of polymers originate in T_d. According to reptation theory

$$T_d \propto \tau_0 M^3 \qquad (2)$$

The effect of temperature is embedded in changes of τ_0 which is linked to the monomeric friction coefficient. The theoretical dependence of T_d on molecular weight (MW) is given by eq 2. Experimentally $T_d \propto M^{3.4\pm0.1}$.

When two linear polymers differing only in molecular weight are blended, it is observed that each chain maintains its individual relaxation time within a wide range of molecular weight ratios and compositions. Such blends have been studied in detail[4-7] and have been modeled successfully.[8-11]

From these results one would surmise that when two different but miscible entangling polymers are mixed, they will retain their individual relaxation processes with individual relaxation times. The isothermal relaxation times of the polymer in the mixture are not identical to or near those observed for the homopolymers because the blend has a single glass transition temperature (T_g) between the T_gs of the homopolymers. A detailed investigation of the temperature dependence of the viscoelastic properties of the blend is thus required. As will be shown, this is not a trivial matter.

In previous studies of the viscoelastic properties of miscible blends time-temperature superposition has usually been observed.[12-17] The temperature shift factors obey a single WLF equation, identical to that for the pure components when the T_g from DSC experiment is used as the reference temperature.[14-17] In the case of polystyrene-poly(2,6-dimethylphenylene oxide) blends, however, the reference temperature is not given by the T_g as measured by DSC because the thermal expansion coefficient varies with the composition of the blend.[12,13]

More recently, however, it has been found that the individual relaxation processes of the components can be observed in the $G''(\omega)$ curves of miscible blends when the components are narrow MWD polymers.[18-20] In those cases, time-temperature superposition has been found to fail because the relaxation time of the polymer with the higher T_g has a stronger temperature dependence than the relaxation time of the blend component with the lower T_g. In the case of blends of 1,4-polybutadiene and polybutadiene (63% 1,2) there is strong qualitative evidence that each component in the blend has a slightly different environment and a different T_g.[20] This is supported by a wide *single* glass transition that is observed in such blends.[20]

In this work we describe viscoelastic measurements on blends of narrow MWD atactic 1,2-polybutadiene (1,2-PBd) and 1,4-polyisoprene (PI). A large body of work has been carried out that shows that high MW atactic 1,2-PBd (86-97% 1,2) and PI (98% cis-1,4, or natural rubber) are miscible in all proportions at room temperature. These blends show a single T_g by DSC and by dynamic loss measurements.[21,22] These and other observations can be used to estimate that the 1,2-PBd-PI interaction param-

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eter is[21,23]

$$\chi = \frac{V_R}{2}\left[\frac{1}{(V_1N_1)^{1/2}} + \frac{1}{(V_2N_2)^{1/2}}\right]^2 \leq 1.7 \times 10^{-4} \quad (3)$$

at room temperature. V_i is the molar volume of each component, N_i the weight-average degree of polymerization, and $V_R = (V_1V_2)^{1/2}$ the reference volume. The miscibility of 1,2-PBd and PI is confirmed by their spontaneous interdiffusion at room temperature.[24]

Recent SANS studies on blends of anionically prepared polyisoprene (7%, 3,4, 69% cis-1,4, and 24% trans-1,4) and deuterated 1,4-polybutadiene with 1,2 content of 12–20% show that miscibility improves with increasing 1,2 content of the polybutadiene. Moreover, the SANS study confirms that χ increases with temperature.[25] From the individual χ values given in Figure 6 of ref 25 it can be estimated that $\chi < 0$ for the 1,2-PBd–PI pair at room temperature. However, a strong temperature dependence of χ predicts an upper critical solution temperature (UCST) which is not observed. Kawahara and co-workers also showed by various techniques that polyisoprene is miscible with polybutadiene containing more than 32% vinyl units.[26,27]

Roland published $G''(\omega)$ master curves of 1,2-PBd and PI blends. Individual relaxations of the components are not resolved, and qualitative superposition of data obtained at different temperatures seems to be achieved.[28] It seems likely that the wide MWD of the polymers erases a large amount of detailed information that can be obtained from a viscoelastic study. Here we describe DSC and density measurements to probe the thermodynamic miscibility of anionically prepared 1,2-PBd and PI. The viscoelastic properties of the polymers and their blends have been determined. All polymers have more entanglements per chain (11–50) than in the study on 1,4-PBd and PBd (63% 1,2). The analysis of the characteristic relaxation times is made more quantitative than in the previous study.[20] The dependence of the characteristic relaxation times on temperature, molecular weight, and blend composition is also described.

Experimental Section

All polymers have been prepared anionically with *sec*-BuLi in benzene at room temperature. The living polymers are terminated with degassed *tert*-butyl alcohol. PI was prepared and characterized by Polysar Rubber Corp. 1,2-PBd was prepared in the presence of excess dipiperidinoethane as described previously.[29] Size exclusion chromatograms obtained with five μStyragel columns (10^6-, 10^5-, 10^4-, 10^3-, and 500-Å nominal pore size) showed a single peak characteristic of a narrow MWD polymer. The molecular weights of the 1,2-PBd samples have been given previously[29] and are shown in Table I. Its microstructure is >99% 1,2-units by NMR. The molecular weights of the PI samples are given in Table I.[30] The microstructure is 70% cis, 23% trans, and 7% 3,4 by ^{1}H and ^{13}C NMR. Blends are made by weight. Both polymers are separately dissolved in benzene and mixed. The homogeneous solution is freeze-dried to constant weight. The blends are protected with 0.1% 2,6-di-*tert*-butylcresol. All blends are water clear.

T_gs of the homopolymers and the blends have been measured with a Du Pont Model 910 DSC under nitrogen at a 10 °C/min heating rate. The sample size is 4–6 mg. Measurements are performed in duplicate or triplicate. The T_g is taken as the midpoint of the heat capacity change. The width of the transition is obtained from the intersection of three tangential lines (see Figure 1). The buoyancy method with water–methanol was used to measure the specific volume of the samples at 25.0 °C. Accuracy is to 1×10^{-4} cm^3/g. Reproducibility is 5×10^{-5} cm^3/g.

The viscoelastic properties are measured with a Rheometrics mechanical spectrometer (Model 605M). Twenty frequencies between 1.58×10^{-2} and 10^2 rad/s are scanned at 7–10 different temperatures. Reversibility with temperature within the time of a temperature change (15 min) has been checked repeatedly.

Table I
Characteristics of Homopolymer Samples

sample	MW × 10^{-3}	T_g, °C	width of transition,[a] °C
1,2-PBd3	2.84[b]	−3	5
1,2-PBd90	84.4[b]	2	4
1,2-PBd180	204.0[b]	2.5	4
PI2	1.76[c]	−72	6
PI60	63.4[d]	−61.4	~5
PI100	103.0[e]	−61	5

[a] From the intersection of three tangential lines. The width of the transition of homopolymers is somewhat reduced due to enthalpic relaxation. [b] M_n.[29] [c] M_n by vapor pressure osmometry. [d] $[\eta]_{Tol}^{35°} = 0.61_6$ with $[\eta] = 1.72_2 \times 10^{-4} M_w^{0.74}$.[30] [e] $[\eta]_{Tol}^{35°} = 0.88_3$ with $[\eta] = 1.72_2 \times 10^{-4} M_w^{0.74}$.[30]

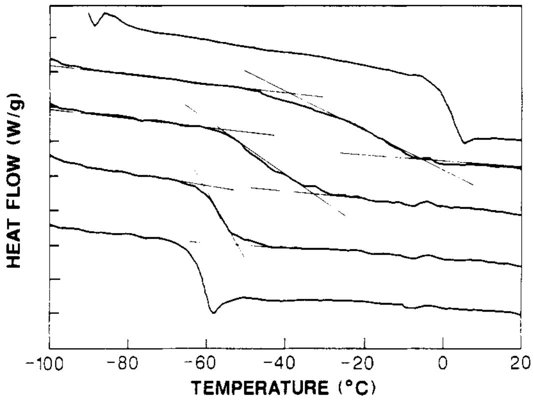

Figure 1. DSC traces of blends of 1,2-PBd180 and PI60 obtained at 10 °C/min heating rate. From top to bottom: 1,2-PBd180; 1,2-PBd180–PI60 (75/25), (50/50), (25/75); PI60.

Results and Discussion

a. Miscibility. The molecular characteristics of the homopolymers used in this work are given in Table I. The miscibility of the 1,2-PBd and PI samples is confirmed by the single T_g of their blends. Examples are shown in Figure 1. Values of T_g and the width of the transition are given in Tables I and II and shown as a function of composition in Figure 2. Mixtures of 1,2-PBd90 and 1,2-PBd180 with PI100 have practically the same T_g and transition width. Blends with a low molecular weight component (1,2-PBd3 or PI2) have somewhat lower T_g. The width of the glass transition is quite large, especially around the 50/50 composition of the blends.[23] This is also true when one component has a low molecular weight. The width of the transition is asymmetric, i.e., blends rich in 1,2-PBd have wider transitions than the corresponding blend rich in PI. All of these observations are in agreement with the dynamic mechanical measurements in the glass transition region.[22] The dependence of T_g on composition does *not* follow a Gordon–Taylor–Wood equation

$$\Delta\alpha_1/\Delta\alpha_2 = w_2(T_{g2} - T_g)/w_1(T_g - T_{g1})$$

Values of $\Delta\alpha_1/\Delta\alpha_2$ are listed in Table II. They decrease with increasing PI fraction of the blend. This behavior

Table II
Glass Transition Temperatures of Blends of 1,2-Polybutadiene and Polyisoprene

sample	w_1, % 1,2-PBd	T_g, °C	width transition, °C	$\Delta\alpha_1/\Delta\alpha_2$
1,2-PBd90 + PI100	75.0	−17	21	0.621
	48.0	−42	26	0.340
	25.0	−55	11.5	0.316
1,2-PBd180 + PI100	75.4	−18	22	0.744
	24.9	−55	10	0.316
1,2-PBd180 + PI60	75	−20	33	0.621
	50	−46	25	0.313
	25	−56	≥8	0.258
1,2-PBd90 + PI2	76	−22	15	0.645
	60	−41	21	0.465
	37.5	−59	14	0.328
	25	−66	9	0.221
	17.5	−68	7	0.202
1,2-PBd3 + PI100	75	−31	30	0.357
	50	−47	15	0.318
	25	−56	8	0.283

Table III
Viscoelastic Properties of Homopolymers at 45.6 °C

sample	η_0, P	$J_e^0 \times 10^7$, cm²/dyn	$G_N^0 \times 10^{-6}$, dyn/cm²	$J_e^0G_N^0$	M_e	v,[a] cm³/g
1,2-PBd3	6.5×10^2	0.6				
1,2-PBd90	7.6×10^6	3.4_5	5.4	1.86		1.1322
1,2-PBd180	1.5×10^8	3.27	6.1	2.1	3860[b]	
PI2	7.9×10^2[d]	0.23[d]				
PI60	$1.2_9 \times 10^4$	4.30				
PI100	$8.4_6 \times 10^4$	4.2_7	4.5	2.0	5350[c]	1.1135

[a] Specific volume at 25.00 °C. [b] $M_e = 3800$.[29] [c] Reference 31. [d] At −20.5 °C.

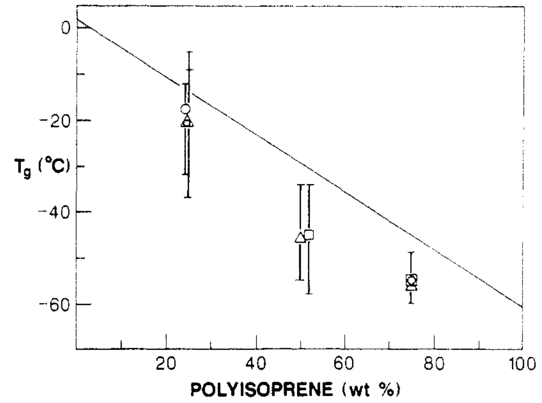

Figure 2. T_g vs composition of 1,2-PBd and PI blends. (○) 1,2-PBd180 + PI100; (△) 1,2-PBd180 + PI60; (□) 1,2-PBd90 + PI100.

of 1,2-PBd–PI blends is in contrast to that of 1,4-PBd and PBd (63% 1,2).[20]

The specific volume (v) as a function of blend composition is shown in Figure 3. The values of v of the homopolymers (Table III) are in good agreement with recent literature values.[21,27] From Figure 3 it can be seen that the specific volume deviates negatively from the weighted average of the pure compounds (volume contraction). Roland did not observe deviation from a simple mixing rule, with 0.004 g/cm³ error bars.[21] Volume contraction is in agreement with results obtained on blends of PI and PBd (32% 1,2) below the lower critical solution temperature (LCST).[27] As can be seen in Figure 3, Kawahara et al. observed also that blends rich in 1,2-PBd have the smallest volume contraction.[27]

b. Viscoelastic Properties of Homopolymers. The terminal properties of the polymers are given in Table III.

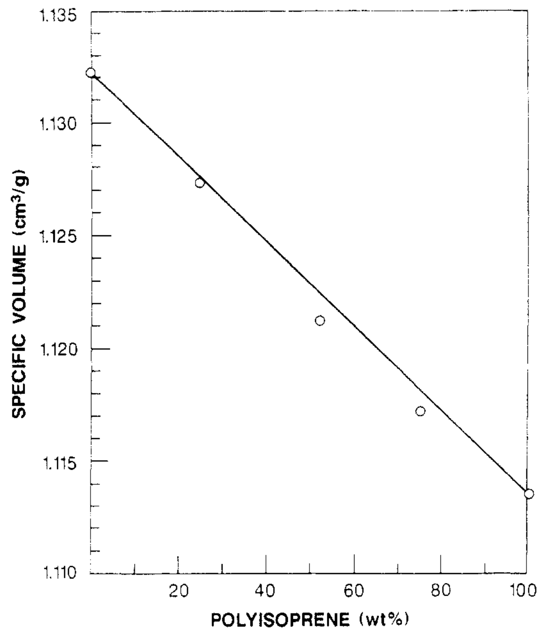

Figure 3. Specific volume against composition of blends of 1,2-PBd180 and PI100 at 25.0 °C. The 50/50 blend data are for 1,2-PBd90 and PI100.

Table IV
WLF Coefficients of Homopolymers

sample	T_g, °C	C_1^g	C_2^g, K	f_0^g[a]	$\alpha \times 10^4$,[b] K⁻¹
1,2-PBd90	2	11.4_5	56.0	0.038	6.8
1,2-PBd180	2	11.3_9	59.2	0.038	6.4
PI60	−61.4	12.2_1	53.7	0.036	6.6
PI100	−61.0	11.7_6	52.9	0.037	6.9

[a] Free volume fraction at T_g. $f_0^g = 1/2.303C_1^g$. [b] Thermal expansion coefficient of free volume $\alpha = f_0^g/C_2^g$.

The zero-shear melt viscosity and the zero-shear recoverable compliance are derived from[31]

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

and

$$J_e^0 = (1/\eta_0^2)\lim_{\omega \to 0}(G'/\omega^2)$$

The plateau modulus is evaluated by[31]

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

The rheological properties of the 1,2-PBd samples have been described previously.[29] Values of $J_e^0G_N^0 \approx 2.0$ indicate that the samples have narrow molecular weight distributions. Values of $M_e = \rho RT/G_N^0$ are in good agreement with literature values.[29,32] The temperature dependence of the horizontal shift factors (a_T) of the homopolymers has been studied in detail. The WLF coefficients are given in Table IV. It is concluded that the relaxation times of 1,2-PBd and PI have the same WLF coefficients within experimental error.

c. Viscoelastic Properties of Blends: Temperature Dependence. Figure 4 shows $G''(\omega)$ curves of the 75/25 blend of 1,2-PBd180 and PI60 at different temperatures. Between 35 and 65 °C $G''(\omega)$ curves show two maxima in the experimentally available frequency window ($-1.8 < \log\omega < 2.0$ rad/s). At 35 °C the maxima are at $\log\omega = -1.35$ and +0.8, respectively. At 65 °C the maxima are at 0.5 and 1.9, respectively. Outside this temperature range only one maximum is observed. Similar behavior is found for the 50/50 blend of 1,2-PBd180 and PI60. At high tem-

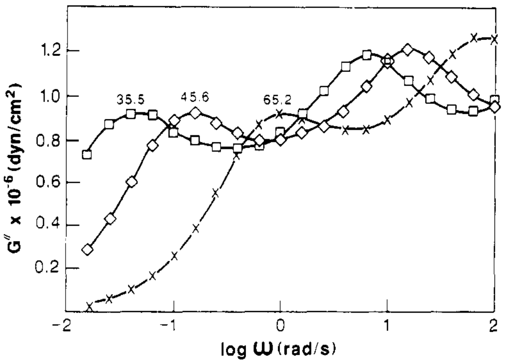

Figure 4. Loss modulus, G'', against log frequency for a 75/25 blend of 1,2-PBd180 and PI60 at different temperatures.

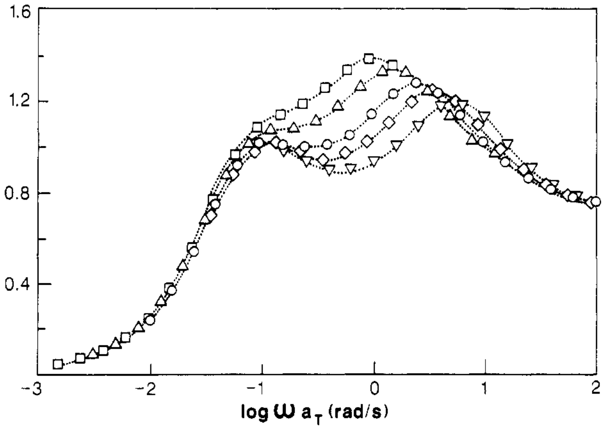

Figure 5. Loss modulus, G'', against log frequency for a 75/25 blend of 1,2-PBd180 and PI100. Data at different temperatures have been shifted by log a_T to superpose at low frequency onto the data obtained at 45.6 °C. (□) 95.8 °C; 65.9 °C; 45.6 °C; (◇) 35.6 °C; (▽) 25.8 °C.

peratures the low-frequency maximum is reduced to a shoulder. In the 25/75 blend, $G''(\omega)$ has only a shoulder in the low-frequency region.

From a comparison of values of $G''(\omega)$ at the maximum with the blend composition it is concluded that the low-frequency process is due to 1,2-PBd and the high-frequency maximum is due to PI. In the molecular weight range studied the component with the higher T_g relaxes more slowly.[20]

Closer inspection of Figure 4 reveals that the difference between the frequencies of the maxima is not constant but increases with decreasing temperature. The blends show thermorheologically complex behavior. This is more clearly shown in Figure 5 for a blend of 1,2-PBd180 and PI100 (75/25). The $G''(\omega)$ curves have been shifted horizontally to superpose at low frequency. This precludes superposition of the high-frequency maximum and construction of master curves of $G''(\omega)$ and $G'(\omega)$. Similar behavior has been observed in blends of 1,4-PBd and PBd (63% 1,2)[20] and in poly(methyl methacrylate)–poly(ethylene oxide).[18] The more slowly relaxing component of the blend has a stronger temperature dependence.

To study the temperature dependence quantitatively, a procedure is required to extract the characteristic relaxation times of each process. The two relaxation times are generally not well resolved. The relaxation time of the slower process is derived in two ways. For the 75/25 and 50/50 blends $\tau_1 = 1/\omega_{G''=G'}$ (s), i.e., the inverse of the crossover frequency in the terminal zone. This procedure is commonly used to determine the longest relaxation time of entangled narrow molecular weight distribution linear polymer. For the 50/50 and 25/75 blends the terminal zone data are compared with the theoretical Rouse model for a linear polymer (see Figure 6). This procedure is used to obtain the longest relaxation time of a minor slowly relaxing component in an entangled blend. It assumes that the relaxation is dominated by constraint release caused by motion of the major fast relaxing component.[33] Values of the characteristic relaxation time of the faster process (PI) are derived from $\tau_2 = 1/\omega_{\max}$(s). The values of τ_1 and τ_2 are given in Table V.

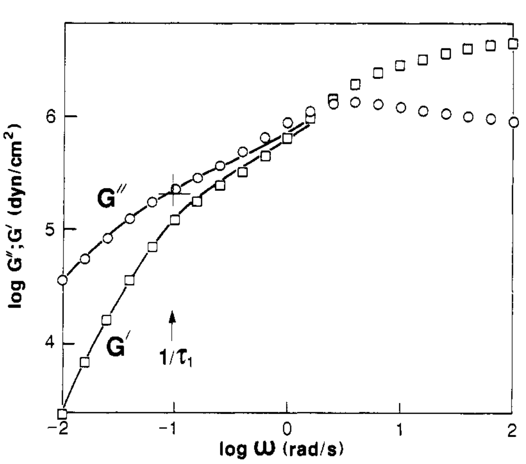

Figure 6. Moduli–frequency data obtained for a 25/75 blend of 1,2-PBd180 and PI100 at 25.8 °C. The lines are for the theoretical Rouse model for a linear polymer. The characteristic time τ_1 for 1,2-PBd is obtained from the theoretical log $\omega\tau_R = 0$.

Blends of 1,2-PBd90 and PI100 have also been studied. The blends show one broad maximum in $G''(\omega)$. The broadness of this maximum is easily quantified by log $\omega_{G''_{\max}}$ − log $\omega_{G''=G'}$. In narrow MWD linear entangled polymers this difference is very small (0.1 log unit) and independent of temperature. In the 1,2-PBd90–PI100 (75/25) blends the difference increases from 0.2 to 0.6 log unit as the temperature decreases from 58 to 16 °C.

A WLF analysis has been used to analyze the temperature dependence of the relaxation times. T_0 is varied in plots of log τ against $1/(T - T_0)$ for each component of each blend. Values of T_0 and the slope of the line with the minimum least squares deviation are recorded. Examples are shown in Figure 7. Even in the most favorable case, when numerous τ data near T_g are available, T_0 is estimated to only ±5 °C. Values of T_g of the components of the blend are obtained from $T_g = T_0 + 55$, where $C_2{}^g = 55$ (see Table IV) is used. The values of T_g are given in Table VI. From the slopes of the log τ against $1/(T - T_0)$ plots values of the thermal expansion coefficient $\alpha = 5.1\text{–}6.9 \times 10^{-4}$ (K^{-1}) are obtained in reasonable agreement with the data for the homopolymers in Table IV.

To assess the possible errors in T_g, T_0 and T_g have also been derived by forcing the experimental data of log τ to a line corresponding to $\alpha = 6.68 \times 10^{-4}$ (K^{-1}), the mean value for the homopolymers. These values of T_g are also given in Table VI. Finally, in Table VI values of T_g obtained by the graphical method based on Colby's work[18] and used in our previous study[20] are also given (see Figure 8).

In general, values of T_g derived by the three methods are in good agreement but occasionally 15 °C differences are observed. From comparison of T_g of one component in different blends of the same composition it is clear that such differences are random and are caused by insufficiently accurate values of τ. From Table VI it can be estimated that the T_g of the PI component is roughly 18, 15, and 12 °C lower than for the 1,2-PBd component when the composition is changed from 75/25 to 25/75. This is in qualitative agreement with the width of the glass

Table V

(A) Characteristic Relaxation Times in 1,2-PBd180 and PI100 Blends

polymer blend composition	temp, °C	log τ_1,[a] s	log τ_2,[b] s	log τ_1/τ_2
75/25	95.7	(−0.84)	−1.80	(0.96)
	65.9	(+0.12)	−1.10	(1.22)
	45.7	(+1.02)	−0.40	(1.42)
	35.8	(+1.58)	0	(1.58)
	25.8		+0.5	
	15.6		+1.1	
	6.8		[$+1.7_5$]	
50/50	66.0	+0.01 (−0.54)	−1.44	1.45 (0.90)
	55.9	+0.36 (−0.16)	−1.18	1.54 (1.02)
	45.8	+0.74 (+0.34)	−0.86	1.60 (1.20)
	35.6	+1.22 (+0.82)	−0.50	1.72 (1.32)
	25.8	(+1.37)	−0.06	(1.43)
	15.5	(+1.94)	+0.42	(1.52)
	7.0		+1.00	
	−0.6		+1.45	
	−10.6			
25/75	95.8	−1.16		
	58.6	−0.23	−1.65	1.42
	45.3	+0.18	−1.28	1.45
	25.8	+1.02	−0.62	1.64
	15.6	+1.52–1.64	−0.18	1.70–1.82
	−10		+0.76	
	−11.1		+1.45	
	−20.4			

(B) Characteristic Relaxation Times in 1,2-PBd180 and PI60 Blends

polymer blend composition	temp, °C	log τ_1,[a] s	log τ_2,[b] s	log τ_1/τ_2
75/25	114.8	(−1.26)		
	95.8	(−0.83)		
	78.5	(−0.36)		
	65.1	(0.09)	−1.88	1.97
	55.5	(0.50)	−1.56	2.06
	45.2	(0.96)	−1.22	2.17
	35.2	(1.48)	−0.84	2.32
	25.7		−0.38	
	15.5		+0.08	
	7.4		[0.70] sh	
50/50	75.8	−0.29 (−0.59)		
	65.3	0.0 (−0.32)		
	55.4	0.40 (0.05)	[−2.0]	2.40 (2.05)
	45.2	0.78 (0.46)	−1.65	2.43 (2.11)
	35.7	1.22 (0.94)	−1.27	2.49 (2.21)
	25.7	1.78 (1.45)	−0.85	2.63 (2.30)
	15.5	(2.02)	−0.38	(2.40)
	6.9		0.18	
	−0.7		0.70	
	−10.9		1.40	
25/75	95.8	−1.18		
	76.0	−0.68		
	58.7	-0.23_5		
	45.2	0.22		
	35.6	0.65	−1.78	2.43
	25.7	1.08	−1.38	2.46
	15.4	[1.56]	−0.95	2.51
	6.9		−0.50	
	−1.0		0.05	
	−10.8		0.60	
	−20.6		1.42	

[a] For 1,2-PBd component. From Rouse analysis of terminal zone, except values in brackets from log $\omega_{G''=G'}$ in terminal zone. [b] For PI from log $\omega_{G''_{\max}}$. Values in square brackets are estimates.

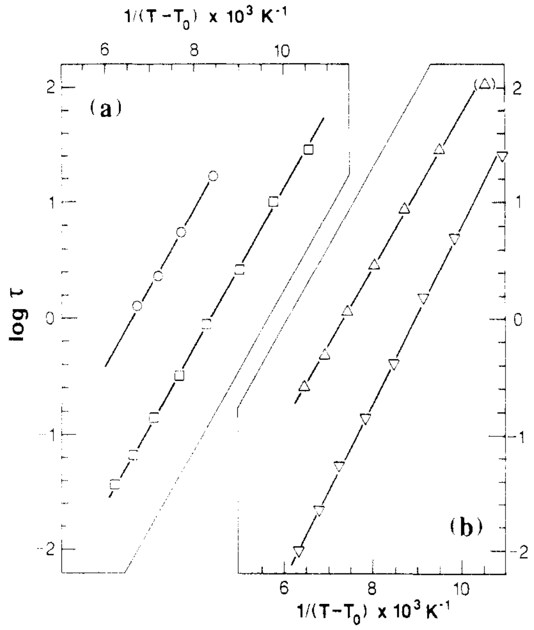

Figure 7. WLF plots for log τ of the components of 50/50 blends of 1,2-PBd and PI. (a) ○, 1,2-PBd180; □, PI100; (b) △, 1,2-PBd180, ▽, PI60.

transition in DSC. From Table VI it can be seen that values of T_g usually fall within the temperature range of the glass transition measured by DSC, although in blends with 25% 1,2-PBd the extracted values of T_g are clearly outside the DSC range. This has also been observed in blends of 1,4-PBd with PBd (63% 1,2). The reason for this is not known. The analysis of the temperature dependence of the characteristic relaxation times supports our earlier hypothesis[20] that the temperature dependence of the relaxation processes of the components of the blends is identical with the temperature dependence observed for the homopolymers. The thermorheological complexity is then uniquely due to the different T_gs that the components of the blend experience.

d. Composition Dependence of Characteristic Relaxation Times. Semilogarithmic plots of isothermal values of τ_1 and τ_2 against composition are shown in Figure 9. The characteristic relaxation time of 1,2-PBd180 decreases with increasing PI in the blend. The decrease is obviously due to the decrease in the glass transition temperature as the PI fraction increases. The decrease of τ_1 is independent of the molecular weight of the polyisoprene. This suggests that constraint release is of little importance for 1,2-PBd180. In blends of 1,2-PBd90 with PI100 the two characteristic times are poorly separated. Nevertheless, estimates of the characteristic times of 1,2-PBd90 show the same decrease with increasing PI fraction as for 1,2-PBd180. The ratio τ_{180}/τ_{90} is practically constant with blend composition and is equal to $(M_{180}/M_{90})^{3.4}$.

The characteristic relaxation times of polyisoprene increase with increasing 1,2-PBd content. Obviously, this is a result of the dominance of the increasing T_g. The characteristic times of PI100 are slightly larger in 1,2-PBd180 than in 1,2-PBd90, suggesting constraint release of PI100 is slightly more hindered in blends with 1,2-PBd180. The ratio $\tau_{\mathrm{PI100}}/\tau_{\mathrm{PI60}}$ is a constant in blends with 1,2-PBd180 and approximately equal to $(M_{\mathrm{PI100}}/M_{\mathrm{PI60}})^{3.4}$.

It would be of interest to remove the effect of the changing T_g of the blends and compare, e.g., the characteristic relaxation times of each component at constant friction factor. In homopolymers, this is usually not an issue or can be determined from T_g and the WLF parameters of each sample.

In the case of mixtures of two chemically different polymers T_g changes considerably. In the case of 1,4-PBd–PBd (63% 1,2) blends the average DSC T_g of each blend was used as the reference point.[20] When this procedure is applied to the present data, it is found that

Table VI
Values of T_g (°C) Derived from the Temperature Dependence of the Characteristic Relaxation Time in Blends

	1,2-PBd			PI			DSC	
sample	WLF[a]	WLF[b]	graphical	WLF[a]	WLF[b]	graphical	from	to
1,2-PBd180–PI100								
75/25	−27	−10	−12	−27	−28	−31	−9	−32
50/50	−28	−23	−27[c] −22[d]	−40	−38	−41	−32	−56
25/75	−36	−33	−36	−48	−46	−48	−51	−61
1,2-PBd180–PI60								
75/25	−13	−25	−12	−33	−34	−34	−5	−38
50/50	−24	−31[c] −33[d]	−22[c] −24[d]	−47	−37	−42	−32	−57
25/75	−36	−47	−31	−60	−48	−49	−52	−60

[a] Least squares method, see text. [b] With $\alpha = 6.68 \times 10^{-4}$ (K^{-1}) and $T_g = T_0 + 55$. [c] Rouse analysis. [d] From crossover $\tau_1 = 1/\omega_{G''=G'}$.

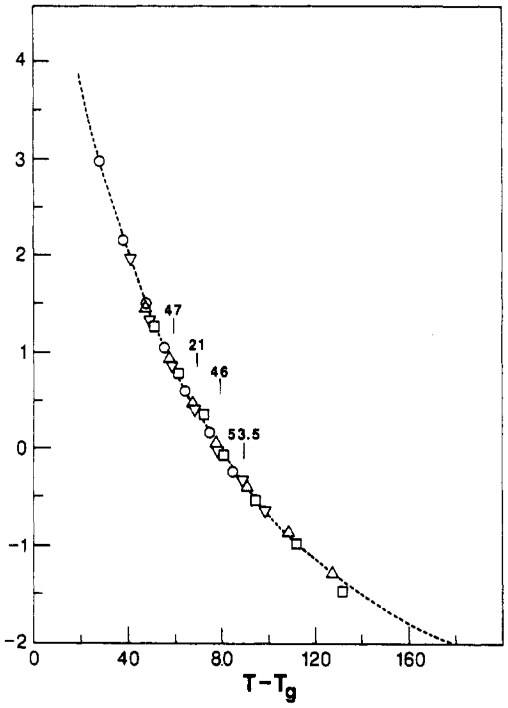

Figure 8. Shift factors a_T against temperature from T_g. Line is for pure 1,2-PBd and PI. (○) PI in 1,2-PBd180–PI60 (25/75) 21 − T_g = 70 °C; (□) 1,2-PBd in 1,2-PBd180–PI60 (25/75) 53.5 − T_g = 90 °C; (▽) PI in 1,2-PBd180–PI60 (75/25) 46 − T_g = 80 °C; (▽) 1,2-PBd in 1,2-PBd180–PI60 (75/25) 47 − T_g = 60 °C.

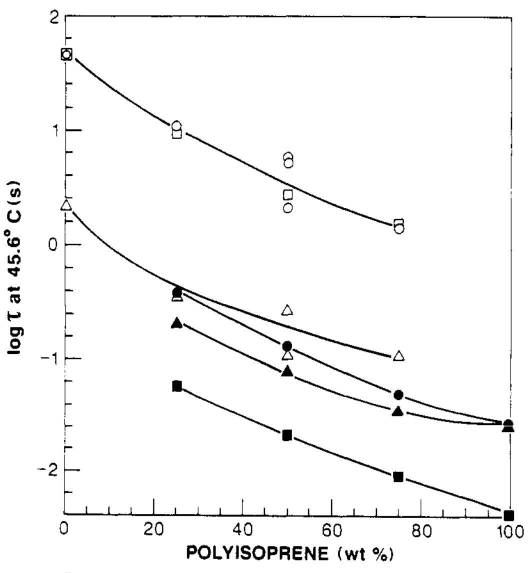

Figure 9. Log τ at 45.6 °C against composition of the blend. (Open symbols) 1,2-PBd; (solid symbols) PI. (Circles) 1,2-PBd180 and PI100; (triangles) 1,2-PBd90 and PI100; (squares) 1,2-PBd180 and PI60.

Table VII
Characteristic Relaxation Times at T_g + 80

	1,2-PBd			PI		
sample composition	T_g + 80, °C	log τ_1, (s)	N	T_g + 80, °C	log τ_2, (s)	N
1,2-PBd180 + PI100						
100/0	82	−0.08	52.8			
75/25	68	0.0	48.$_2$	50	−0.57	24.3
50/50	55	0.39[a] −0.18[b]	44.3	40	−0.66	22.4
25/75	44	0.26	41.0	31	−0.82	20.7
0/100				19	−0.72	19.2
1,2-PBd180 + PI60						
100/0	82	−0.08	52.8			
75/25	68	0	48.2	50	−1.36	15.0
50/50	55	0.39[a] −0.18[b]	44.3	40	−1.42	13.8
25/75	44	0.26	41.0	31	−1.56	12.7
0/100				19	−1.58	11.8

[a] Rouse. [b] Crossover.

the characteristic time of 1,2-PBd increases 10-fold from that of the homopolymer in the 50/50 and 25/75 blends. The characteristic time of polyisoprene, on the other hand, is almost constant down to the 50/50 blend with 1,2 PBd and *decreases* by a factor of 3 for the 75/25 blend.

As shown in Table VI the individual T_gs of the components of the blends as determined by the Colby analysis and the WLF analysis are rather consistent. These estimated T_gs have been used as reference temperatures for the analysis of the characteristic times of the components of the blends. Values of τ at T_g + 80 are given in Table VII and are shown in Figure 10. From Figure 10a it can be seen that τ increases for 1,2-PBd when diluted with polyisoprene. This is contrary to expectation. Dilution of the more slowly relaxing 1,2-PBd with polyisoprene should decrease the relaxation time due to enhanced constraint release. This effect may be small, however.[5] A decrease in relaxation time is also expected because of a reduced number of entanglements per 1,2-PBd chain when blended with polyisoprene. Values of the number of entanglements per chain calculated according to[34]

$$N_i = M_i/(\phi_i Me_i + \phi_j Me_j)$$

are given in Table VII.

Dilution of PI with more slowly relaxing 1,2-PBd is expected to increase the relaxation time by reducing constraint release (≤3 times)[5] and by increasing the number of entanglements per polyisoprene chain (factor of 2.2 at 25/75). Small increases in τ_2 are observed with increasing 1,2-PBd (see Figure 10a).

e. Terminal Properties of Blends. In Figure 11 the isothermal (45.6 °C) zero-shear viscosities of the blends are shown as a function of blend composition. The three

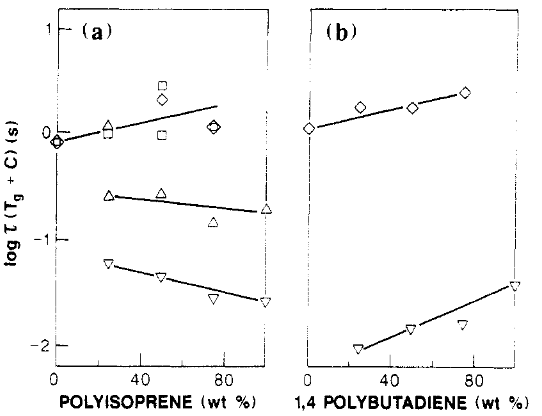

Figure 10. (a) Log τ at $T_g + 80$ against composition of the blend. (□) 1,2-PBd in 1,2-PBd180–PI100; (◇) 1,2-PBd in 1,2-PBd180–PI60; (△) PI100 in 1,2-PBd180–PI100; (▽) PI60 in 1,2-PBd180–PI60. (b) Log τ at $T_g + 50$ against composition of the blend. (▽) 1,4-PBd in AD; (◇) PBd (63% 1,2) in AD.[20]

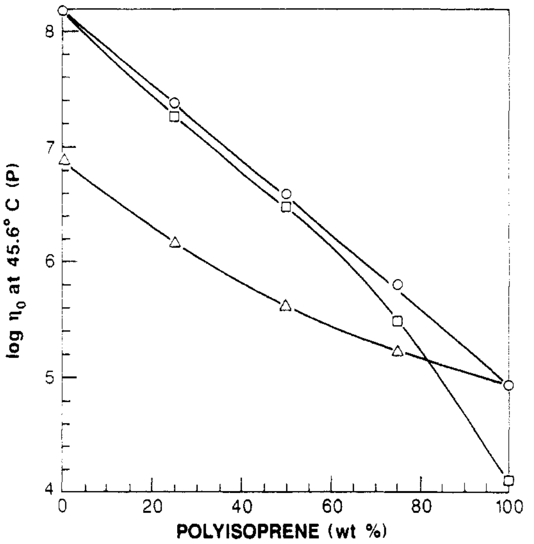

Figure 11. Zero-shear melt viscosities at 45.6 °C of blends of 1,2-PBd and PI. Symbols are as in Figure 9.

possible cases are observed. Blends of 1,2-PBd180 with PI100 show a linear dependence of log η_0 on blend composition. Blends of 1,2-PBd90 with PI100 have a convex and blends of 1,2-PBd180 with PI60 have a concave dependence of log η_0 on blend composition.

The plots of log J_e^0 against blend composition are typical for binary blends of narrow molecular weight homopolymers[4,5] and in blends.[20] A small fraction of a polymer with a long relaxation time increases J_e^0 substantially. Adding 1,2-PBd180 to PI60 increases J_e^0 more than adding the same amount of 1,2-PBd180 to PI100. Blends of 1,2-PBd90 with PI100 have a nearly constant value of J_e^0 as expected from their almost equal relaxation times. Note that the characteristic relaxation time of the polymer *in the blend* is important, not that of the homopolymer.

At the transition from the terminal to the plateau zone G'' either goes through a maximum (see Figure 4) or has a shoulder. When the relaxation times of the components are well separated, values of G''_{max} consist almost entirely of contributions from the 1,2-PBd component. In homopolymer blends values of G''_{max} vary according to $\phi_1^2(G''_{max})_1$,[5-11] where ϕ_1 is the volume fraction of the high molecular weight component and $(G''_{max})_1$ is the value of the maximum for the homopolymer. It can be seen that the same dilution rule applies roughly to blends of two polymers. For the 1,2-PBd180–PI60 blends with 75, 50, and 25% 1,2-PBd, $G''_{max} = 9.2 \times 10^5$, 4.3×10^5, and 1.3×10^5 dyn/cm^2, respectively. The calculated values are 8.9×10^5, 4.0×10^5, 4.0 and 1×10^5 dyn/cm^2, respectively. The experimental values of G''_{max} are increasingly larger than the calculated ones due to increasing contributions of PI to the modulus as 1,2-PBd is diluted.

Summary and Conclusions

It is of interest to compare the results on 1,2-PBd and PI blends described in this work with the results obtained previously on blends of PBd (63% 1,2) and 1,4-PBd.[20] Both systems are rubbers with low T_gs that can be studied from −50 to 100 °C. Strong interactions between the polymers are absent because the polymers have no polar groups. All blends studied are clear to the eye at room temperature. (Blends of 1,2-PBd with 1,4-PBd are cloudy, however.) The small positive interaction parameter for PBd (63% 1,2) and 1,4-PBd is well established[35] and limits miscibility to polymers of rather low molecular weight or small ranges of composition. There is evidence that 1,2-PBd–PI is more miscible. The interaction parameter is close to zero with a possible LCST.[21,36] However, we confirm that the T_gs of 1,2-PBd–PI blends are broad,[22,36] actually broader than for the PBd (63% 1,2)–1,4-PBd blends that have been studied. Moreover, the T_gs do not follow a simple Gordon–Taylor–Wood rule, which suggests that χ is strongly composition dependent.

Despite the subtle thermodynamic differences between the two systems, the same thermorheological complexity is observed. Relaxation times of the more slowly relaxing component have a stronger temperature dependence than the relaxation times of the more quickly relaxing component. In each cases, the more slowly relaxing component has the higher glass transition temperature. It would be of interest to perform experiments in which this situation is reversed, e.g., by changing the molecular weight ratio of the components.

In both studies we ascribe the thermorheological complexity to a modulated blend composition or microheterogeneity that causes different T_gs for the components. In the analysis, the assumption has been made that the free volume and thermal expansion coefficient of the free volume in each part of the blend is the same as that of the homopolymers. This has not been proven and may not be correct, e.g., when mixing is accompanied by volume changes. We are not sufficiently confident, however, that the small decrease in specific volume of 1,2-PBd–PI blends is genuine. Roland did not find this phenomenon,[36] but others have observed it in similar systems.[27] In principle, the detailed study of the temperature dependence of the relaxation times should allow one to resolve this point, but the resolution of the individual relaxation processes and accuracy of the values of τ are presently too crude. In this regard, interesting results may be expected if the temperature dependence is studied by other techniques, for example, by dielectric spectroscopy, where a normal mode process is observed at low frequencies for PI but not for PBd.[37,38]

Our suggestion of large amplitude composition fluctuation is not irreconcilable with the ^{1}H NMR results which indicate that the two polymers are mixed to a 0.5–1.0-nm level.[39] Indeed, the study of the temperature dependence of ^{13}C line widths shows that the T_g of polyisoprene is about 15 °C lower than that for 1,2-PBd. This is in good agreement with the T_g difference deduced from the viscoelastic measurements. The dynamic microheterogeneity proposed by Miller et al. to explain the different values of T_g[39] is not supported by the identical fractional free volume data given in Table IV for the hompolymers.

Recent dielectric relaxation results for miscible blends of 1,4-PBd and 1,2-PBd have also been interpreted as due to concentration flucutations with a length scale of about 2.5 nm.[40] The viscoelastic results suggest that the length scale is of the order of the radius of gyration of the polymers. Under Θ conditions, R_Gs for 1,2-PBd90 and 1,2-PBd180 are 9.2 and 14.4 nm, respectively.[29] For PI60 and PI100 R_G = 8.4 and 10.7 nm, respectively.[30]

When isocomposition and isothermal properties are investigated as a function of molecular weight, it is observed that the characteristic relaxation times of each component follow roughly the "entangled polymer" dependence ($M^{3.4}$) independent of whether the component is the more slowly or quickly relaxing one.

When the isothermal properties are compared as a function of blend composition, it is found that the relaxation times and the zero-shear viscosity depend overridingly on the T_g of the blend. Since J_e^0 is less temperature dependent, its composition dependence is typical of blends of polymers.[4-6] Addition of a small amount of a component with a long relaxation time causes a large increase in J_e^0.

Attempts have been made to extract the iso-free volume relaxation times of the components and to determine their composition dependence. Such relaxation times have been determined at (T_g + constant) °C and therefore depend critically on the value of T_g. For the PBd (63% 1,2)–1,4-PBd blends the average DSC value of T_g has been used because the rheological T_g for each component was available only for the AD pair.[20] Moreover, the values of T_g lie in the upper half or above the DSC glass transition region (Table V in ref 20). The values of the rheological T_gs lie within the DSC transition for the 75/25 blend of 1,2-PBd–PI. But the agreement worsens as the 1,2-PBd is diluted with more PI in the same way as observed previously.[20] The reason for this discrepancy is still not clear. Note also that large tails are omitted from the DSC transitions by the tangent method (see Figure 1).

Inspection of Table VI in ref 20 and Table VII and Figure 10 show that in all cases the iso-free volume relaxation times vary very little with composition. It has been shown previously that relaxation times of PBd (63% 1,2) increase on dilution with 1,4-PBd, the result of an increased number of entanglements, thereby overriding the opposite small effect of increased constraint release.[20] The same argument leads to the observed decrease of the relaxation times of 1,4-PBd (see Figure 10b). Constraint release effects are expected to be less important in the blends of 1,2-PBd with PI because each chain has many entanglements. On dilution with PI the relaxation time of 1,2-PBd is expected to decrease because PI has M_e = 5350. This is not observed. It is possible that we have not properly accounted for iso-free volume when we determined T_g for the 1,2-PBd component and set T_g + 80 as the temperature of comparison. The expected increase in the relaxation time of PI on dilution with 1,2-PBd is found (see Figure 10a). It is probably premature to attempt such a detailed analysis of the relaxation times when the analysis of the moduli–frequency curves and the determination of T_g are still too qualitative.

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