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Effects of Polydispersity on the Linear Viscoelastic Properties of Entangled Polymers. 3. Experimental Observations on Binary Mixtures of Linear and Star Polybutadienes

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ABSTRACT: The effect of polydispersity on the viscoelastic response of entangled polymers was explored with binary mixtures of nearly monodisperse linear and 3-arm star polybutadienes. Storage and loss moduli were measured over a wide range of frequencies for one series of star–star mixtures and four series of linear–star mixtures. Results at several temperatures were reduced to master curves at 25 °C, and the values of viscosity η_0 and recoverable compliance J_e^0 were obtained. Some observations about the influence of the matrix on the relaxation of individual components are recorded and compared with results from other laboratories. The dependences of η_0 and J_e^0 on composition when one or both of the components is a star polymer are described.

The effect of polydispersity on the rheological behavior of homopolymer melts is a subject of both theoretical and practical interest.[2] For linear polymers the molecular weight or chain length distribution alone defines the polydispersity. The situation is more complicated for polymers with long branches because a diversity of structures as well as molecular weights is usually encountered. Moreover, the polymerization mechanisms that lead to branching typically broaden the distribution of molecular weights, and it is difficult to distinguish effects caused by the presence of branched molecules from those caused simply by an increase in the distribution breadth.[3]

From studies on model systems it is clear that the viscoelastic response of highly entangled polymers depends strongly on chain architecture. Thus, for example, the terminal relaxation spectrum for nearly monodisperse linear polymers is relatively narrow and has a form that is practically independent of chain length.[4] The spectra for nearly monodisperse star and comb polymers are much broader[4,5] and have forms that depend strongly on branch length.[6] The dependence of zero-shear viscosity η_0 and recoverable compliance J_e^0 on molecular weight is also quite different for linear and branched polymers in the entangled regime.[7] A recent theory based on the tube model suggests that the relaxation mechanisms are also different, entangled linear chains in a monodisperse melt moving primarily by reptation along their tubes[8] and entangled branched chains moving by some combination of tube length fluctuations and tube renewal.[6,9-12] Thus, it seems reasonable to expect that rheological mixing laws will also depend on chain architecture.

Mixture of monodisperse components are used to investigate the influence of polydispersity. Previous papers in this series[13,14] have dealt with binary mixtures of nearly monodisperse linear polybutadienes. Master curves of the dynamic modulus $G^*(\omega)$ were obtained for a wide range of compositions. The contributions of individual components are relatively easy to identify in such systems, the spectral range of response for linear polymers being narrow even in mixtures. The compositional dependence of the contributions was examined in some detail in those papers and related theoretically to changes in the tube renewal rates introduced by polydispersity. The compositional dependences of η_0 and J_e^0 were compared with results calculated according to various empirical mixing rules[13] and predicted by reptation theory with the tube renewal contributions handled by a simple constraint release model.[14]

The present paper deals with mixtures that contain 3-arm star polybutadienes. In contrast with the extensive work on mixtures of linear polymers, only a few studies of branched polymer mixtures have been reported. Berglund, Carriere, and Ferry have examined the relaxation of a linear polybutadiene dispersed dilutely in a 4-arm star matrix.[15] Graessley and Raju have obtained values of η_0 for mixtures of linear and 3-arm star hydrogenated polybutadiene with nearly matched component viscosities.[16] Hadjichristidis and Roovers have measured viscoelastic properties for mixtures of 3- and 4-arm star polybutadienes with the same arm length,[17] and Roovers has analyzed the relaxation of 4- and 18-arm star polybutadienes dispersed dilutely in several linear polybutadiene matrices.[18] Rheological measurements on mixtures of branched and linear commercial polyethylenes have also been published,[19-21] and Dobrescu has developed a method for predicting their flow curves from data on the components.[20] We have found no general proposals of linear viscoelastic mixing rules for branched systems, again in contrast to the great variety that have been suggested for linear polymers.[12,13]

Five series of binary mixtures were investigated, four with linear and star components (the linear–star series) and one in which both components are stars (the star–star series). In one of the linear–star series, the linear component has a smaller radius of gyration R_G than the star. In another the R_G values are nearly matched. In the third, the linear component has a larger R_G, and in the fourth, the component viscosities are nearly matched. The chains are well entangled in all cases. Dynamic modulus master curves were obtained, as in the earlier study of linear–linear mixtures,[13] but the interpretation here is somewhat more limited. The inherently broad spectrum of star polymers makes individual component contributions less easy to assign. The molecular theory for entangled monodisperse stars is also less settled than for linear chains, particularly regarding the relative importance of tube length fluctuations and tube renewal on relaxation. Some matrix effects in the relaxation of individual components are noted, but most attention is devoted to the compositional dependence of η_0 and J_e^0.

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Table I
Molecular Characteristics of Pure-Component Polybutadienes

sample	$[\eta]$,[a] dL g^{-1}	$M \times 10^{-4}$	R_G,[b] nm	microstructure		
				% cis	% trans	% vinyl
41L	0.65	3.68	7.0	42	50	8
105L	1.33	10.0	11.5	49	44	7
174L	1.93	16.8	14.9	51	42	7
75S	0.81	7.46	9.0	43	48	9
127S	1.365	12.7	11.7	44	46	10

[a] Intrinsic viscosity in tetrahydrofuran at 25 °C. [b] Radius of gyration for linear chains at the Θ-condition calculated from $R_G = 0.0364 M^{1/2}$.[25] Values for the star polymers were calculated with $g = (R_G^2)_{\text{star}}/(R_G^2)_{\text{linear}} = 0.82$ for 3-arm stars at the Θ-condition.

Experimental Section

The three linear polybutadiene components—samples 41L, 105L, and 174L—were prepared by anionic polymerization in cyclohexane at 50 °C by using a capped-bottle technique.[22] The two 3-arm star polybutadiene components—samples 75S and 127S—were prepared by anionic polymerization and trichloromethylsilane linking in benzene at ambient temperature and under vacuum line conditions.[23] The initiator was *sec*-butyllithium in all cases. The stars were fractionated to remove unlinked arms. All samples had narrow molecular weight distributions, $M_w/M_n < 1.1$, according to size-exclusion chromatography.

Molecular weights were determined by light scattering in cyclohexane (Chromatix KMX-6), and intrinsic viscosities were obtained in tetrahydrofuran at 25 °C. Samples 41L and 174L were used in the study of linear–linear mixtures.[13] Based on subsequent work,[24] the molecular weights of those samples have been revised slightly; the modified values are given in Table I. Chemical microstructure was characterized by infrared spectroscopy. The proportions of 1,4-cis, 1,4-trans, and 1,2-vinyl additions were determined as described elsewhere.[13] Results are given in Table I. The linear polymers and stars have slightly different vinyl contents, presumably the result of the different conditions used in their preparation.

Mixtures of the components were prepared as described previously.[13] Values for the radius of gyration R_G were calculated for the various components in the melt state on the basis of data obtained at the Θ-condition[25,26] (Table I). The components R_G's are nearly matched in the 105L/127S series; R_G for the branched component is larger in the 41L/127S series and smaller in the 174L/127S series. The component melt viscosities are nearly matched in the 105L/75S series (see below).

Dynamic storage and loss moduli, $G'(\omega)$ and $G''(\omega)$, were measured in the frequency range 10^{-3} s^{-1} $< \omega <$ 10^2 s^{-1} with a Rheometrics mechanical spectrometer by procedures described earlier.[13] Data were collected at 25, 50, and 75 °C for each mixture, then shifted along the frequency axis to generate master curves[2] at the reference temperature T_0 = 25 °C. Superposition was excellent in all cases. Viscosity and recoverable compliance were obtained from[2]

$$\eta_0 = \lim_{\omega \to 0} \frac{G''(\omega)}{\omega} \tag{1}$$

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

Values of the frequency–temperature shift factors a_T were obtained from

$$a_T = \eta_0(T)/\eta_0(T_0) \tag{3}$$

since the change in modulus shift factor b_T is negligible over this relatively narrow temperature range.[24] The pure component values of a_{50} and a_{75} are somewhat different for linear and star polymers, probably caused by their slightly different microstructures but perhaps also due to some slight thermorheological complexity in the star polymer behavior.[27] Rheological properties for the individual components are given in Table II and for the mixtures in Table III. Some measurements made on concentrated solutions of star sample S127 in a commercial hydrocarbon oil, Flexon 391,[4] are also given there.

All mixtures are well entangled. The entanglement molecular weight M_e is 1850 for undiluted polybutadiene;[13] the number of

Table II
Viscoelastic Properties of Pure-Component Polybutadienes

sample	$M \times 10^{-4}$	N[a]	η_0 (25 °C, P)	a_{50}	a_{75}	$J_e^0 \times 10^7$, cm^2 dyn^{-1}
41L	3.68	20	1.35×10^4	0.39	0.19	1.78
105L	10.0	54	4.37×10^5	0.37	0.17	1.95
174L	16.8	91	2.95×10^6	0.35	0.15	1.82
75S	7.46	40	4.79×10^5	0.28	0.10	8.31
127S	12.7	69	2.75×10^7	0.30	0.11	13.5

[a] $N = M/M_e$, where M_e = 1850 for undiluted polybutadiene of this microstructure.[13]

Table III
Viscoelastic Properties of the Binary Mixtures

ϕ_B	η_0 (25 °C, P)	a_{50}	$J_e^0 \times 10^7$, cm^2 dyn^{-1}
	41L/127S Series		
0.05	2.24×10^4	0.32	11.7
0.10	2.95	0.33	18.6
0.20	6.03	0.30	24.0
0.30	1.20×10^5	0.30	29.5
0.50	5.43	0.29	25.1
0.75	3.80×10^6	0.27	18.2
	105L/127S Series		
0.05	5.37×10^5	0.33	4.60
0.10	6.31	0.32	6.02
0.15	7.16	0.32	9.33
0.20	8.51	0.32	12.3
0.30	1.20×10^6	0.32	15.1
0.50	2.63	0.28	16.6
0.75	8.13	0.28	17.8
	174L/127S Series		
0.05	3.24×10^6	0.33	5.01
0.10	3.55	0.32	5.89
0.20	4.27	0.32	8.51
0.30	5.50	0.30	10.5
0.50	8.03	0.30	14.1
	105L/75S Series		
0.05	5.01×10^5	0.32	2.63
0.10	4.90	0.33	2.95
0.20	4.90	0.33	3.63
0.30	5.41	0.31	4.17
0.50	5.65	0.30	5.49
0.70	5.50	0.29	6.91
0.80	5.37	0.29	7.07
0.90	5.13	0.28	7.58
0.95	5.01	0.27	7.94
	75S/127S Series		
0.05	5.69×10^5		10.6
0.10	7.35		14.1
0.20	1.11×10^6		15.8
0.30	1.63		17.4
0.50	3.63		18.2
0.70	8.79		18.2
0.85	1.58×10^7		15.5
	Flexon 391/127S Series		
0.21	1.09×10^3		63.0
0.32	8.03×10^3		38.0
0.52	1.59×10^5		24.5
0.77	2.67×10^6		17.8

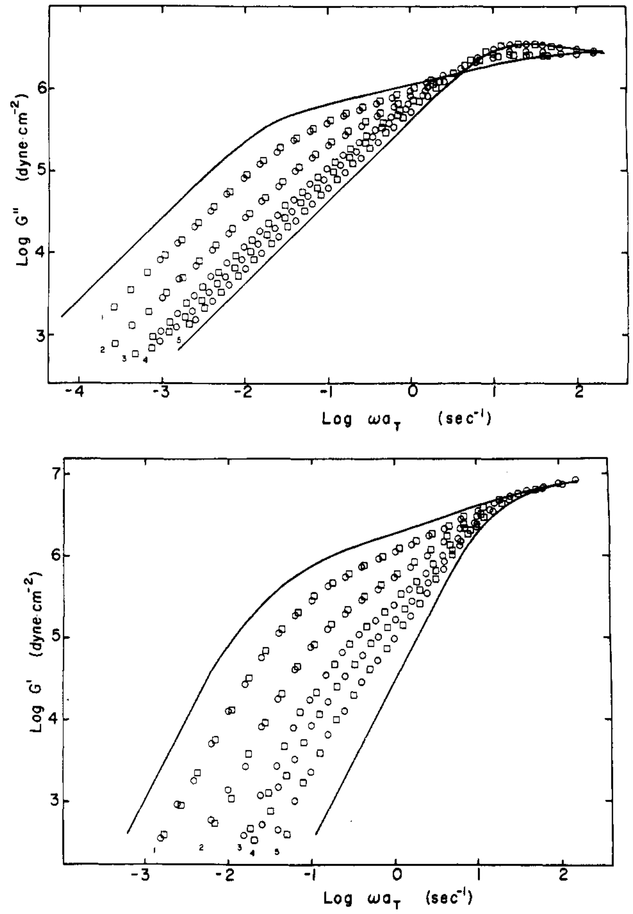

Figure 1. (Top) Master curves of the dynamic storage modulus for selected compositions of the 105L/127S series. Solid lines represent the pure component data; the points represent measurements on the mixtures at 25 (○) and 50 °C (□), the latter reduced to the reference temperature $T_0 = 25$ °C. The numbers indicate mixture composition; volume fraction of star component $\phi = 0.75$ (1), 0.50 (2), 0.30 (3), 0.20 (4), and 0.10 (5). (Bottom) Master curves of the dynamic loss modulus for selected compositions of the 105L/127S series. The designations are the same as those given above.

entanglements per molecule, $N = M/M_e$, is listed in Table II for the pure components.

Results and Discussion

A. General Observations. Master curves of $G'(\omega)$ and $G''(\omega)$ for the 105L/127S series are shown in Figure 1. Results for the other series have a similar appearance. The most slowly relaxing component in each series is a star polymer, and the low-frequency peak in loss modulus, a prominent feature in linear–linear mixtures called the L or long chain peak,[13] is not observed owing to the inherently broad relaxation spectrum of entangled stars. A loss peak at high frequency, associated with the linear component in the linear–star series and called the S or short chain peak in linear–linear mixtures,[13] was observable in some cases, however. The effect of mixture composition on the frequency of that peak, $(\omega_m)_s$, could therefore be monitored. The S peak for the 41L/127S series occurred beyond the range of our measurements, but values of $(\omega_m)_s$ for various compositions of the other linear–star series were obtainable and are given in Table IV.

In linear–linear mixtures $(\omega_m)_s$ was found to shift to lower frequency with increasing concentration of the long-chain component, approaching a reduction factor of about 4.5 in the limit of pure long-chain matrix.[13] We attributed that behavior to a suppression of tube renewal contributions in the relaxation of the short-chain component. In the linear–star mixtures, however, $(\omega_m)_s$ is practically unaffected by the presence of a more slowly relaxing star in the 105L/75S series where the component viscosities are nearly the same and also in the 174L/127S series, where the viscosity of the star component is larger by a factor of ~9. Some reduction in $(\omega_m)_s$ with increasing star component was found in the 105L/127S series, where the star component viscosity is larger by a factor of ~60. However, the effect is clearly weaker (we estimate a maximum reduction factor of about 2) than in linear–linear mixtures with comparable ratios of the component viscosities.[13] An earlier study had found no difference in relaxation behavior for linear chains (a) in their own melt or (b) dispersed dilutely in a star polymer of much higher viscosity.[15] From our results, a star matrix can alter the relaxation behavior of linear chains, but the effect is weaker than that produced by a linear matrix of the same viscosity.

Table IV
Loss Peak Frequency for the Linear Component in Linear–Star Polybutadiene Mixtures at 25 °C

	$(\omega_m)_s$, s^{-1}		
ϕ_B	105L/127S	174L/127S	105L/75S
0.00	25	4.0	25
0.05	25	4.0	25
0.10	25	4.0	25
0.15	22.5		
0.20	25	4.0	25
0.30	20	4.0	25
0.50	16	4.0	25
0.75	16		

Table V
Estimates of Longest Relaxation Time for 3-Arm Star Polybutadienes When Dilutely Dispersed in Various Matrices at 25 °C

test polymer	matrix	τ_1, s	τ'_1, s	τ_1, s (eq 4)
127S	41L	0.60	0.09	0.23
127S	105L	3.2	1.3	3.1
127S	174L	32.0	17.0	12.0
75S	105L	2.5	0.70	0.95
127S	75S	9.3	2.3	

Roovers investigated the relaxation of 4-arm and 18-arm polybutadiene stars as dilutely dispersed test molecules ($\phi \leq 0.025$) in linear polybutadienes matrices of much lower viscosity.[18] He estimated τ_1, the terminal relaxation relaxation time of the stars, as the reciprocal of the frequency at which the storage compliance $J'(\omega) = G'(\omega)/[G'(\omega)^2 + G''(\omega)^2]$ reached 90% of its low-frequency limit J_e^0. His results, reduced to $T_0 = 27$ °C, are well described by[18]

$$\tau_1 = 1.8 \times 10^{-23} M_a^{2.2} P^{2.6} \text{ (s)} \tag{4}$$

where M_a is the arm molecular weight of the stars and P is the molecular weight of the linear matrix. Roovers also applied the procedure of Montfort, Marin, and Monge[28] and found that it gave smaller values of the relaxation time (by factors of 2–6) but similar variations of relaxation time with matrix molecular weight.

We applied the Roovers procedure to obtain τ_1 for the 3-arm stars in this study. Data at $\phi_B = 0.05$ were used, the most dilute condition available. Results are given in Table V. We also applied a slight variant of the procedure of Watanabe, Sakamoto, and Kotaka,[29] according to which the weight-average relaxation time of the dilute component is obtained from the increments that component produces in η_0 and $J_e^0 \eta_0^2$:

$$\tau_w = \frac{\Delta(\eta_0^2 J_e^0)}{\Delta \eta_0} \tag{5}$$

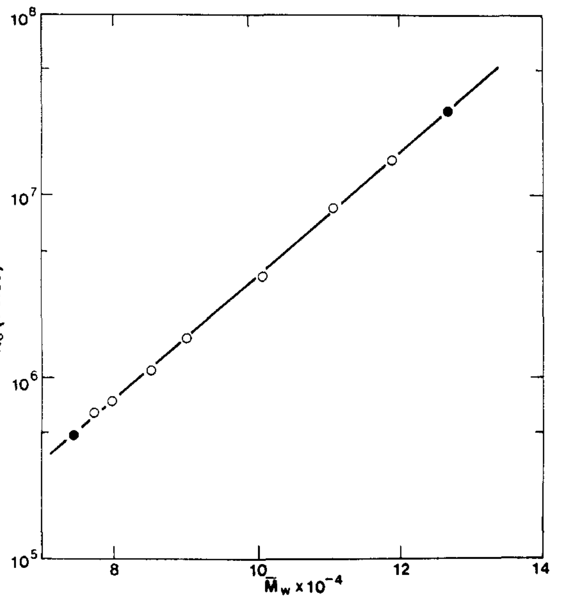

Figure 2. Viscosity as a function of weight-average molecular weight for the 75S/127S series. The filled symbols indicate pure component values; the open symbols indicate values for the mixtures.

The values of τ_w were converted to τ'_1, the longest relaxation time for free-draining star polymers, by using an expression easily derived from the spectra for Rouse model stars:[30]

$$\tau'_1 = \frac{60}{\pi^2}\frac{3f-2}{15f-14}\tau_w \tag{6}$$

where f is the number of arms in the star ($\tau'_1 = 1.37\tau_w$ for 3-arm stars). The results are recorded in Table V along with values of τ_1 calculated with the Roovers equation (eq 4), using the values of P and M_a for our mixtures. The calculated results were adjusted to 25 °C and also multiplied by 0.8 to correct from the slightly faster relaxation of 3-arm stars relative to stars with 4 or more arms.[17,31,32]

The values of τ_1 and τ'_1 obtained from our experimental data are similar in magnitude, although τ'_1 is consistently smaller; much as found by Roovers[18] when he compared the results of his procedure with those obtained by the Montfort–Marin–Monge procedure. Values of τ_1 calculated from eq 4 fall somewhere in the middle, a comforting result especially since the ranges in P and M_a are somewhat different here than in the Roovers study.[18] Our concentration of $\phi = 0.05$ is probably not dilute enough to avoid test chain interactions, however, and in view of this we have not attempted a more detailed interpretation.

B. Viscosity. The viscosities of the linear components at 25 °C are in good agreement with other results on polybutadienes of similar microstructure in the same range of molecular weights:[24]

$$(\eta_0)_L = 4.01 \times 10^{-12} M^{3.41} \tag{7}$$

The viscosity of well-entangled star polymers varies exponentially with arm molecular weight M_a.[6] We used that form with a constant preexponential factor and the data for our two 3-arm star components to obtain

$$(\eta_0)_B = 1.47 \times 10^3 \exp(M/12900) \tag{8}$$

where $M = 3M_a$.

The viscosity of linear–linear mixtures is described with surprising accuracy if M in the power law for mondisperse polymers (eq 7 in this case) is replaced by the weight-average molecular weight of the mixtures:[12,13]

$$\bar{M}_w = \phi_1 M_1 + \phi_2 M_2 \tag{9}$$

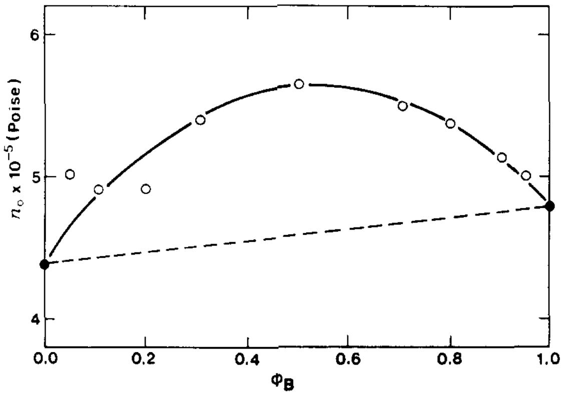

Figure 3. Viscosity versus volume fraction of the star component in the 105L/S75 series. Designations are the same as in Figure 2. The dashed line corresponds to a linear interpolation of pure-component values.

Table VI
Star and Linear Equivalent Molecular Weights of Pure-Component Polybutadienes in Linear-Star Mixtures

sample	$M \times 10^{-4}$	$M^* \times 10^{-4}$	$M^{**} \times 10^{-4}$
41L	3.68	2.86	
105L	10.0	7.35	
174L	16.8	9.81	
75S	7.46		10.2
127S	12.7		33.4

There is no theory that justifies that result; it is simply an empirical observation. We found a parallel situation to exist for the star–star mixtures, namely, that the monodisperse form (eq 8 in this case) was applicable when $\bar{M}_w$ was used in place of M. The result is shown in Figure 2. Thus, for both linear–linear and star–star mixtures, the experimental data on viscosity are accommodated by the form

$$\eta_0 = F(\bar{M}_w) \tag{10}$$

where $\eta_0 = F(M)$ is the applicable relationship for pure components.

The four linear–star series involve mixtures of components with different architectures. The component viscosities are nearly the same for the 105L/75S series, and the viscosities of the mixture change very little across the composition range. The results are shown in Figure 3. There is a weak maximum around $\phi = 0.5$, as was seen in an earlier study of linear–star mixtures with matched component viscosities,[16] but the difference from values based on a linear interpolation of pure component data is never more than about 20%. Thus, to a first approximation, mixtures of isoviscous components with different architectures are isoviscous.

The pure-component viscosities differed considerably in the other three linear–star series. We explored the possibility of describing the viscosities of those mixtures by one of the constant-architecture mixing rules. There are two ways this can be done, either by establishing a "star-equivalent" molecular weight M^* for the linear component and applying the mixing law for stars or by establishing a "linear-equivalent" molecular weight M^{**} for the star component and applying the mixing rule for linear polymers. Values of M^* for the linear components were calculated from η_0 by using the relationship for stars (eq 8), and values of M^{**} for the star components were calculated from η_0 by using the relationship for linear chains (eq 7). The results are given in Table VI. The star polymer mixing rule was tested by plotting log η_0 versus $\bar{M}_w^*$, where $\bar{M}_w^* = \phi_1 M_1^* + \varphi_2 M_2$, the subscript 2 denoting

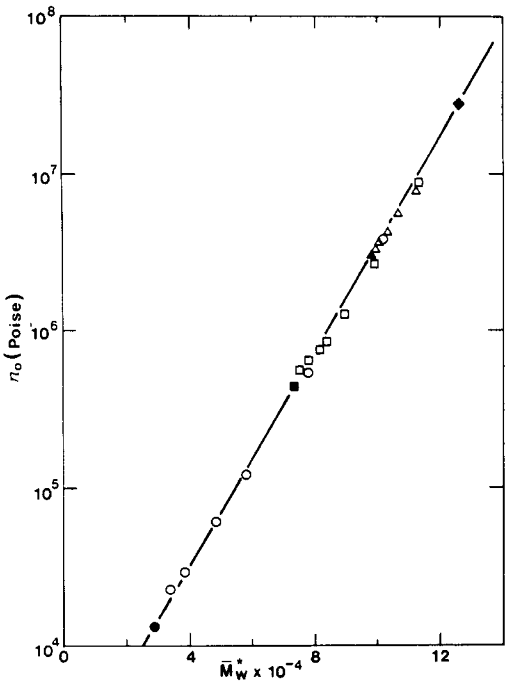

Figure 4. Test of the star polymer mixing law for three linear–star series with star-equivalent molecular weights used for the linear component values. The filled symbols indicate M^* for linear samples 41L (●), 105L (■), and 174 (▲) and M for star sample 127S (◆). Open symbols indicate corresponding values for the mixtures; the solid line represents eq 8.

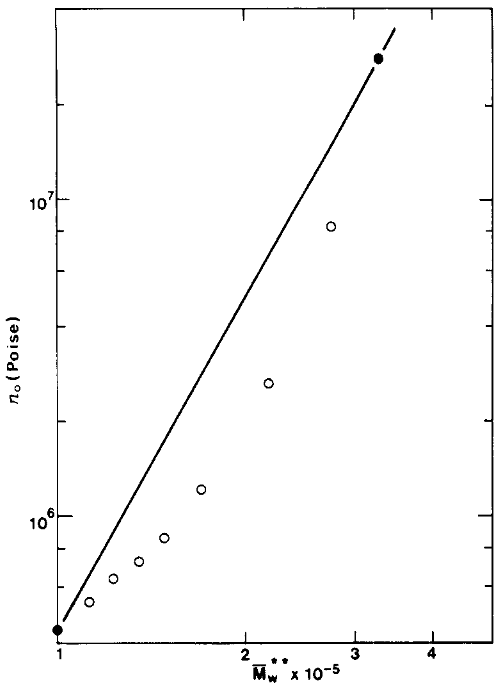

Figure 5. Test of the linear polymer mixing law for the 105L/127S series using a linear-equivalent molecular weight for the star component. Filled circles correspond to M for the linear component and M^{**} for the star; open circles indicate values for the mixtures. The solid line represents eq 7.

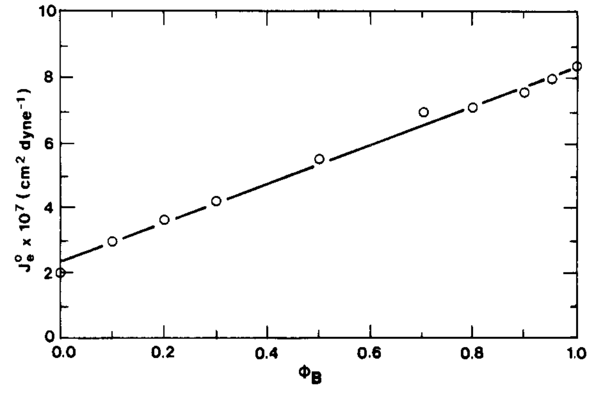

Figure 6. Recoverable compliance versus volume fraction of the star component in the 105L/S75 series.

the star component. Results for the 41L/127S, 105L/127S, and 174L/127S series are shown in Figure 4. The viscosity behavior is described remarkably well: departures of η_0 from the star mixing law are never greater than 20% and usually much less.

Results for the linear polymer mixing rule were much less satisfactory. Tests were performed by plotting log η_0 versus log $\bar{M}_w^{**}$, where $\bar{M}_w^{**} = \phi_1 M_1 + \phi_2 M_2^{**}$; subscript 2 again denotes the star component. The comparison for the 105L/127S series is shown in Figure 5. Large and systematic departures from the linear polymer mixing rule are evident in this series and also in corresponding examinations of viscosity for the 41L/127S and 174L/127S series (not shown).

The better fit provided by the star polymer mixing rule may be due in part to the fact that the viscosity of the star component was always larger in the systems examined here. The linear and star mixing rules predict similar results where the component viscosities are nearly the same (the 105L/75S series). We have no results with which to compare the rules when the linear component has the higher viscosity. Of course, the linear polymer rule must apply eventually because, in the limit, the star would behave simply as a monomeric diluent of the linear polymer.

Finally, it is worth noting that the mixing rules can be tested without computing values of M^* and M^{**}. Predictions for mixtures require only the component viscosities, $(\eta_0)_1$ and $(\eta_0)_2$, and volume fractions, ϕ_1 and ϕ_2. Thus, the mixing law based on $\bar{M}_w$ for linear polymers ($\eta_0 = (\text{const})(\bar{M}_w)^\alpha$) can be written

$$\eta_0 = [\phi_1(\eta_0)_1^{1/\alpha} + \phi_2(\eta_0)_2^{1/\alpha}]^\alpha \qquad (11)$$

and the mixing law based on $\bar{M}_w$ for star polymers ($\eta_0 = (\text{const})\exp(\beta\bar{M}_w)$) can be written

$$\eta_0 = (\eta_0)_1^{\phi_1}(\eta_0)_2^{\phi_2} \qquad (12)$$

C. Recoverable Compliance. The values of J_e^0 for the pure-component stars are in reasonably good agreement with the experimental observations and theory for star polymers:[6]

$$J_e^0 = 0.6\frac{M_a}{\rho RT} \qquad (13)$$

where ρ is melt density, R is the universal gas constant, and T is the temperature. Thus, $J_e^0 = 8.31 \times 10^{-7}$ cm^2/dyn is found for sample 75S, and eq 13 ($\rho = 0.895$ mL/g at $T = 298$ K) predicts 6.73×10^{-7}. Also $J_e^0 = 1.35 \times 10^{-6}$ cm^2/dyn is found for sample 127S, and eq 13 predicts 1.15 $\times 10^{-6}$. Results for the linear–star mixtures are shown in Figure 6 and 7 as functions of ϕ_B, the volume fraction of branched polymer. Results for the star–star mixtures are shown in Figure 8, ϕ_B in this case referring to the higher molecular weight sample S127.

Although we have examined several possibilities, some based on molecular arguments and some empirical, we have been unable to find any simple description of J_e^0 that is quantitatively acceptable for all the mixtures. We note, however, that the mixing rule of Ninomiya and Ferry,[33] based on the Rouse model, behaves in a qualitatively

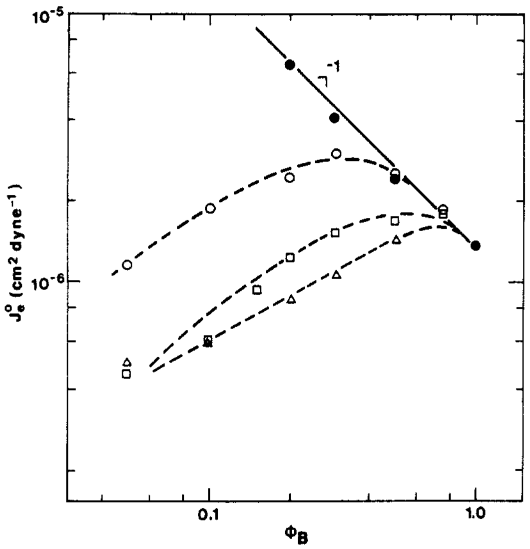

Figure 7. Recoverable compliance versus volume fraction of the star component for three linear–star series of mixtures. The filled circles indicate values for pure-star component S127 and its solutions in the monomeric diluent Flexon 391 (see ref 2). The open symbols indicate values for the mixtures of sample S127 with 41L (○), 105L (□), and 174L (△). Dashed lines are used to suggest trends.

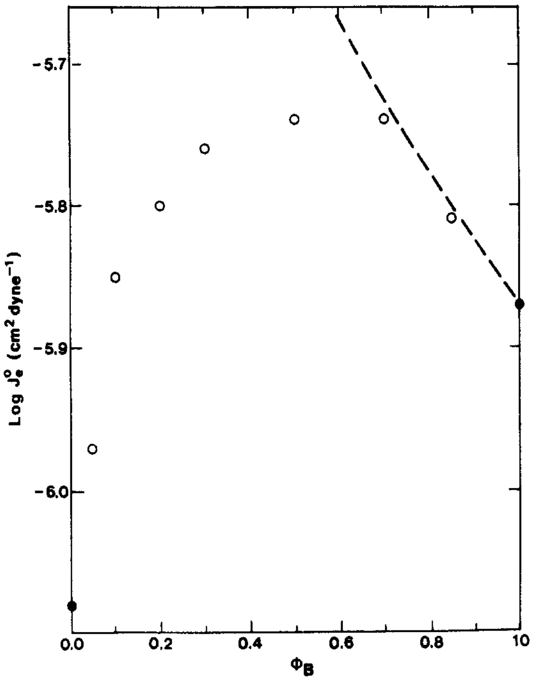

Figure 8. Recoverable compliance versus fraction of the star component in the 75S/127S series. The dashed line represents data for solutions of sample S127 in Flexon 391 (see Figure 7).

correct fashion and might therefore provide the basis for some more accurate description in the future. The Ninomiya–Ferry rule for mixtures can be written

$$J_e^0 = \frac{\phi_1 (J_e^0)_1 M_1^2 + \phi_2 (J_e^0)_2 M_2^2}{\phi_1 M_1^2 + \phi_2 M_2^2} \tag{14}$$

where the $(J_e^0)_i$ and M_i are pure-component values and the ϕ_i is the volume fractions. We applied this equation to the mixtures using the "star-equivalent" molecular weight M^* (Table VI) for the linear components. Some of the results in Figures 6–8 are nicely consistent with that somewhat arbitrary procedure. Thus, for example, M^* is practically identical with the star polymer molecular weight M_B in the isoviscous 105L/75S series, in which case the molecular weight cancels from eq 14 and J_e^0 is predicted to vary linearly with ϕ_B. Within experimental error, this is indeed the result found for that series (Figure 6). Also, $J_e^0 \propto \phi_B^{-1}$ is predicted for a monomeric diluent, as observed for stars;[4] and when the diluent is a polymer of somewhat lower molecular weight than the star, J_e^0 is also predicted to vary as ϕ_B^{-1} near $\phi_B = 1$. The latter tendency can be seen both in Figure 7 for the linear–star mixtures and in Figure 8 for the star–star mixtures.

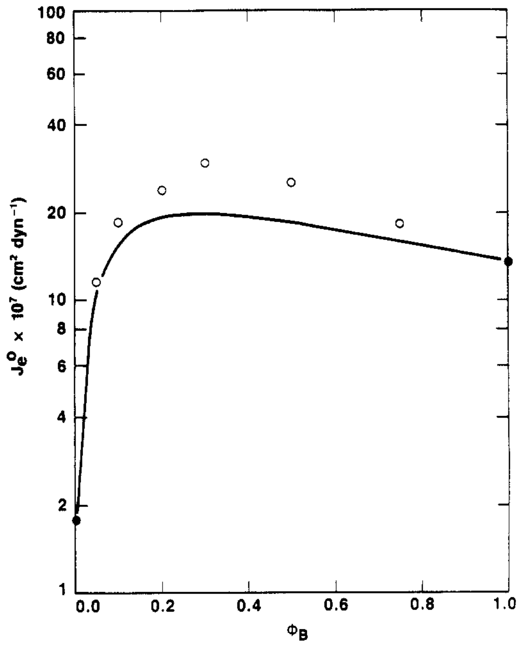

Figure 9. Comparison of recoverable compliance for the 41L/127S series with predictions based on the Ninomiya–Ferry mixing rule. The points represent experimental data; the curve was calculated with eq 14.

Despite these attractive features, however, the values of J_e^0 calculated with eq 14 are smaller than the measured values, as shown by the example of the 41L/127S series in Figure 9. Unfortunately, our selection of eq 14 has no basis in theory, and it is not obvious how to improve its ability to fit data while retaining such good features as the result for the isoviscous 105L/75S series. Also, like the mixing rule for η_0 (eq 12), the rule for J_e^0 in the linear–star mixtures can only describe the regime in which the star is the slower relaxing component. When the reverse is true, the quite different rules for linear polymers[13] must eventually emerge.

Conclusions

We have found that the relaxation rate of entangled linear polymers is reduced in a more viscous star matrix, but less so than in a linear matrix having the same viscosity as the star. Entangled 3-arm star polymers in a linear matrix of lower viscosity have terminal relaxation times which are roughly consistent with values estimated from the more extensive results of Roovers (eq 4). The viscosity of star–star mixtures varies exponentially with $\bar{M}_w$ of the mixture. The viscosity for linear–star mixtures obeys the star polymer mixing rule (eq 12) when the star is the more viscous component. We were unable to discover a unified and quantitatively correct description of recoverable compliance for entangled mixtures that contain star polymers.

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Glass Transition and Melting Behavior of Poly(ethylene-2,6-naphthalenedicarboxylate)

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ABSTRACT: On the basis of thermal analysis the heat capacities of both solid (230–350 K) and liquid (390–600 K) poly(ethylene-2,6-naphthalenedicarboxylate) (PEN) have been established by measurements on over 30 samples. The heat capacity of the solid is structure-independent to 300 K. Between 300 and 390 K, a pre-glass transition increase in heat capacity is observed for the amorphous samples of the polymer. It contributes about 9.5 J/(K mol) to the heat capacity increase [80.1 J/(K mol)]. Above the glass transition temperature (390 K), poorly crystallized PEN shows a rigid-amorphous fraction (up to 0.2). The rigid-amorphous fraction starts to gain mobility at about 430 K and reaches zero after melting of the low melting fraction of the polymer. The glass transition temperature on cooling changes logarithmically ($T_g = 382.3 + 2.03 \ln q$, q in K/min). The hysteresis of amorphous samples has been analyzed. The crystallization range was studied from 450 to 530 K by crystallizing on cooling from the melt and heating from the glass. Four types of crystallinities must be distinguished: w^c(H), w^c(M), w^c(L), and w^c(C), with fusion peaks at high, middle, and low temperatures. The last fraction, w^c(C), forms on cooling after crystallization and causes an increase in C_p starting at about 450 K. The metastability, sequence of crystallization, stepwise crystallization, and annealing phenomena are analyzed. The equilibrium melting parameters have been estimated to be $T_m^\circ = 610$ K, $\Delta H_f = 25 \pm 2$ kJ/mol, and $\Delta S_f = 41 \pm 3.3$ J/(K mol).

Introduction

Poly(ethylene-2,6-naphthalenedicarboxylate) (PEN) is a relatively well-known polymer used for engineering purposes. Most research on PEN has concentrated on photochemical properties, such as absorption,[1] fluorescence, and chemiluminescence.[2] A special property of PEN is the formation of liquid crystalline polymers when polymerized with suitable comonomers.[3]

The crystal structure of PEN was reported to be triclinic with dimensions of $a = 0.651$ nm, $b = 0.575$ nm, and $c = 1.32$ nm and angles of $\alpha = 81°21'$, $\beta = 144°00'$, and $\gamma = 100°00'$.[4] Only brief reports for liquid-induced crystallization of PEN in dioxane, aniline, and methylene chloride were published.[5,6] A distinct spherulitic texture was found in these crystallizations, and their time and temperature dependence was also studied.[5,6] Infrared spectra of PEN have been reported several years ago.[7] A detailed thermal analysis of PEN has not been reported so far.

In this paper, we describe the thermal analysis of amorphous and various semicrystalline PEN samples. The solid and liquid heat capacities have been measured. Special attention has been paid to the temperature range between 300 K and T_g, where possible local molecular motion in the amorphous state causes an increase in heat capacity. A similar increase was found earlier for poly-

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