Entanglement and Flow Behavior of Bidisperse Blends of Polystyrene and Polybutadiene

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ABSTRACT: The relaxation of highly entangled bidisperse blends of polystyrene and bidisperse blends of polybutadiene were studied experimentally. The main objective was to quantify the effect that the interaction of short and long chains has on the relaxation of the blend. For the analysis of dynamic mechanical data, the simplest model for the relaxation time spectrum of the blend, $H(\lambda)$, was found to be satisfactory. It consists of a linear superposition $H(\lambda) = \sum_{i=1}^{2} B_i H_i(\lambda/A_i)$ where the spectra of the nearly monodisperse components, $H_i(\lambda)$, were described by the BSW model. The interaction of the two blend components is expressed phenomenologically by the shift factors A_i and B_i whose values arise naturally when fitting G' and G'' data of the blends. They depend on the weight fractions, w_i, and the molecular weights, M_i. The characteristic relaxation time of the short chains gets extended by the blending while the characteristic relaxation time of the long chain is reduced. The pattern in the shift factors suggests a blending rule for *slightly* polydisperse melts, i.e. for blends in which the molecular sizes are so close together that the characteristic time constants of the components are not noticeably affected by the blending.

Introduction

Molecular dynamics theories and experimental observations have given a clear picture of the viscoelastic behavior of *monodisperse* linear flexible polymers, but questions remain concerning the effects of polydispersity. For example, it remains unclear how the longest relaxation time, $\lambda_{\max}$, of a polydisperse system depends on molecular weight distribution. One approach to understanding polydispersity effects is to study bidisperse blends of two components, each of them having a narrow molecular weight distribution, and to decompose the relaxation behavior of the blend into the contributions of the two components. This bidisperse blend approach has been taken by many researchers and the viscoelastic behavior is well documented. Most efforts have focused on polystyrene blends[1–8] but several researchers have looked at other blends, including poly(vinyl acetate),[9] polybutadiene,[10] and polyisoprene.[11] All of these blends exhibit the same general G' and G'' patterns which suggests a universal format for the blending rule.

In this study we only address the linear viscoelastic behavior of polymer blends in which both components are of sufficiently high molecular weight (above the so-called "entanglement molecular weight"). Contribution of smaller molecules could be included like a solvent effect but this is not the objective here.

Expectations are high for potentially inverting the blending rule and predicting molecular weight distributions from linear viscoelastic data. Most well known are the attempts of Tuminello and co-workers who predicted molecular weight distributions from a variety of linear viscoelastic material functions.[12–14] Tuminello's efforts as well as several other methods for relating viscoelastic behavior with the molecular weight distribution have been reviewed by Wasserman and Graessley[15] (who, in the same paper, also developed a very promising blending rule). We will return to this inversion problem in the discussion section below.

Empiricists typically express blending behavior in terms of the relaxation time spectrum, $H(\lambda)$, while theoretical work has focused on the relaxation modulus, $G(t)$. The relaxation modulus and $H(\lambda)$ contain the same material information and are related via a Laplace transform

$$G(t) = \int_0^\infty H(\lambda) e^{-t/\lambda}\, d\lambda/\lambda \qquad (1)$$

So far no definitive blending rule is known which can accurately predict the stress relaxation of the blend over a large time window and for a wide range of molecular weights and compositions. The earliest blending rule,[9] one which is consistent with the original reptation theory,[6] proposes the simple linear superposition

$$H(\lambda) = \sum_{i=1}^{N} w_i H_i(\lambda) \qquad (2)$$

where w_i is weight fraction of the ith component of the blend and H_i is the relaxation spectrum of a monodisperse melt with molecular weight M_i. Any continuous molecular weight distribution, $w(M)$, can be represented as a blend of discrete fractions, w_i, with molecular weight M_i. However, Ninomiya[9] already recognized that the stress relaxation behavior of the blends could not be described by a simple addition of the behavior of the monodisperse constituents. He recognized that blending affects the characteristic time scales of the components and proposed that the simple linear superposition rule would be improved by incorporating time shift factors, A_i, for each component in the blend:

$$H(\lambda) = \sum_{i=1}^{N} w_i H_i(\lambda/A_i) \qquad (3)$$

While this resulted in a significant improvement, it failed to capture the behavior of the blends over the entire time window of the experiments. Subsequently, Bogue et al.[1] argued that a quadratic blending rule was

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Table 1. Empirical Blending Rules Found in Literature

author(s)	blending rule
Ninomiya[9] (1959)	$H(\lambda) = \sum_{i=1}^{N} w_i H_i(\lambda/A_i)$
Bogue et al.[1] (1970)	$H(\lambda) = \sum_{i=1}^{N} \sum_{j=1}^{N} w_i w_j H_{ij}(\lambda/A_{ij})$
Prest and Porter[2,17] (1973)	$H(\lambda) = \sum_{i=1}^{N} B_i H_i(\lambda/A_i)$
Kurata et al.[3] (1974)	$H(\lambda) = \sum_{i=1}^{N} \sum_{j=1}^{N} \sum_{k=1}^{N} w_i w_j w_k H_{ijk}(\lambda/A_{ijk})$

required to represent relaxation data:

$$H(\lambda) = \sum_{i=1}^{N} \sum_{j=1}^{N} w_i w_j H_{ij}(\lambda/A_{ij}) \tag{4}$$

where H_{ij} represents some unknown relaxation function of the i chain entangled with the j chain and the time shifts, A_{ij}, are adjustable parameters. The empirical approach of Bogue and others[3,6,17] was to set the H_{ii} terms equal to H_i and then determine H_{ij} and A_{ij} from bidisperse blend experiments. This procedure was hampered by the fact that many parameters had to be determined from limited data.

A comparison of linear and quadratic blending rules lead Prest[2,17] to conclude that a quadratic blending rule was not necessary to represent the data but that a more general form of the linear blending rule was sufficient. He formalized an expression for the generalized linear blending rule

$$H(\lambda) = \sum_{i=1}^{N} B_i H_i(\lambda/A_i) \tag{5}$$

where B_i values are a function of the molecular weight distribution and are not equal to w_i. Prest was unable, however, to formulate an adequate expression for H_i, the relaxation spectrum of a sample of molecular weight M_i. We show in this work that with an appropriate function, $H_i(\lambda)$, to describe the monodisperse behavior, the generalized linear blending rule is sufficient to describe bidisperse blends.

Several blending rules (for dilute and concentrated blends) were proposed by Watanabe[6,7] on the basis of direct numerical calculations of the relaxation spectra of bidisperse blends. From such calculations, the weighting of the relaxation spectra of the long and short chains in the blend was inferred. In the case of dilute blends, an additional wedge-like spectrum was proposed to describe the behavior of a long chain completely surrounded by shorter chains. This involves additional parameters which might be difficult to evaluate or confirm by experiments. By using the linear blending rule of eq 5, we can test whether it is necessary to introduce such additional wedge-like spectra. A summary of proposed empirical blending rules is shown in Table 1. Once one has chosen a blending rule (e.g. eqs 2–5 or Table 1), a variety of linear viscoelastic material functions can be calculated.[18]

Much novel insight concerning entanglement behavior in polymers came from the reptation model[16,19] which predicts a simple linear blending rule (eq 2). Early efforts to predict the behavior of polydisperse polystyrene from the reptation model were not successful.[20–21] Later modifications of reptation considered concepts of constraint release/tube renewal[15,22–28] and of tube enlargement,[29] and better agreement with experiment was found.

Several of these models, including the double reptation concept of des Cloizeaux[28] and the Rubinstein, Helfand, and Pearson approach (RHP),[26] arrive at a quadratic blending rule (eq 4). These models have been formulated in terms of the relaxation modulus, $G(t)$:

$$G(t) = \sum_{i=1}^{N} \sum_{j=1}^{N} w_i w_j G_{ij}(t) \tag{6}$$

and give expressions for the cross term $G_{ij}(t)$ without introducing adjustable parameters. This makes these models very attractive, but the corresponding functions for $H_{ij}(\lambda)$ are not easily evaluated since they are related to the prescribed $G_{ij}(t)$ via an integral

$$G_{ij}(t) = \int_0^{\infty} H_{ij}(\lambda) e^{-t/\lambda} \, d\lambda/\lambda \tag{7}$$

It should be noted that these models do not require time shift factors ($A_{ij} = 1$), although experimental work[6–8,30] has clearly demonstrated the existence of such shifts in the longest relaxation time, $\lambda_{\max}$, of bidisperse blends. Blending rules based on the double reptation model (Table 2) have been proposed by several researchers with notable success (Tsenoglou,[35] Wasserman et al.[15]). Their range of validity might, however, be restricted to blends in which the molecular weights are fairly close together (slightly polydisperse blends, as defined below). This suggests the possibility that the molecular dynamics models have captured important aspects of the physics involved but require modification to account for time shifts.

Watanabe and Tirrell[27] developed a model which does include time shifts and which might effectively be expressed by eq 5. Their configuration-dependent constraint release model (CDCR), introduces the argument

Table 2. Theoretical Blending Rules Found in Literature

author(s)	blending rule	comments
Graessley and Struglinski[24] (1986)	$G(\mathrm{t}) = G_N^0 \sum_{i}^{N} w_i \mu_i(\mathrm{t}) R_i(t/A_i)$	$\mu_i(t)$ defined by reptation model; $R_i(t)$ defined by constraint release mechanism[a]
Rubinstein, Helfand, and Pearson[26] (1987)	$G(t) = G_N^0 \sum_{i}^{N} \sum_{j}^{N} w_i w_j \mu_i(t) R_j(t/A_j)$	$\mu_i(t)$ defined by reptation model; $R_i(t)$ defined by constraint release mechanism.[a]
Watanabe and Tirrell[27] (1989)	$G(t) = \sum_{i}^{N} w_i B_i' G_i(t/A_i)$	reptation + constraint release[a] (nonseparable)
Tsenoglou[35] (1987), des Cloizeaux[28] (1990)	$G(t) = (\sum_{i}^{N} w_i G_i^{1/2}(t))^2$	double reptation

[a] Constraint release modeled in each case as if the tube surrounding the chain behaves like a Rouse chain (Rouse, 1953).[36]

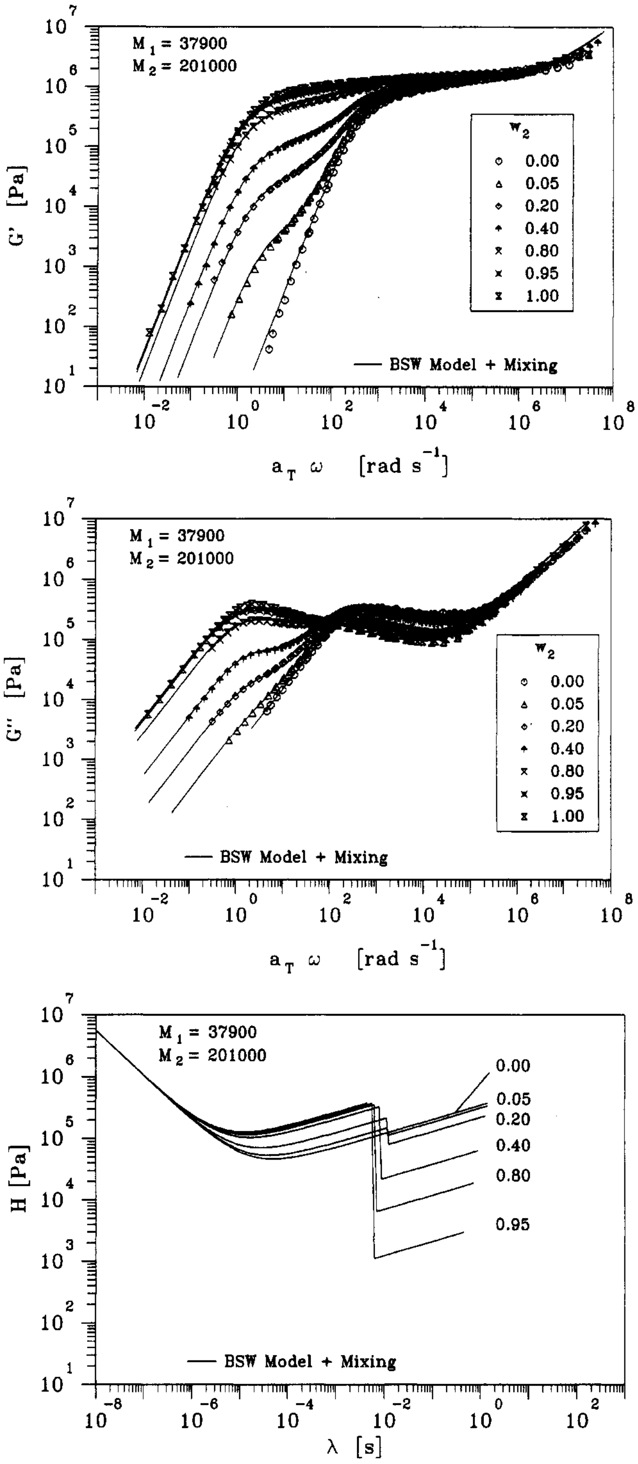

Figure 1. The (a) storage and (b) loss moduli of bidisperse polybutadiene (PBD) blends measured at 28 °C (the line through the data represents the model described by eq 4) and (c) the relaxation time spectra of bidisperse polybutadiene blends used to model the dynamic moduli in parts a and b. Both M_1 and M_2 are highly entangled. The BSW parameters are given in Table 3 and the shift factors are listed in Table 4. The BSW parameters are given in Table 3 and the shift factors are listed in Table 4.

that the constraint release mechanism and the reptation mechanisms are coupled. While the CDCR model does not capture all of the features of the linear viscoelastic behavior and was formulated only for the case of a small amount of long chains entangled in a matrix of shorter chains, its assumptions may give the correct functional form for the blending rule.

Table 3. The BSW Parameters of Polystyrene and Polybutadiene[34]

parameer	PS	PBD
G_N^0 (Pa)	228000	1650000
n_e	0.23	0.23
n_g	0.67	0.73
λ_c (s)	3e−4	4.04e−7
M_c (g/mol)	15200	2714
z	3.43	3.52
C_1	5.02	4.17
C_2 (K)	125.3	196.8
T_{ref} (°C)	180	28

Table 4. Shift Factors of Polybutadiene Blends: M_1 = 37 900 and M_2 = 201 000 g/mol

w_2	B_2	A_2	A_1
0.00	0.000		1.00
0.05	0.008	0.334	1.30
0.10	0.015	0.334	1.30
0.20	0.050	0.500	1.50
0.40	0.170	0.650	1.90
0.60	0.370	0.900	2.70
0.80	0.630	0.950	2.70
0.90	0.780	0.980	2.70
0.95	0.900	0.990	2.70
1.00	1.000	1.000	

In this study we analyze G' and G'' data with the most simple proposal of a blending rule, eq 5, that of a linear superposition of the component behavior. This provides important information since it shows that, if the most simple model already suffices within experimental error of the data, more sophisticated blending rules might not be extractable from the data. We represent the relaxation spectrum of the ith (nearly) monodisperse component, $H_i(\lambda)$, with the empirical BSW spectrum[31] and the generic parameters[34] of polystyrene or polybutadiene, respectively. These generic parameters are considered fixed in this approach. Only the vertical and horizontal shifting factors for the ith component, B_i and A_i respectively, are allowed to be adjustable. They will be evaluated by fitting eq 5 to the dynamic mechanical data of the blends. As will be shown, the linear blending rule is quite effective in describing the observed relaxation behavior, so that we can proceed to the main objective of this study which is the search for patterns in A_i and B_i as functions of composition, molecular weight, and molecular weight ratio. Particularly interesting is the effect of blending on the longest relaxation time, λ_{max}, of each component. We search for these patterns since they are an expression of the still unknown blending rules.

Experimental Section

Polybutadiene blends were prepared from two nearly monodisperse polymers with molecular weights of 201 000 and 37 900 g/mol respectively. Both of these polybutadiene molecular weights are highly entangled. The ratio of M_w/M_n is below 1.3 for both molecular weights and the cis, trans, and vinyl content is approximately 44:48:8 for both samples. The (nearly) monodisperse components were solution blended in toluene and then placed in a vacuum oven at 55 °C for 2 weeks. After that, the samples were weighed to ensure that the toluene had been removed. The dynamic moduli were measured on a Rheometrics Dynamic Spectrometer 7700 and parallel plate geometry. Strain levels were kept below 5% to remain in the linear viscoelastic limit. $G'(\omega)$ and $G''(\omega)$ master curves of the polybutadiene blends, Figure 1, were prepared by time-temperature shifting of dynamic mechanical data to a reference temperature of 28 °C. The temperature shift factors are listed in Table 3. The molecular weights and weight fractions for each blend are listed in Table 4.

Data on polystyrene blends was taken from Watanabe et al.'s work and the details of the experimental procedures have been published.[6,7] Tables 5 and 6 list the molecular

Table 5. Shift Factors of Polystyrene Blends: M_1 = 38 900 and M_2 = 427 000 g/mol

w_2	B_2	A_2	A_1
0.00	0.000		1.00
0.01	0.003	0.030	1.06
0.03	0.005	0.045	1.17
0.05	0.007	0.060	1.50
0.10	0.020	0.070	1.78
0.20	0.050	0.110	2.89
0.40	0.170	0.230	3.89
1.00	1.000	1.000	

Table 6. Shift Factors of Polystyrene Blends: w_2 = 0.01 and M_2 = 2 810 000 g/mol

M_1	B_2	A_2	A_1
23 400	0.001 00	0.000 23	0.90
38 900	0.000 80	0.001 00	1.10
72 400	0.000 55	0.006 50	1.00
124 000	0.000 40	0.040 00	1.20

weights and weight fractions for each blend. The ratio M_w/M_n for the polystyrene fractions was below 1.1.

The first set of polystyrene blends[6] consists of different compositions of two molecular weights (38 900 and 42 7000 g/mol). The lower molecular weight is very close to the entanglement molecular weight of polystyrene while the higher molecular weight is highly entangled. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, are displayed in Figure 2 at a reference temperature of 167 °C.

The second set of polystyrene blends[7] contains 1% of a high molecular weight component (2 810 000 g/mol) blended with 99% of several lower molecular weights. The high molecular weight in each blend is highly entangled, but the lower molecular weights (23 400, 38 900, 72 400, 124 000 g/mol) range from slightly entangled to highly entangled. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, are displayed in Figure 3 at a reference temperature of 167 °C.

Spectrum of Linear Flexible Monodisperse Polymers

Before one can advance the relaxation spectrum of bidisperse blends, a representation of the viscoelastic behavior of the monodisperse fractions should be chosen. There are several choices for modeling the linear viscoelastic behavior of a monodisperse linear flexible polymer. While several theoretical models seem to describe the monodisperse polymer well (reptation and constraint release,[26] reptation with contour length fluctuations[32]), these models are numerically cumbersome and cannot be easily adapted to the format of a generalized linear blending rule. One might choose to use the viscoelastic data of the monodisperse polymer itself as input to a blending rule, but it is difficult to separate the effects of the glass transition (independent of MWD for $M > M_c$) from the effects of the entanglement regime (dependent on MWD) in such data. For the purposes of this study, we use an empirical relaxation time spectrum (BSW spectrum) which has been shown to represent the viscoelasticity of (nearly) monodisperse polymers well and which conveniently separates the glass transition regime from the entanglement regime.[31] With "nearly" monodisperse polymers we mean polymers with M_w/M_n so close to unity that they behave rheologically like a perfectly monodisperse polymer.

The BSW spectrum for linear flexible monodisperse polymers may be defined as

$$H(\lambda) = \begin{cases} n_e G_N^0\left[\left(\dfrac{\lambda}{\lambda_{\max}}\right)^{n_e} + \left(\dfrac{\lambda}{\lambda_c}\right)^{-n_g}\right] & \text{for } \lambda \le \lambda_{\max} \\ 0 & \text{for } \lambda > \lambda_{\max} \end{cases} \tag{8}$$

where G_N^0 is the plateau modulus, $\lambda_{\max}$ is the longest

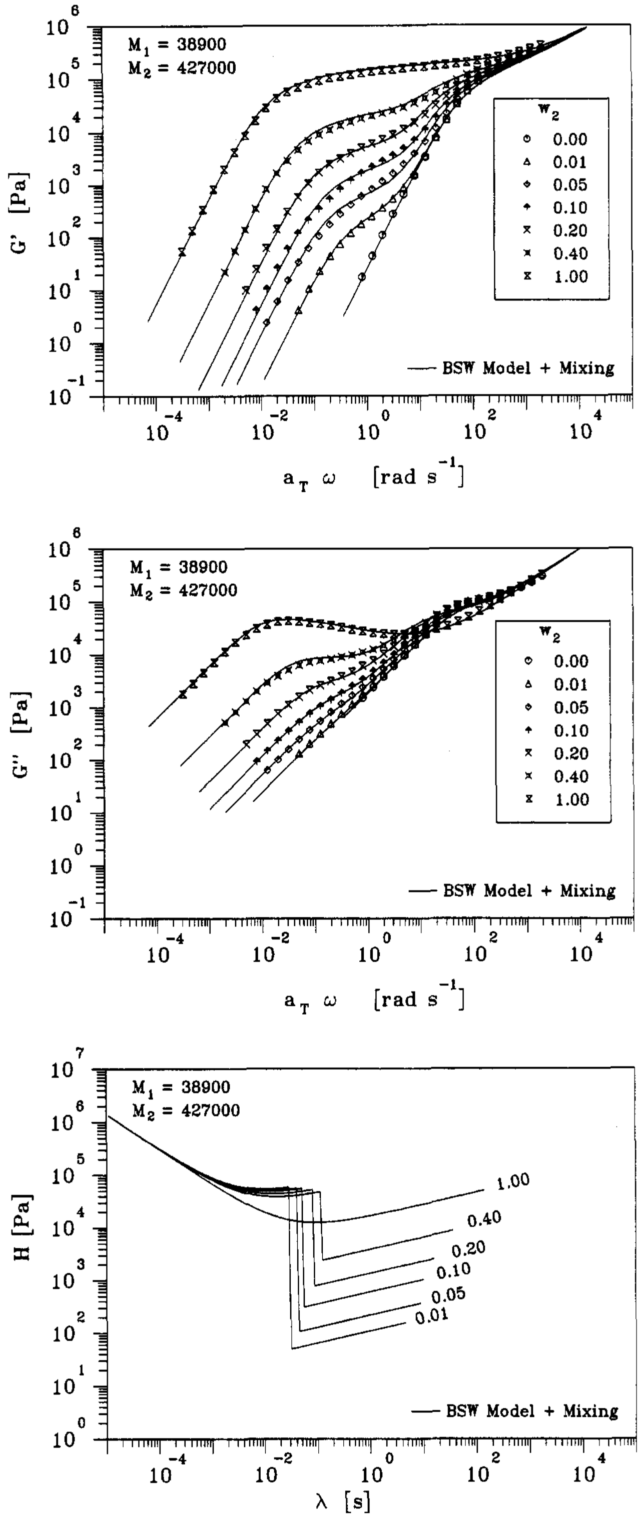

Figure 2. The (a) storage and (b) loss moduli of bidisperse polystyrene (PS) blends measured at 167 °C (Watanabe et al., 1984)[6] and (c) the relaxation time spectra of bidisperse polystyrene blends used to model the dynamic moduli in parts a and b. Component 1 is slightly entangled and component 2 is highly entangled. The line through the data represents the model described by eq 4. The BSW parameters are given in Table 3 and the shift factors are listed in Table 5.

relaxation time, n_e and n_g are the slopes of the spectrum in the entanglement and glass transition zones, respectively. The first term in eq 8, $H_e = n_e G_N^0(\lambda/\lambda_{\max})^{n_e}$, represents entanglement behavior while the second term, $H_g = n_e G_N^0(\lambda/\lambda_c)^{-n_g}$, represents the short time glass transition behavior. The longest relaxation time,

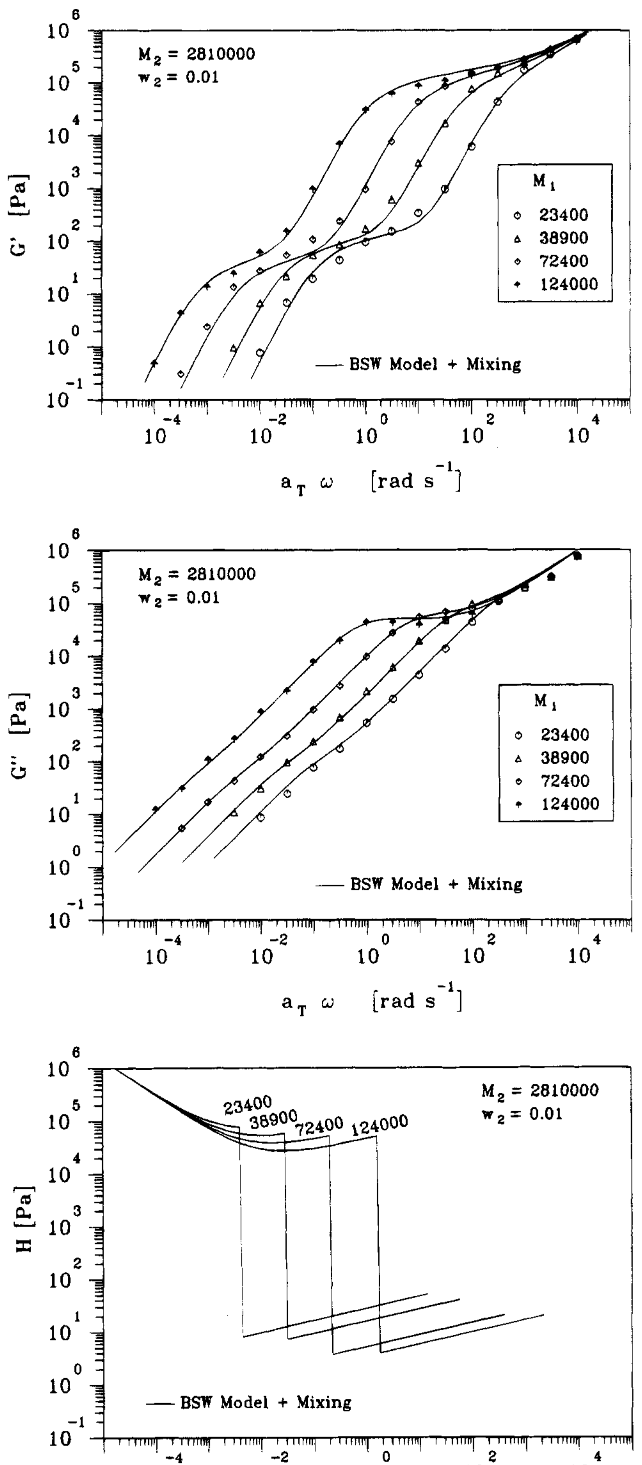

Figure 3. The (a) storage and (b) loss moduli of bidisperse polystyrene blends measured at 167 °C (Watanabe et al., 1985)[7] and (c) the relaxation time spectra of bidisperse polystyrene blends used to model the dynamic moduli in parts a and b. The 1 chain in the blend varies from slightly entangled (M_1 = 23 400 g/mol) to highly entangled (M_1 = 124 000 g/mol). The 2 chain is highly entangled. The line through the data represents the model described by eq 4. The BSW parameters are given in Table 3 and the shift factors are listed in Table 5.

$\lambda_{\max}$, scales with the molecular weight, M:

$$\lambda_{\max} = \lambda_c (M/M_c)^z \tag{9}$$

where M_c is a characteristic molecular weight for the onset of entanglement behavior and z is the scaling exponent of the viscosity–molecular weight relation which has values between 3.3 and 3.7.[33] A schematic of the BSW spectrum is shown in Figure 4. Jackson et al.[34] developed a method for determining the BSW parameters for a given material and gave generic parameter values for polystyrene and polybutadiene, see Table 3.

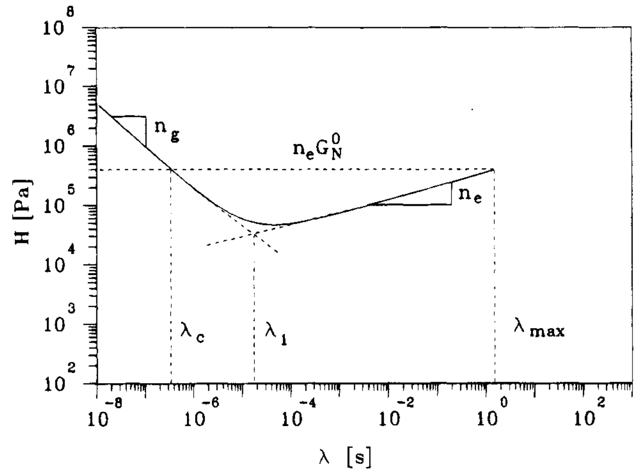

Figure 4. A schematic of the BSW model for the relaxation spectrum of a monodisperse linear flexible polymer. The five parameters that define the spectrum are the glass transition slope (n_g), the entanglement slope (n_e), the plateau modulus (G_N^0), the crossover relaxation time (λ_c), and the longest relaxation time ($\lambda_{\max}$).

The longest relaxation time, $\lambda_{\max}$, as defined by eq 9 can be compared to the definition of the average relaxation time of the system, $\langle\lambda\rangle$:

$$\langle\lambda\rangle = \frac{\int_0^\infty H_e(\lambda)\lambda\, d\lambda}{\int_0^\infty H_e(\lambda)\, d\lambda} = \left(\frac{n_e + 1}{n_e + 2}\right)\lambda_{\max} \tag{10}$$

where H_e is the entanglement portion of the relaxation time spectrum as defined by the first term in eq 8. For the monodisperse material $\lambda_{\max}$ and $\langle\lambda\rangle$ are proportional, but this does not hold for the polydisperse case. Efforts have been made[7] to track the dependence of $\lambda_{\max}$ on the molecular weight distribution by evaluating eq 10 for the highest molecular weight component of the blend. To do so, however, one is forced to propose a blending rule which may influence the evaluation of $\lambda_{\max}$.

The zero shear viscosity, η_0, and the recoverable compliance, J_e^0 of a nearly monodisperse polymer can also be represented in terms of the BSW parameters[31]

$$\eta_0 = \int_0^{\lambda_{\max}} H_e(\lambda)\, d\lambda = \frac{n_e}{n_e + 1} G_N^0 \lambda_c (M/M_c)^z \tag{11}$$

$$J_e^0 = \frac{1}{\eta_0^{\,2}} \int_0^{\lambda_{\max}} H_e(\lambda)\lambda\, d\lambda = \frac{1}{G_N^0}\left(1 + \frac{1}{n_e^{\,2} + 2n_e}\right) \tag{12}$$

These material constants have been measured by numerous researchers to determine their dependence on molecular weight and molecular weight distribution.[4,6,17,33]

Modeling with the Generalized Linear Mixing Rule

We postulate that the relaxation behavior of polydisperse melts is largely determined by the generic BSW parameters of the polymer. These parameters are known from modeling of nearly monodisperse melts with different molecular weights. The only additional parameters in the generalized linear blending rule (eq 5) are the shift factors A_i and B_i. This leads to the following expressions for the *longest relaxation time*, $\lambda_{\max,ib}$, of the ith component of the blend

$$\lambda_{\max,ib} = A_i \lambda_{\max,i} \tag{13a}$$

and the *average relaxation time*, $\langle\lambda\rangle_{ib}$, of the ith component of the blend

$$\langle\lambda\rangle_{ib} = A_i \langle\lambda\rangle_i \tag{13b}$$

where $\lambda_{\max,i}$ is calculated from eq 9 and the average relaxation time of the pure component $\langle\lambda\rangle_i$, is calculated from eq 10. The zero shear viscosity, η_0, and equilibrium compliance, J_e^0, of the polydisperse blend can also be expressed in terms of the generalized linear mixing rule

$$\eta_0 = \sum_{i=1}^{N} B_i A_i \eta_{0,i} \tag{14}$$

$$J_e^0 = \sum_{i=1}^{N} B_i A_i^2 J_{e,i}^0 \eta_{0,i}^2 / \left(\sum_{i=1}^{N} B_i A_i \eta_{0,i}\right)^2 \tag{15}$$

where the subscript i refers to the component with molecular weight M_i and the parameters $\eta_{0,i}$, and $J_{e,i}^0$ are calculated from eqs 11 and 12. A successful blending rule should accurately predict the behavior of η_0 as a function of M_w. An even more severe criterion for a successful blending rule is the prediction of J_e^0 which is very sensitive to the molecular weight distributions.[17]

Finally, the vertical shift factors, B_i, of the generalized linear mixing rule are constrained by a plateau modulus, G_N^0, which does not depend on molecular weight or molecular weight distribution. Given the definition of the plateau modulus

$$G_N^0 = \int_0^{\lambda_{\max}} H_e(\lambda)\, d\lambda/\lambda \tag{16}$$

it can be demonstrated from eq 5 that

$$G_N^0 = G_N^0 \sum_{i=1}^{N} B_i \rightarrow \sum_{i=1}^{N} B_i = 1 \tag{17}$$

This constraint on the vertical shift factors reduces the number of fitting parameters by one.

Procedure for Modeling Bidisperse Blend Data

The modeling of the dynamic moduli of the blends proceeds in five steps.

1. Calculation of Monodisperse Relaxation Spectra. The monodisperse spectra (Figure 4) for each component, $H_i(\lambda)$, are calculated from eqs 8–9 using the parameters for polystyrene and polybutadiene listed in Table 3.

$$H_1(\lambda) = n_e G_N^0 \left(\frac{\lambda}{\lambda_c}\left(\frac{M_c}{M_{w1}}\right)^z\right)^{n_e} + H_g(\lambda) \tag{18a}$$

$$H_2(\lambda) = n_e G_N^0 \left(\frac{\lambda}{\lambda_c}\left(\frac{M_c}{M_{w2}}\right)^z\right)^{n_e} + H_g(\lambda) \tag{18b}$$

The subscript 1 refers to the shorter chain in the bidisperse blend while the subscript 2 refers to the longer chain. The term $H_g(\lambda)$ is the contribution of the short time glass transition which does not depend on molecular weight.

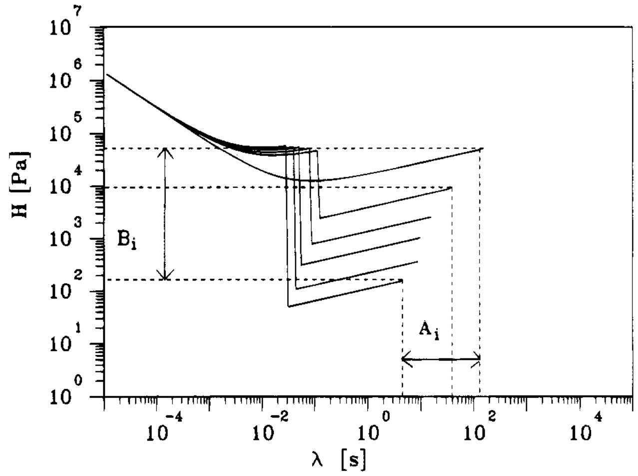

Figure 5. A schematic of the relaxation time spectrum of a bidisperse blend as a linear superposition of the spectra of the monodisperse components. The monodisperse spectra are shifted on both the time axis and the modulus axis. The monodisperse spectra are defined by the BSW parameters. The vertical shift factor of the ith fraction is denoted B_i and the horizontal shift factor of the ith fraction is denoted A_i.

2. Initialization of Time Shift Factors and Weighting Factors. The time shift factors, A_1 and A_2, and the weighting factor, B_2, are initialized.

$$A_1 = 1 \tag{19a}$$

$$A_2 = 1 \tag{19b}$$

$$B_2 = (w_2)^2 \tag{19c}$$

The second weighting factor B_1 is calculated from eq 17.

$$B_1 = 1 - B_2 \tag{19d}$$

It is clear that B_2 goes to zero for pure component 1 and that B_2 goes to 1 for pure component 2.

3. Evaluation of the Generalized Linear Blending Rule. The above parameter values are entered as initial values into the blending rule for disperse blends. The relaxation spectrum of the blend (Figure 5) is calculated from eq 5 using $H_i(\lambda)$ as calculated in step 1 and using the shift factors from step 2:

$$H(\lambda) = B_1 H_1(\lambda/A_1) + B_2 H_2(\lambda/A_2) \tag{20}$$

where $H(\lambda)$ is the spectrum of the blend.

4. Calculation of the Moduli. The dynamic moduli can be defined in terms of the relaxation spectrum:[18]

$$G'(\omega) = \int_0^\infty H(\lambda) \frac{\omega^2\lambda^2}{1+\omega^2\lambda^2} \frac{d\lambda}{\lambda} \tag{21}$$

$$G''(\omega) = \int_0^\infty H(\lambda) \frac{\omega\lambda}{1+\omega^2\lambda^2} \frac{d\lambda}{\lambda} \tag{22}$$

The relaxation spectrum from step 3 is substituted into eqs 21–22 to evaluate $G'(\omega)$ and $G''(\omega)$ and an on-screen graphical comparison is made between the modeled moduli and the data.

5. Iteration. If the model fails to agree with the data then values of A_1, A_2, and B_2 and changed incrementally and the procedure is repeated. This manual iteration continues until the best graphical superposi-

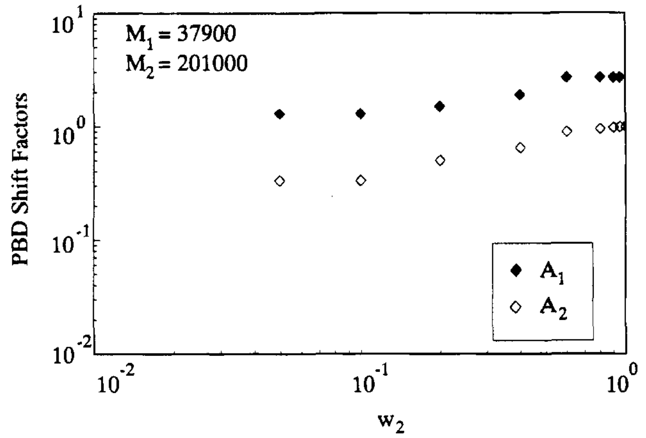

Figure 6. The horizontal shift factors of each molecular weight in the bidisperse polybutadiene blends displayed in Figure 1a–c.

tion of modeling and data is achieved. Once the final parameters have been obtained, the zero-shear viscosity and equilibrium compliance are calculated from eqs 14 and 15.

Modeling Results

The dynamic moduli for each of the blends were calculated with the above procedure (eqs 21 and 22) and are shown as solid lines in Figures 1a,b, 2a,b, and 3a,b. The corresponding relaxation spectra from eq 20 are displayed in Figures 1c, 2c, and 3c, respectively. The BSW constants of polystyrene and polybutadiene were evaluated from nearly monodisperse data[34] and are used without adjustment, while the shift parameters A_1, A_2, and B_2 are taken from the best fit of the measured moduli as described in step 5 above.

The time shift factors, A_1 and A_2, for the highly entangled polybutadiene blends are displayed in Figure 6. Tabulated values of the shift factors are listed in Table 4. By definition the time shift factors, A_i, are given as

$$A_i = \lambda_{\max,ib}/\lambda_{\max,i} \tag{23}$$

where $\lambda_{\max,ib}$ is the longest relaxation time of the ith chain in the blend and $\lambda_{\max,i}$ is the longest relaxation time of the ith chain in a monodisperse sample. As w_i approaches one, A_i must approach one. This trend is evident in Figures 6 where A_2 goes to one as w_2 goes to one, allowing recovery of the pure component properties.

The polystyrene blends of Figure 2 have time shift factors (Table 5) which show similar trends to the polybutadiene blends, even though the polystyrene blends are much less entangled. The time shift factors, A_1 and A_2, for these polystyrene blends are displayed in Figure 7. It is evident that A_1 and A_2 of the polybutadiene blends in Figure 6 are much closer to one than the polystyrene factors plotted in Figure 7. These factors show the same limiting behavior as w_2 goes to one as the polystyrene factors in Figure 6.

Likewise, the weighting factors, B_2, of the blends must go to zero as w_2 goes to zero and must go to one as w_2 goes to one in order to recover the monodisperse behavior. This behavior is observed for the polybutadiene weighting factors in Figure 8 (Table 4). The polystyrene factors, B_2, in Figure 8 (Table 5) appear to lie nearly on the same curve as the polybutadiene weighting factors. There may be differences as w_2 goes to zero that cannot be seen in Figure 8 due to the lack of polybutadiene data. This suggests that above some threshold composition, $w_c \cong 0.1$, B_2 is independent of molecular weight.

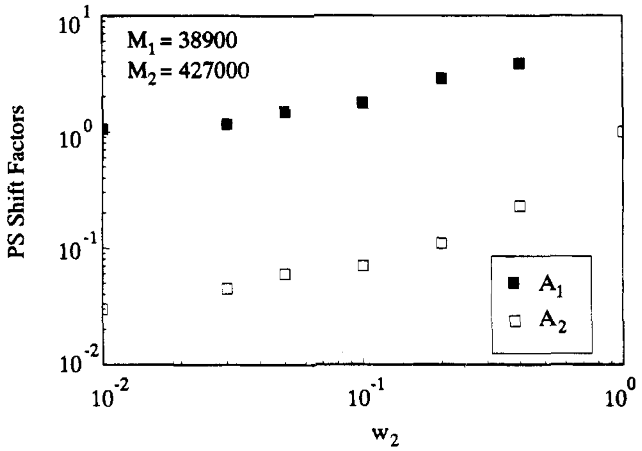

Figure 7. The horizontal shift factors of each molecular weight in the bidisperse polystyrene blends displayed in Figure 2a–c.

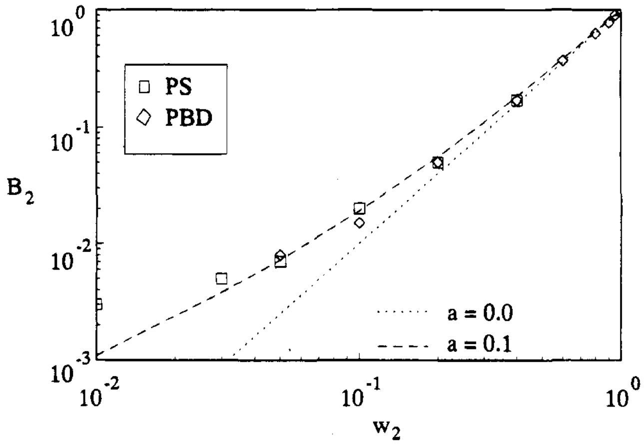

Figure 8. The vertical shift factors of the high molecular weight component of the polystyrene and polybutadiene blends in Figures 1a–c and 2a–c. The vertical shift factor of the low molecular weight component for each blend is $B_1 = 1 - B_2$. The dashed line represents eq 27 with $a = 0.1$. The dotted line represents eq 27 with $a = 0.0$.

The polystyrene data of Figure 3 were also modeled with the above procedure and the shift factors obtained are tabulated in Table 6. These blends range from slightly entangled (M_1 = 23 400 g/mol) to highly entangled (M_1 = 124 000 g/mol). The composition of high molecular weight is $w_2 = 0.01$ in all of these blends. The time shift factors of the high molecular weight component of these blends, A_2, are plotted in Figure 9 (open diamonds). Since the variable being changed in these blends is M_1, A_2 is plotted versus the ratio M_1/M_2. Also included in Figure 9 is one data point from the blends listed in Table 5 for the case of $w_2 = 0.01$ (open circle). It is evident that A_2 approaches one as M_1/M_2 approaches one. For these blends, the time shift factor, A_1, of the major component (Table 6) is nearly one and does not change noticeably.

The weighting, B_2, of the polystyrene blends in Figure 5 (Table 6) are plotted in Figure 10 (open diamonds) versus the ratio M_1/M_2. For these blends, the value of M_2 = 2 810 000 g/mol is constant. It appears that B_2 goes to $(w_2)^2$ as M_1 approaches M_2. This suggests that there is a region of M_1 and M_2 where $B_2 \cong (w_2)^2$. The blend with $w_2 = 0.01$ from Figure 2 (Table 5) is also displayed (open circle). The weighting factor, B_2, of this blend (Table 5) does not have the same dependence on the ratio M_1/M_2 as the blends of Figure 3 (Table 6).

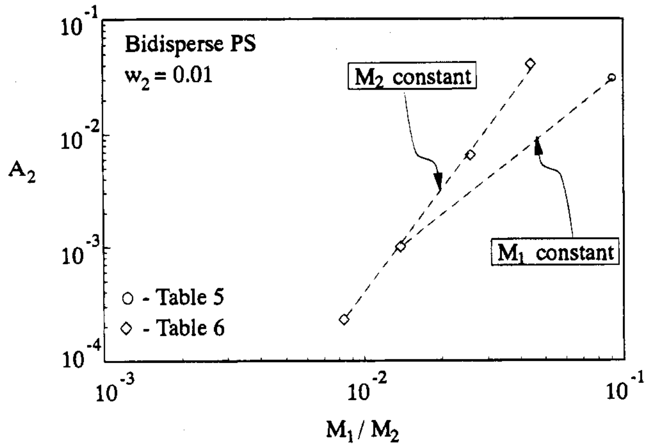

Figure 9. The horizontal shift factors, A_2 (open diamonds), of the high molecular weight component of the polystyrene blends displayed in Figure 3a–c. The low molecular weight of the blend has $A_1 \simeq 1$. One data point for the blend with $w_2 = 0.01$ from the polystyrene blends in Figure 2a–c is also included (open circle).

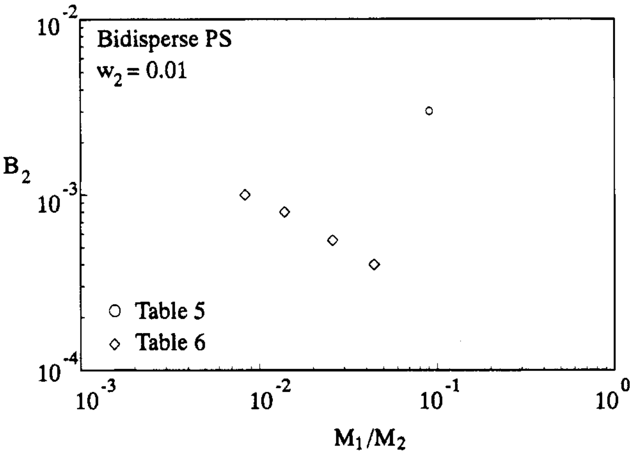

Figure 10. The vertical shift factors (open diamonds) of the high molecular weight component of the polystyrene blends displayed in Figure 3a–c. The vertical shift factor of the low molecular weight component for each blend is $B_1 = 1 - B_2$. One data point for the blend with $w_2 = 0.01$ from the polystyrene blends in Figure 2a–c is also included (open circle). The dashed line represents eq 27 with $a = (bM_1^cM_2^c)/M_c^{2c}$ where $b = 0.0461$ and $c = -0.66$.

To further demonstrate the agreement between the model and the data, the zero-shear viscosity and the equilibrium compliance were calculated from eqs 14 and 15 for each of the PBD blends in Figure 1. The BSW parameters were taken from Table 3 and the shift factors from Table 4. A comparison of the model predictions and the measured viscosities (limit of $\eta^*(\omega)$ and ω goes to zero) is made in Figure 11. Likewise, a comparison of the measured compliances (limit $J'(\omega)$ as ω goes to zero) and the model is made in Figure 12.

Discussion

We approach the polydispersity problem by gradually increasing the complexity. The starting condition is set by the relaxation of the monodisperse polymer. In this study we experimented with a range of bidisperse polymers and propose a simple blending rule for slightly polydisperse polymers. Highly polydisperse polymers will be studied in the future but they are not considered in this paper.

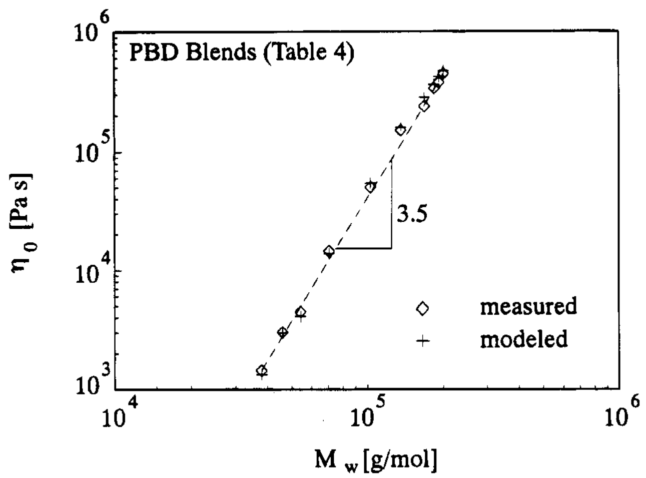

Figure 11. The zero-shear viscosities, η_0, of the polybutadiene blends in Figure 1. The diamond symbols represent the measured dynamic viscosities, η^*, in the limit of low frequency and the crosses represent the calculated viscosities from eq 14. The BSW parameters used are in Table 3 and the shift factors are in Table 4.

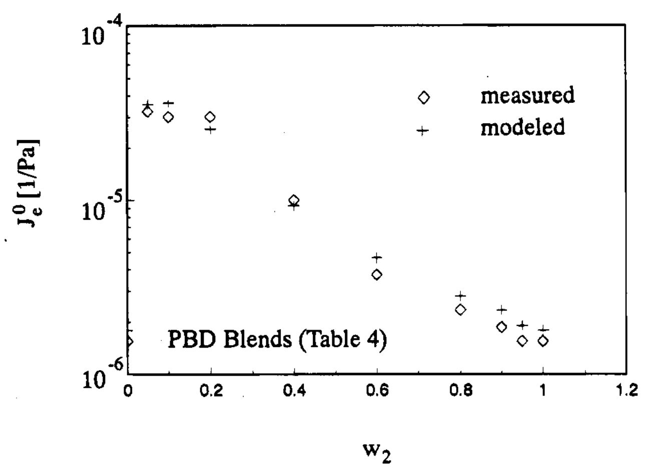

Figure 12. The equilibrium compliances, J_e^0, of the polybutadiene blends in Figure 1. The diamond symbols represent the measured storage compliances, $J'(\omega)$, in the limit of low frequency and the crosses represent the calculated viscosities from equation 15. The BSW parameters used are in Table 3 and the shift factors are in Table 4.

Implications of the Generalized Linear Blending Rule. We compare the generalized linear blending rule to the quadratic blending rule of eq 3 in order to derive an expression for the weighting factors B_i which is consistent with the data in Figures 8 and 10. If we set the two rules equal

$$\sum_{i=1}^{N} B_iH_i = \sum_{i=1}^{N}\sum_{j=1}^{N} w_iw_jH_{ij} \tag{24}$$

we can develop constraints on the quadratic rule which make it equivalent to the generalized linear rule. Any definition of H_{ij} as a linear superposition of H_i and/or H_j will reduce to a generalized linear blending rule. When we specify H_{ij} in the simplest form

$$H_{ij} = a_{ij}H_i \tag{25}$$

or conversely $H_{ji} = a_{ji}H_j$, we can express the vertical shift factor B_i

$$B_i = w_i\sum_{j=1}^{N} a_{ij}w_j \tag{26}$$

For a bidisperse blend, $a = a_{21} = 2 - a_{22}$ and $a_{11} = a_{22}$

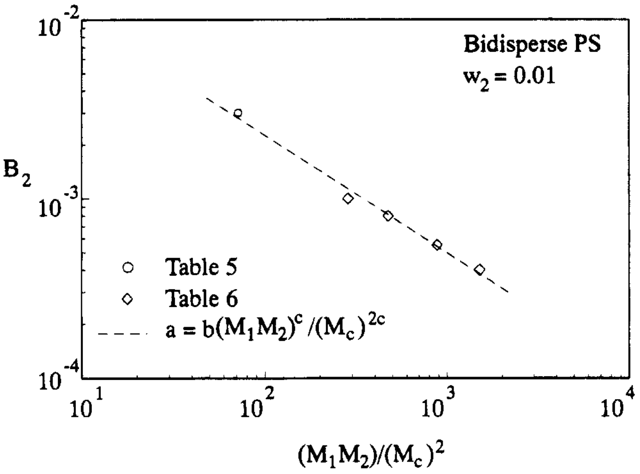

Figure 13. The vertical shift factors (open diamonds) of the high molecular weight component of the polystyrene blends displayed in Figure 3a–c. One data point for the blend with $w_2 = 0.01$ from the polystyrene blends in Figure 2a–c is also included (open circle). The dashed line represents eq 27 with $a = (bM_1^cM_2^c)/M_c^{2c}$ where $b = 0.0461$ and $c = -0.66$.

$= 1$. This gives a simple form for B_2

$$B_2 = w_2^{\,2} + aw_2w_1 \tag{27}$$

The dashed line in Figure 8 is calculated from eq 27 with $a = 0.1$ One can also compare the predictions of eq 27 to the weighting factors in Figure 10. In this case, the molecular weight dependence of B_2 is contained in the parameter a. The dashed line in Figure 13 was calculated using the relation, $a = (bM_1^cM_2^c)/M_c^{2c}$, and equation 27 with $b = 0.0461$ and $c = -0.66$. Thus, a possible interpretation of the generalized linear blending rule is that it is a special case of the quadratic blending rule where the H_{ij} terms are constrained to the form of eq 25.

This interpretation allows us to express the relaxation modulus as

$$G_{ij} = a_{ij}G_i \tag{28}$$

which can be easily compared to two of the models presented in Table 2[26,28]

$$G_{ij} = (G_iG_j)^{1/2} \text{ (des Cloizeaux, 1990)} \tag{29a}$$

$$G_{ij} = \mu_iR_j \text{ (Rubinstein et al., 1987)} \tag{29b}$$

where the subscript i refers to the chain and the subscript j refers to the matrix. There are two important implications resulting from eq 28:

(1) The a_{ij} term is not *necessarily* separable. This would indicate that the reptation mechanism (i-chain) and the constraint release mechanism (j-tube) may be coupled. This would be consistent with the assumptions of the CDCR model.

(2) In the event that the a_{ij} term is separable, i.e. $a_{ij} = f_ig_j$, it is not time dependent. This would mean that the constraint release mechanism (j-tube) is not time dependent in contrast to the examples in eq 29.

Simple Blending Rule for Slightly Polydisperse Polymers. There are some simplified heuristics one can draw from the data in Figures 6–10. It can be seen that the time shift factors, A_i, approach unity. Also, the PBD factors in Figure 6 are noticeably closer to unity than the corresponding factors for PS in Figure 7. This occurs because M_1/M_2 for PBD is closer to one. This is confirmed by the data in Figure 9 where it is evident that A_2 is approaching one as M_1/M_2 approaches one. This result allow us to set $A_i = 1$ for blends in which the molecular weights of the components are sufficiently close to each other. This leads to the definition of *slightly polydisperse* polymers for which the molecular sizes are so close together that the rheological time constants of the components are not altered, $A_i \approx 1$.

The weighting factor, B_i, can also be simplified for slightly polydisperse polymers that are highly entangled. In Figure 8, it is evident that the shift factors approach $(w_2)^2$ for $w_2 > w_c$, where w_c is some cut off. Figure 10 then shows that for the case of $w_2 = 0.01$, B_2 approaches $(w_2)^2$ as M_1M_2 increases. This implies that the value of w_c goes to 0 as M_1M_2 increases. Therefore, for a slightly polydisperse polymer that is highly entangled, B_2 can be represented as $(w_2)^2$ (dotted line in Figure 8). It has previously been shown that when this result is extended to the polydisperse case one obtains a blending rule[8]

$$B_i = w_i(w_i + 2\sum_{j=i+1}^{N} w_j) \qquad M_i < M_{i+1} \tag{30}$$

We can rewrite the blending rule now,

$$H(\lambda) = \sum_{i=1}^{N} w_i(w_i + 2\sum_{j=i+1}^{N} w_j)H_i(\lambda) \tag{31}$$

This simplified rule may be applied to slightly polydisperse polymers.

The bidisperse approach can be extended to highly polydisperse systems only after an analytical expression has been derived for the time shift factors, A_i, and the weighting factors B_i, as a function of M_1 and M_2. This can be done experimentally by considering additional bidisperse blends. Furthermore, molecular dynamics models may be modified to bring their predictions in line with the experimental evidence.

Conclusions

We have demonstrated that a generalized linear blending rule can successfully describe $G'(\omega)$ and $G''(\omega)$ for bidisperse blends. This class of blending rule may be interpreted as a linear approximation of the well-known quadratic blending rules. Furthermore, this type of blending rule is consistent with the form of blending rule obtained from the CDCR model.

Use of the generalized linear blending rule has allowed an experimental determination of the shifts, A_i, of the relaxation times associated with each component of the blend. These time shift factors clearly depend upon the molecular weight and the molecular weight ratio. Further work on bidisperse blends with high molecular weights and different M_1/M_2 ratios might be required to clarify the patterns in these shift factors.

The weighting factors, B_i, associated with the generalized linear blending rule are not equal to w_i. They are reasonably well described by the relation

$$B_2 = (w_2)^2 + aw_1w_2 \tag{32}$$

where a has a value of about 0.1 for moderate differences between M_1 and M_2. Beyond that, it is a function of M_1 and M_2. Additional work should include a complete mapping of a as a function of M_1/M_2 for weight fractions of w_2 less than 0.1.

The patterns suggested from the weighting factors (Figures 8 and 10) and the time shift factors (Figures 6, 7, and 9) should reflect the blending rule of these materials. Comparison of these results with the predictions of constraint release theories may help in a reformulation of such theories to better reflect the viscoelastic behavior of polydisperse systems.

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