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Molecular Weight Polydispersity Effects on the Viscoelasticity of Entangled Linear Polymers

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ABSTRACT: A molecular model is developed to explain the viscoelastic behavior of entangled homopolymer blends of an arbitrary molecular weight distribution in the terminal relaxation regime. This is accomplished by analyzing the entanglement architecture and molecular dynamics of the temporary network formed by the intermeshing species. It is assumed that coupling between any two macromolecular components along a single chain is random and that this occurs proportionally to the fractional participation of these same components in the blend as a whole. The population densities and lifetimes of the various types of entanglements among chains of similar or dissimilar length are thus calculated and related to the composition and corresponding properties of the monodisperse polymeric precursors. These results are then utilized in the derivation of simple blending rules for the time-dependent relaxation modulus, the dynamic moduli, the viscosity, and the recoverable compliance of the dense homopolymer mixtures. The theoretical predictions are compared with experimental evidence for the binary case.

Introduction

The study of the effect of molecular weight distribution on the rheology of polymer melts is one of the central concerns of macromolecular science.¹⁻²² This knowledge contributes to the optimization of material formulations by matching them to particular processing and product needs. The present work is an attempt to provide a molecular explanation of the terminal viscoelastic behavior in homopolymer blends, i.e., in polymer mixtures composed of two or more entangled polymeric species of identical chemistry and molecular architecture but dissimilar molecular weight. This is accomplished by calculating the number of densities and lifetimes of the various kinds of entanglements formed between chains of equal and unequal size. The knowledge on the dynamics of dissolution and renewal of the temporary polymeric network is then used to predict the rate of stress relaxation progression and to estimate the viscosity, elasticity, and dynamic moduli of the polydisperse homopolymer blends.

The fundamental property describing the linear viscoelastic behavior of a liquid composed of long, flexible polymer chains is the shear stress relaxation modulus, $G(t)$, defined as the time decaying ratio of stress, $\sigma(t)$, over strain, γ , after a step-strain shear deformation:

$$G(t) = \sigma(t)/\gamma \quad (1)$$

The zero shear rate viscosity, η , and recoverable compliance, J_e° , which are corresponding measures of the polymer fluidity and elasticity, may then be obtained from the following relationships:^{23,24}

$$\eta = \int_0^\infty G(t) dt \quad (2)$$

$$\eta^2 J_e^\circ = \int_0^\infty t G(t) dt \quad (3)$$

According to the network theories of dense polymer systems, the stress relaxation modulus depends on the extent of physical coupling between macromolecules and the rate of conformational renewal of the individual chains. In a fluid composed of entangled polymers of uniform molecular weight, M_i , a measure of the interchain associations is the number of primitive steps per chain, N_{i0} (i.e., the number of chain subsegments confined by two

consecutive entanglements). This is equal to

$$N_{i0} = M_i/M_e \quad (4)$$

where M_e is the molecular weight between entanglements, a physical parameter independent of the polymer molecular weight, but which decreases with chain flexibility and increases with dilution in a low molecular weight solvent. At quiescent conditions or under small deformations N_{i0} remains constant in value, although the entanglements of an individual chain with its neighbors are continuously dissolved and reformed, subject to the Brownian motion of the polymer molecules.

A measure of the molecular agility and, consequently, of the rate of network renewal is the time decaying fraction, $F_i(t)$, of the original steps still surviving at time t after an initial observation:

$$N_i(t) = N_i(0)F_i(t) = (M_i/M_e)F_i(t) \quad (5)$$

Here, $N_i(t)$ is the number of the original segments still remaining intact, $N_i(0) = N_{i0}$ and, evidently, $F_i(0) = 1 \geq F_i(t) \geq 0 = F_i(\infty)$. The functional form of $F_i(t)$ depends on the large-scale architecture of the macromolecular unit (linear, star, branched, etc.). Its rate of decrease with time is controlled by the molecular size and frictional resistance during the molecular motion. For the case of flexible linear chains, the most credible way of estimating $F_i(t)$ is provided by the reptation theory.²⁵⁻²⁷ According to this theory, entangled chains rearrange their conformations by curvilinear diffusion along their own contours. This motion is assumed to take place within a medium of permanent topological obstacles representing the surrounding entanglements. For a monodisperse system, the reptation theory predicts

$$F_i(t) = F(t/\tau_i) \simeq \exp(-t/\tau_i) \quad (6)$$

where τ_i is the characteristic relaxation time

$$\tau_i \simeq \frac{\langle R_i^2 \rangle}{36D_i} \simeq \frac{N_i(0)\langle R_i^2 \rangle M_i \zeta}{12kTm} = \alpha M_i^3 \quad (7)$$

$\langle R_i^2 \rangle$ is the end-to-end distance of the chain ($\langle R_i^2 \rangle \sim M_i/m$), D_i the self-diffusion coefficient, ζ the monomeric friction coefficient, m molecular weight of the monomeric unit, k the Boltzmann constant, and T the temperature.

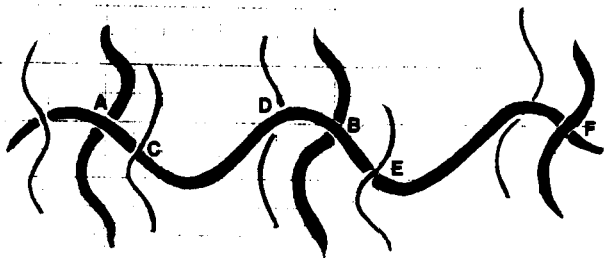


Figure 1. Entanglements and molecular segmentation in a homologous binary blend. Lines of variable thickness signify polymers of dissimilar length (e.g., thick line represents a long chain) and entanglements are represented by (lettered) line interceptions. Segments AB and BF are LL steps while segments CD or DE are LS steps (e.g., LS signifies a step lying on a long chain and defined by two successive entanglements with short chains).

In order to calculate the time-dependent stress relaxation modulus, the classical theory of rubber elasticity is adopted for the case of temporary networks. In other words, it is assumed that the stress value at any time t after a sudden strain imposition is proportional to the number density of the original ($t = 0$) primitive steps still surviving at that time:

$$G_i(t) = kT\nu_i N_i(t) = (RT\rho/M_e)F_i(t) = G_N^0 F_i(t) \quad (8)$$

where ν_i is the number of i chains per unit volume:

$$\nu_i = \rho N_A / M_i \quad (9)$$

ρ is the polymer density, N_A is the Avogadro number, R is the gas constant, and G_N^0 ($RT\rho/M_e$) is the plateau modulus, an index of material rigidity.

Molecular Dynamics in Polydisperse Networks

In a network of chains of unequal size, as opposed to a monodisperse system, there is no qualitative equivalence between the different interchain associations and the primitive steps they define. The average lifetime of a particular entanglement is proportional to the combined length of the two chains from which it is formed. Consequently, primitive steps lying on and defined by the longest chains are the last to relax. The number of different steps in the network and their corresponding lifetimes can actually be calculated. Let us consider a homopolymer blend composed of entangling molecules of n different sizes; the molecular weight of the i th component ($i = 1, 2, \dots, n$) is equal to M_i and its volume fraction is ν_i . Provided that all $M_i \gg M_e$, the number of entanglements (or primitive steps) per chain (N_{i0}) is again given by eq 4.

Let the index ij characterize a primitive step lying on an i polymer chain (of molecular weight M_i) and defined by two consecutive entanglements with two j chains (of molecular weight M_j) (Figure 1). This deliberately abstracted way of looking at the network (in terms of overlapping segments) establishes a convenient regrouping of the primitive step constituents according to their origin and lifetime expectancy.²⁹ The number of the ij steps surviving at time t after an initial counting is $N_{ij}(t)$ and the total number of steps per i chain in the mixture is $N_i(t)$. Neglecting end effects ($N_i \gg 1$), the total number of steps along a single chain is equal to the sum of the number of entanglements formed along its path, irrespective on whether these physical junctions are caused by neighbors of similar or dissimilar length:

$$N_i(t) = \sum_{j=1}^n N_{ij}(t) \quad (10)$$

It is also reasonable to assume that the number of couplings

of an i chain with chains of its own size decreases linearly with the volume fraction of the i species in the blend, and that the ii steps are renewed at a rate identical with the one prevailing in the unmixed state:

$$N_{ii}(t) = (M_i/M_e)\nu_i F_i(t) \quad (11)$$

On the other hand, the fraction of entanglements along an i chain caused by random interactions with j chains should be equal to the fractional participation of the j steps in the total step population in the blend:

$$\frac{N_{ij}(t)}{N_i(t)} = \frac{\nu_j N_j(t)}{\sum_{i=1}^n \nu_i N_i(t)} \quad (12)$$

An alternative way of explaining the physical meaning of eq 12 is to say that the topological segmentation along a single chain is representative of that in the bulk of the mixture.

From the last two relationships and eq 9 it can be shown that the entanglement probability between dissimilar chains is proportional to the geometric average of the entanglement probabilities between similar chains:

$$N_{ij}(t) = \nu_j \left[\frac{N_{ii}(t)N_{jj}(t)}{\nu_i \nu_j} \right]^{1/2} = \nu_j \left(\frac{M_i}{M_e} \right) [F_i(t)F_j(t)]^{1/2} \quad (13)$$

Consequently, the relaxation function and the characteristic relaxation time of an i molecule in the blend (F_{iB} and τ_{iB}), representing the rate of conformational renewal of this molecule in an environment of dissimilar neighbors, may be related to the corresponding properties of the unmixed (monodisperse) state in the following manner:

$$F_{iB}(t) = \frac{N_i(t)}{N_i(0)} = \sum_{j=1}^n \nu_j [F_i(t)F_j(t)]^{1/2} \quad (14a)$$

$$\tau_{iB} = \int_0^\infty F_{iB}(t) dt \quad (14b)$$

The utility of this analysis in estimating the rheological properties of polydisperse systems is demonstrated in the next section.

Viscoelasticity of Homologous Polymer Blends

An expression for the stress relaxation modulus of an entangled homopolymer blend, $G_B(t)$, can be derived by following the same reasoning used for eq 8, i.e., by assuming that it is proportional to the step density and surviving memory of the original network topology:

$$G_B(t) = kT \sum_{i=1}^n \nu_i N_i(t) = kT \sum_{i=1}^n \sum_{j=1}^n \nu_i \nu_j N_{ij}(t) \quad (15)$$

Combination of eq 15 with eqs 9, 10, and 13 results in the following blending law relating the viscoelastic behavior of the mixture to that of its individual monodisperse components:

$$G_B(t) = \left(\frac{RT\rho}{M_e} \right) \left[\sum_{i=1}^n \sum_{j=1}^n \nu_i \nu_j \sqrt{F_i(t)F_j(t)} \right] \Rightarrow G_B^{1/2}(t) = \sum_{i=1}^n \nu_i G_i^{1/2}(t) \quad (16)$$

This relationship always predicts a weaker modulus than the one estimated by a mere linear averaging, since it

accounts for the accelerated relaxation of an entangled chain due to the earlier disengagement of its shorter neighbors.

The expression for the time-dependent relaxation modulus (eq 16) may be introduced in eqs 2 and 3 for the prediction of the zero shear viscosity, η_B , and recoverable compliance, J_{eB}^0 , of the blend. This requires a detailed knowledge of the individual moduli of the monodisperse components. For the case of linear polymers, explicit relationships between the properties of the polydisperse mixtures and the corresponding properties of the monodisperse precursors (η_i and J_{ei}^0 , which is independent of M_i in the entangled regime) may be produced by approximating the relaxation function of each of these components with a single-exponential term [$F_i(t) = e^{-t/\tau_i}$]:

$$\eta_B = 2 \frac{RT\rho}{M_e} \sum_{i=1}^n \sum_{j=1}^n v_i v_j \frac{\tau_i \tau_j}{\tau_i + \tau_j} = 2 \sum_{i=1}^n \sum_{j=1}^n v_i v_j \frac{\eta_i \eta_j}{\eta_i + \eta_j} \quad (17)$$

$$J_{eB}^0 = \frac{4}{\eta_B^2} \frac{RT\rho}{M_e} \sum_{i=1}^n \sum_{j=1}^n v_i v_j \left(\frac{\tau_i \tau_j}{\tau_i + \tau_j} \right)^2 = \frac{4}{\eta_B^2} J_{e1}^0 \sum_{i=1}^n \sum_{j=1}^n v_i v_j \left(\frac{\eta_i \eta_j}{\eta_i + \eta_j} \right)^2 \quad (18)$$

Consequently, one may also examine the manner the individual $F_i(t)$ and τ_i [or $F_{iB}(t)$ and τ_{iB}] affect the overall relaxation function [$F_B(t) = G_B(t)/G_N^0$] and characteristic relaxation time ($\tau_B = \eta_B/G_N^0$) of the blend as a whole. The same technique utilized in the derivation of eqs 17 and 18 may be applied in expressing the storage and loss modulus of the mixture, $G'_B(\omega)$ and $G''_B(\omega)$, which are frequency-dependent functions, of importance in characterizing viscoelastic materials under oscillatory flow conditions:

$$G'_B(\omega) = \omega \int_0^\infty G_B(t) \sin(\omega t) dt \simeq G_N^0 \sum_{i=1}^n \sum_{j=1}^n v_i v_j \left[1 + \frac{1}{4} \left[\left(\frac{G_N^0}{G'_i(\omega)} - 1 \right)^{1/2} + \left(\frac{G_N^0}{G'_j(\omega)} - 1 \right)^{1/2} \right]^2 \right]^{-1} \quad (19)$$

$$G''_B(\omega) = \omega \int_0^\infty G_B(t) \cos(\omega t) dt \simeq G_N^0 \sum_{i=1}^n \sum_{j=1}^n v_i v_j (G_{ij} + 1/G_{ij})^{-1} \quad (20a)$$

and where

$$G_{ij} = \frac{G_N^0 - G'_i(\omega)}{2G''_i(\omega)} + \frac{G_N^0 - G'_j(\omega)}{2G''_j(\omega)} \quad (20b)$$

These theoretical predictions are compared with the experimental results of Struglinski and Graessley³ from a series of binary blends of linear polybutadienes in the undiluted and 50% diluted state, at 25 °C (Figures 2–8). It is observed that the model slightly underestimates the fluidity and is relatively less accurate in predicting the elasticity of the mixtures. Possible explanations of these discrepancies may include the deviations from absolute monodispersity of the utilized precursor components, the introduction of the single-exponential approximation in the derivation of eqs 17–20, neglect of path fluctuations² as an additional mechanism of macromolecular relaxation, and deviations from the linear concentration dependence of the entanglement spacing upon dilution (eq 11).²⁸

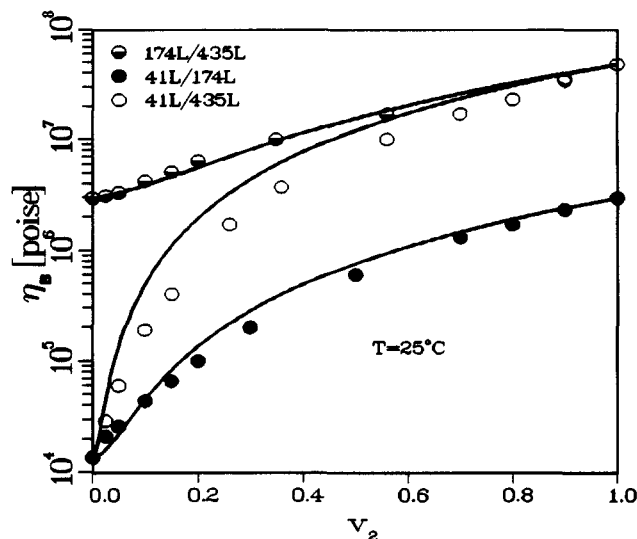


Figure 2. Blend viscosity vs volume fraction of the long-chain component. Points represent the experimental data from ref 3, at 25 °C for the following combinations of molecular weights (in 10³ g/mol): 174/435 (○), 41/435 (○), and 41/174 (●). Continuous curves represent the corresponding predictions of eq 17.

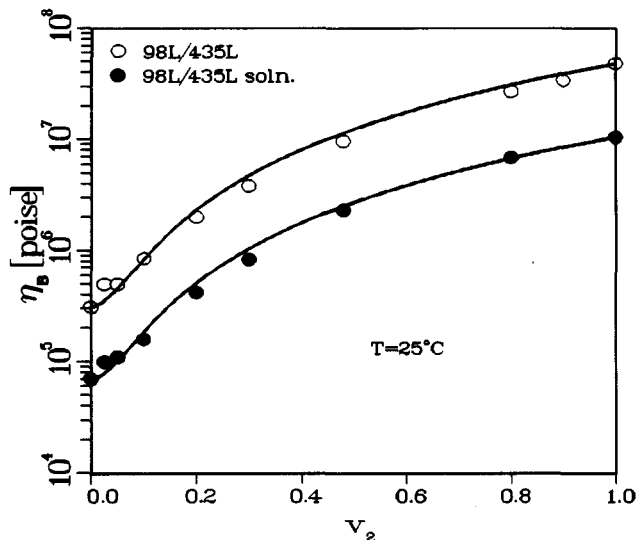


Figure 3. Viscosity vs volume fraction of the long-chain component. Points represent the experimental data from ref 3, at 25 °C, for a series of 98/435 mixtures (molecular weights in 10³ g/mol) in the melt state (○), and in a 50% solution in Flexon 391 (●). Continuous curves represent the predictions of eq 17.

Continuous Molecular Weight Distributions

The developments of the previous section may readily be extended to apply for continuous molecular weight distributions. This may be accomplished by converting discrete component summations into integrations with respect to molecular weight and by recalling that, for the range of sizes under consideration ($M_i \gg M_e$), volume fractions are equivalent to weight fractions ($v_i \simeq w_i$). Following this logic, the expression for the time-dependent relaxation modulus of the blend assumes the form

$$\sqrt{G_B(t)} = \sqrt{G_N^0} \int_{M_e}^\infty w(M) \sqrt{F(t/\tau)} dM \quad (21)$$

where $w(M)$ is the volume (or weight) fraction probability density, and $\tau(M)$ is the molecular weight dependent relaxation time.

Application of eq 21 necessitates in general the utilization of numerical tools. One of the few examples where a closed-form integration is possible occurs in a blend of

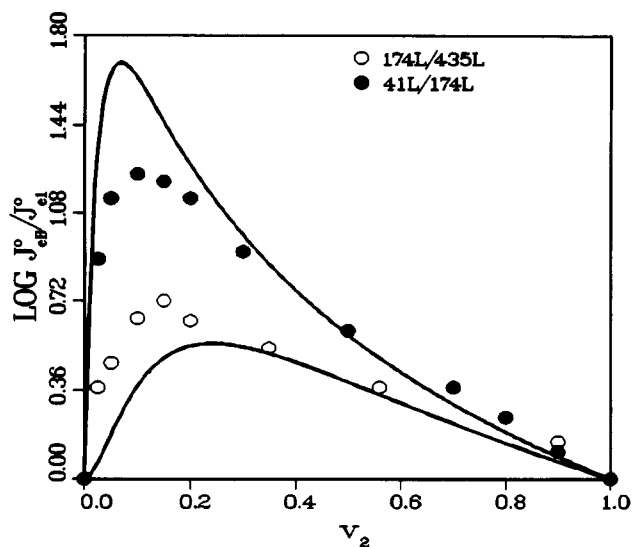


Figure 4. Reduced recoverable shear compliance vs volume fraction of the long-chain component. Points represent the experimental data,³ at 25 °C, for the following combinations of molecular weights (in 10³ g/mol): 174/435 (○) and 41/174 (●). Continuous curves represent the predictions of eq 18.

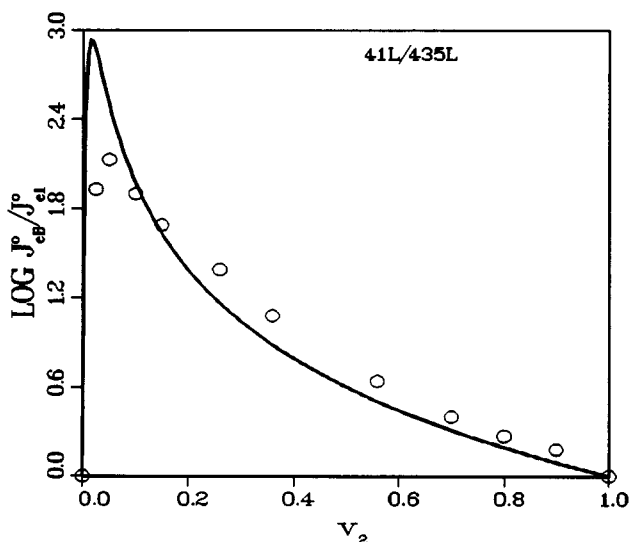


Figure 5. Reduced recoverable shear compliance vs. volume fraction of the long-chain component. Points represent the experimental data for a series of 41/435 mixtures (molecular weights in 10³ g/mol), at 25 °C.³ Continuous curve represents the predictions of eq 18.

homologous polymers whose individual viscoelastic behavior is adequately described by the reptation theory (eqs 6–8) and where

$$\text{and } \begin{cases} w(M) = 3M_1^3/M^4 & \text{for } M \geq M_1 > M_e \\ w(M) = 0 & \text{for } M < M_1 \end{cases} \quad (22)$$

This implies that the probability distribution function is $W(M) = 1 - (M_1/M)^3 \geq 0$, and that the number-average and weight-average molecular weights are respectively equal to $M_n = 4M_1/3$ and $M_w = 3M_1/2$. A naive attempt to predict the stress relaxation modulus of the blend (based on a M_w -dependent τ_B) would therefore result in

$$G_B(t) = G_N^0 \exp(-8t/27\tau_1) \quad (23)$$

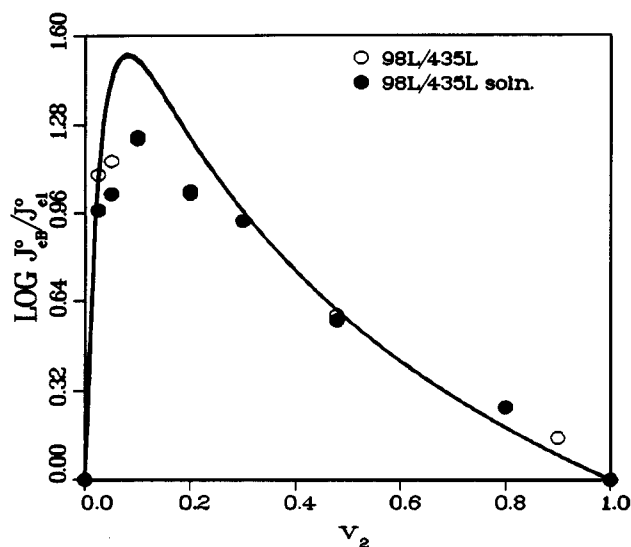


Figure 6. Reduced recoverable shear compliance vs volume fraction of the long-chain component. Points represent the experimental data³ for a series of 98/435 mixtures (molecular weights in 10³ g/mol), in the melt state (○) and in a 50% solution in Flexon 391 (●). Continuous curves represent the predictions of eq 18, for either case.

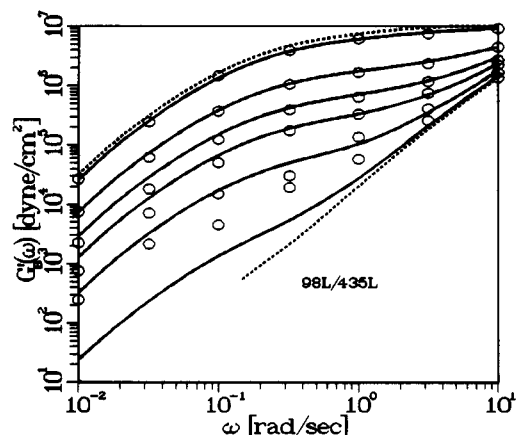


Figure 7. Storage modulus vs frequency of oscillation. Points represent the experimental data,³ at 25 °C, for a series of 98/435 blends, of long-chain composition equal to (from top to bottom) $v_2 = 0.8, 0.48, 0.3, 0.2, 0.1$, and 0.05 . Dashed curves represent the experimental measurements for the monodisperse precursors and continuous curves the estimates of eq 19.

where $\tau_1 = \alpha M_1^3$. Equation 21 suggests instead

$$G_B(t) = G_N^0 \left(\frac{2\tau_1}{t} \right)^2 \left[1 - \exp\left(\frac{-t}{2\tau_1} \right) \right]^2 \quad (24)$$

The predictions of the last two expressions are contrasted in Figure 9, where it is demonstrated how a seemingly mild sample polydispersity introduces a significant broadening in the relaxation spectrum.

Discussion

By calculation of the population densities and hierarchy of dissolution and renewal of the various types of entanglements in a composite network formed by linear chains of dissimilar length, blending laws have been derived concerning the viscoelastic and molecular dynamic properties of these mixtures in the terminal relaxation region. The basic findings of this work generalize the results of our earlier investigation on binary systems²⁹ by indicating that the stress relaxation modulus of a mixture is subject to a square-root additivity rule (eq 16 or 21) and that,

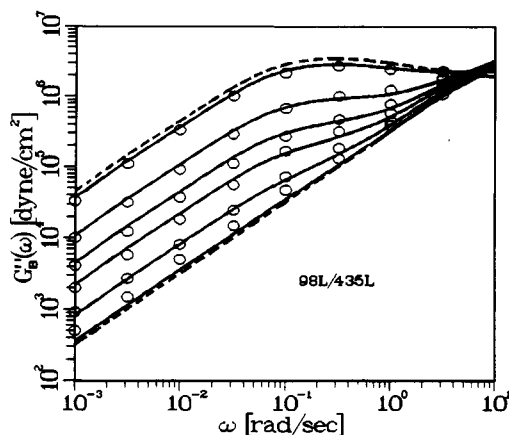


Figure 8. Loss modulus vs frequency of oscillation. Points represent the experimental data,³ at 25 °C, for a series of 98/435 blends, of long-chain composition equal to (from top to bottom) $v_2 = 0.8, 0.48, 0.3, 0.2, 0.1$, and 0.05 . Dashed curves represent the experimental measurements for the monodisperse precursors and continuous curves the estimates of eq 20.

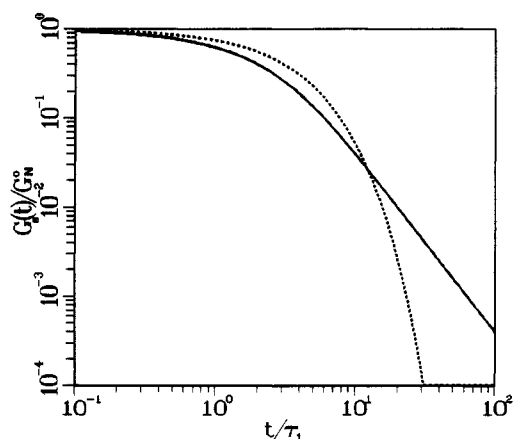


Figure 9. Theorizing on the effects of a continuous molecular weight distribution (eq 22) on the stress relaxation modulus. Dashed curve represents the estimates of eq 23. Continuous curve illustrates the predictions of eq 24 ($M_w/M_n = 9/8$).

consequently, all rheological properties of the blend are subtly related to the corresponding properties of the precursor components without any need of introducing additional molecular parameters or physical assumptions other than that of randomness in interchain associations (eqs 11 and 12).

A derivative benefit from the present analysis is a simple method of correcting the original reptation theory result by accounting for the accelerated relaxation due to constraint release.^{2,30-32} It is known from eq 14 that the molecular relaxation time in a binary mixture is equal to

$$\tau_{1B} = v_1\tau_1 + \frac{2v_2\tau_1\tau_2}{\tau_1 + \tau_2} \quad (25)$$

This implies that a single linear chain of finite length ($v_1 \rightarrow 0, \tau_1 < \infty$) moving in a permanent network environment ($v_2 = 1 - v_1 \rightarrow 1, \tau_2 \rightarrow \infty$) will relax in double the time it would in an environment of free chains of its own kind, $\tau_{1B} = 2\tau_1$.

A methodology similar to the one followed in this work may also be employed for the study of other homogeneous multicomponent polymeric systems. For example, explanations may be offered for the rheological behavior of miscible heteropolymer blends^{33,34} and the mechanical properties of imperfect rubber networks,³⁵ which may be considered as "blends" of fixed cross-linked strands mixed with mobile tethered chains.

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Glossary

D	self-diffusion coefficient (cm^2/s)
$F(t)$	molecular relaxation function
$G(t)$	shear stress relaxation modulus (dyn/cm^2)
G_N^0	plateau modulus (dyn/cm^2)
J_e^0	shear compliance (cm^2/dyn)
k	Boltzmann constant (erg/K)
M	polymer molecular weight (g/mol)
m	monomer molecular weight (g/mol)
M_e	molecular weight between entanglements (g/mol)
N	primitive steps (or entanglements) per chain
n	number of polymer components in the blend
N_A	Avogadro number (molecule/mol)
R	gas constant = kN_A ($83.2 \times 10^6 \text{ erg/mol K}$)
$\langle R_i^2 \rangle$	mean squared end-to-end distance (cm^2)
T	temperature (K)
t	time (s)
v	volume fraction
$W(M)$	cumulative probability distribution of molecular weights
$w(M)$	probability density function of molecular weights
α	proportionality constant of eq 7
γ	shear strain
ζ	monomeric friction coefficient (g/s)
η	viscosity ($\text{dyn-s}/\text{cm}^2 = \text{poise}$)
ν	chains/volume
ρ	density (g/cm^3)
σ	shear stress (dyn/cm^2)
τ	relaxation time (s)
ω	oscillatory frequency (rad/s)

Subscripts

B	blend
i	i chain, of molecular weight M_i
iB	i chain in the blend
ij	step on an i chain, formed by two successive j constraints
j	j chain, of molecular weight M_j

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