A Molecular Model for the Viscoelastic Properties of Entangled Homogeneous Block Copolymers

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ABSTRACT: A molecular model has been proposed to describe the viscoelastic properties of homogeneous entangled block copolymers. It combines the basic concepts embodied in two recently developed models: (1) the transient network model for entangled homopolymers and (2) a block copolymer model for homogeneous unentangled block copolymers. In the present model a block copolymer is represented by a collection of beads and springs. The viscous retardation effect of entanglements is modeled by assigning enhanced frictional coefficients to the corresponding beads, where the enhanced frictional coefficients assume the high-friction-inside distribution. The elastic effect of the entanglements is modeled by connecting pairs of entanglements with coupling springs, whose strength is assumed to be inversely proportional to the interbead distance. Inherent differences in monomeric friction associated with the different blocks of the copolymer are taken into account by multiplying the assigned frictional coefficients of the beads (entangled as well as unentangled) by the corresponding ratio between the monomeric frictional coefficients. The derived force balance matrix equation is then solved for the relaxation times, from which all the linear viscoelastic properties can be calculated. Good agreement is seen between model prediction and literature data on a set of butadiene–isoprene diblock copolymers.

In recent years, block copolymers have been widely used in various engineering applications. These polymer systems generally exhibit the phenomenon of microphase separation as a result of the positive Gibbs free energy of mixing. Many of the useful properties of such polymers are in fact attributed to the incompatible nature of their components. There are, however, some block copolymers that do not show phase separation at room temperature, e.g., polystyrene and poly(α-methylstyrene),[1] polybutadiene and polyisoprene,[2] nitrocellulose and poly(vinyl acetate),[3] and poly(α-methylstyrene) and poly(2,6-dimethyl-1,4-phenylene).[4] Still others, which are phase separated at room temperature, would presumably be homogeneous when $T > T_s$, where T_s is the separation temperature described by Leary and Williams.[5] These homogeneous block copolymers deserve special attention, as an understanding of the relationship between their viscoelastic properties and the block compositions forms the basis for future work on the more complicated phase-separated systems. This paper reports some preliminary results of our investigation into modeling of the viscoelastic properties of these homogeneous block copolymers.

In this work the Rouse–Bueche–Zimm (RBZ) bead-and-spring model of viscoelasticity[6-8] is modified to apply to entangled homogeneous block copolymers. The extension is based on some recent developments in describing the viscoelastic behavior of entangled homopolymers[9,10] and computing the maximum relaxation times of homogeneous block copolymers.[11,12] First, a transient network model[10] based on the RBZ molecular theory has been developed to apply to entangled homopolymers, where the effects of entanglements are modeled by assigning enhanced frictional coefficients to entangled beads and by connecting all pairs of entangled beads with elastic coupling springs. The same basic RBZ theory has also been extended to compute the maximum relaxation times of homogeneous block copolymers. However, the latter model is not capable of predicting the viscoelastic properties of entangled block copolymers because the effects of entanglements have not been incorporated into the mathematical framework of the model. This deficiency is remedied by the model proposed in this work, which combines the basic concepts of the transient network model for entangled homopolymers and the block copolymer theory originally designed for unentangled systems.

Theory

The original block copolymer model, which predicts maximum relaxation time as a function of block copolymer composition, assigns different frictional coefficients to beads (submolecules) along different component blocks.[11,12] The ratio of the frictional coefficients for the different blocks is obtained from the ratio of the monomeric frictional coefficients, numbers of monomeric segments per submolecule, and the characteristic lengths of the block constituents. A schematic representation of this model for a diblock copolymer is shown in Figure 1a. The size of a bead reflects the magnitude of its frictional coefficient. The more viscous block is represented by the larger (shaded) beads.

The transient network model developed recently is capable of calculating the viscoelastic properties for entangled homopolymers. The effects of entanglements are modeled by enhanced friction associated with the entangled beads and by additional elastic coupling connecting topologically paired entanglements. The former effect is due to a reduction in chain mobility caused by entanglements. The latter effect comes from the elastic force which is transmitted throughout the entire entangled network as a result of coupling among the entanglements. Since all the entangled points on any given chain are elastically coupled through the network, the elastic force originating from a given entanglement ultimately affects the motion of the other entanglements along the same chain. The coupling force is assumed to be inversely proportional to the contour distance between the entangled beads because statistically the force must be transmitted via a large number of chains as the distance increases. However, entanglements are less effective than permanent cross-links in transmitting elastic forces since the interacting chains can still slip by each other. This slippage is taken into account by introducing a material parameter, α ($0 < \alpha < 1$), whose value depends on the flexibility of the polymer backbone. Thus the elastic coupling effect is modeled by eq 1, where ϵ_{ij} is the coupling spring constant between entanglements at positions i and j.

$$\epsilon_{ij} = \alpha/|i - j| \qquad (1)$$

Entanglements are assumed to have different complexities; hence different entangled beads experience different degrees of retardation. This presumption is

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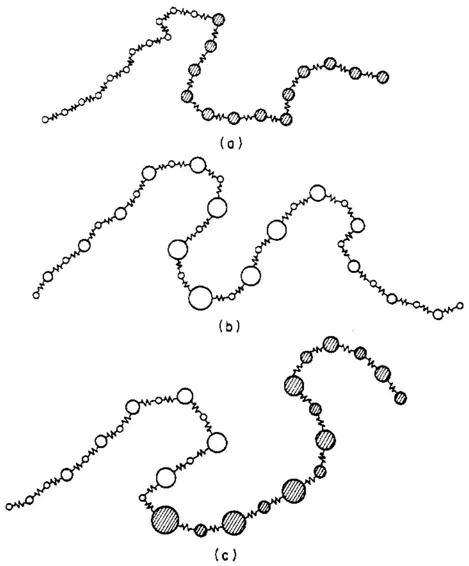

Figure 1. Schematic representation of the molecular models. Circles (beads) represent submolecules. The sizes of the circles correspond to the magnitudes of their frictional coefficients. (a) An unentangled diblock copolymer. Shaded beads represent the more viscous block. (b) An entangled homopolymer where every other bead is an entangled bead. The entangled beads assume the high-friction-inside distribution. (c) A homogeneous entangled diblock copolymer with alternating entangled and unentangled intervening beads. Shaded beads represent the more viscous block.

modeled by associating different enhanced frictional coefficients with entanglements at different positions of the chain. A number of distributions for the enhanced frictional coefficients have been investigated,[10] and the high-friction-inside distribution has been found to give the best agreement with experimental data. The high-friction-inside distribution is given by

$$\delta_e^I \equiv f_e^I / f_u = I^4 \tag{2}$$

where f_e^I is the enhanced frictional coefficient of entanglement at position I, f_u is the frictional coefficient of unentangled beads, and I is counted from chain ends toward the chain center. The transient network model is represented schematically in Figure 1b, where the numerous elastic coupling springs are omitted in order to simplify the figure.

The above modifications must all be incorporated into the new molecular model to calculate the viscoelastic properties of entangled block copolymers. First, the unentangled beads along different blocks are assumed to have frictional coefficients proportional to their respective monomeric frictional coefficients. Next, the additional retardation effect introduced by the entanglements must also be included. It can be approximated by the high-friction-inside distribution, since the block copolymer under investigation is homogeneous and a given entanglement has equal tendency to entangle with any of the other entanglements in the system. The overall retardation effect results from both topological constraint of the entwined chains and the inherently different viscous nature of the monomeric units constituting the various submolecules. The combined effect is thus modeled by assigning an enhanced frictional coefficient which is equal to the product of that calculated from the high-friction-inside distribution and the ratio of the frictional coefficients of the unentangled beads.

A schematic representation of this new model is shown in Figure 1c for an entangled diblock copolymer. Shaded circles correspond to beads along the more viscous block. Note the frictional coefficients associated with entangled beads still assume the high-friction-inside distribution. However, those on the more viscous block now have their frictional coefficients further enhanced by the ratio of the frictional coefficients of the unentangled beads along the component blocks.

Summarizing these concepts and transforming them into the mathematical framework of the model, we have, for unentangled beads along blocks A and B, the ratio of frictional coefficients[12]

$$\delta_r = \frac{b_A^2 f_A}{b_B^2 f_B} = \frac{a_A^2 m_A^2 \xi_A}{a_B^2 m_B^2 \xi_B} \tag{3}$$

a is the characteristic length, m is the number of monomer units per submolecule, and ξ is the monomeric frictional coefficient. The characteristic length, a, is related to the mean-square end-to-end distance, b, of the submolecule by the relationship

$$b^2 = ma^2 \tag{4}$$

For entangled beads along the more viscous block (here taken to be block A), the frictional coefficients become

$$\delta^I = \delta_e^I \delta_r = I^4 (a_A^2 m_A^2 \xi_A / a_B^2 m_B^2 \xi_B) \tag{5}$$

where I is counted from chain ends toward the chain center (regardless of the blocks). This is a reasonably accurate assumption since the block copolymers under consideration are homogeneous. The viscous retardation due to topological constraints is assumed to be evenly distributed throughout the entire chain.

The concepts embodied in eq 4 and 5 are expressed in matrix notation by force balance eq 6,[10] where $\dot{\mathbf{x}}$ and $\mathbf{x}$ are

$$\dot{\mathbf{x}} = \mathbf{V}_x^s - D_B \mathbf{D}^{-1} \frac{\partial \ln \psi}{\partial \mathbf{x}} - \sigma_B \mathbf{D}^{-1} \mathbf{Z} \mathbf{x} \tag{6}$$

column vectors of the bead velocities and positions, $\mathbf{V}_x$ is a column vector of the velocities of the surrounding medium, $D_B = kT/f_B$ is the diffusion coefficient of an unentangled submolecule of the less viscous block (block B), $\partial \ln \psi / \partial \mathbf{x}$ is the gradient of the configurational potential, and $\sigma_B = 3kT/b_B^2 f_B$. Matrix $\mathbf{D}$ in eq 6 accounts for the enhanced friction, whereas matrix $\mathbf{Z}$ accounts for the elastic coupling effect of the network. The exact forms of these matrices depend on the block copolymer configuration and composition. As an example, for a diblock copolymer where every other bead is taken to be an entangled bead, matrix $\mathbf{D}$ assumes the following form:

$$\mathbf{D} = \begin{bmatrix} (\delta_r) & & & & & & & \\ & (\delta_r) & & & & & \bigcirc & \\ & & \ddots & & & & & \\ & & & (\delta_r) & & & & \\ & & & & 1 & & & \\ & & & & & \ddots & & \\ & \bigcirc & & & & & 1 & \\ & & & & & & & 1 \end{bmatrix} \bullet \begin{bmatrix} 1 & & & & & & & & & & \\ & (\delta_e^1) & & & & & & & \bigcirc & & \\ & & 1 & & & & & & & & \\ & & & (\delta_e^2) & & & & & & & \\ & & & & 1 & & & & & & \\ & & & & & (\delta_e^3) & & & & & \\ & & & & & & \ddots & & & & \\ & & & & & & & (\delta_e^2) & & & \\ & & \bigcirc & & & & & & 1 & & \\ & & & & & & & & & (\delta_e^1) & \\ & & & & & & & & & & 1 \end{bmatrix} \tag{7}$$

Matrix $\mathbf{Z}$ is identical with that for an entangled homo-

Table I
Values for the Parameters Used in Determining the Ratio of Frictional Coefficients

polym	$10^8 a$,[a] cm	m[b]	ξ(0 °C),[a] (dyn s)/cm
isoprene	6.8	5.0[c]	2.8×10^{-6}
butadiene	6.0	5.4[d]	5.0×10^{-7}

[a] Reference 13. [b] Reference 14. [c] Weighted average for 90% cis-1,4, 10% trans-1,4. [d] Weighted average for 45% cis-1,4, 45% trans-1,4, 10% vinyl.

Table II
Molecular Characteristics and Model Parameters for the Diblock Copolymers

	butadiene content		isoprene content					
diblock no.	mol %	wt %	mol %	wt %	N_{eB}	N_{eI}	f_I/f_B	α
2143	0.50	0.44	0.50	0.56	17	16	6.2	0.1
2144	0.66	0.61	0.34	0.39	25	12	6.2	0.1
2148	0.34	0.29	0.66	0.71	12	22	6.2	0.1

$$\mathbf{Z} = \begin{bmatrix} 1 & -1 & 0 & 0 & 0 & 0 & \text{--} \\ -1 & (2+\gamma_2) & -1 & -\epsilon_{24} & 0 & -\epsilon_{26} & \text{--} \\ 0 & -1 & 2 & -1 & 0 & 0 & \text{--} \\ 0 & -\epsilon_{42} & -1 & (2+\gamma_4) & -1 & -\epsilon_{46} & \text{--} \\ 0 & 0 & 0 & -1 & 2 & -1 & \text{--} \\ \text{--} & \text{--} & \text{--} & \text{--} & \text{--} & \text{--} & \text{--} \end{bmatrix} \tag{8}$$

polymer[10] where

$$\gamma_j = \sum_{j,\, i \neq j} \epsilon_{ij} \tag{9}$$

The eigenvalues of matrix $\mathbf{D}^{-1}\mathbf{Z}$ can be obtained numerically to yield the relaxation-time spectrum, from which can be calculated the various linear viscoelastic functions,[9] such as the stress-relaxation moduli, dynamic mechanical moduli, steady-state shear compliance, and zero-shear viscosity.

Results and Discussion

The viscoelastic properties predicted by the model depend on the model parameters. For a diblock copolymer, these parameters include the ratio of frictional coefficients of the blocks, δ_r, the number of entanglements on the blocks, N_{eA} and N_{eB}, and the slippage parameter, α, for the system. We will illustrate the procedure to determine these values by using butadiene–isoprene diblock copolymer systems as an example. The ratio of frictional coefficients of the blocks, δ_r, is given by eq 3. Estimation of this ratio requires knowledge of the characteristic length, the number of monomer units per submolecule, and the monomeric frictional coefficient for the constituent blocks. These have been compiled for a number of polymers.[13,14] Literature data for polybutadiene and polyisoprene are summarized in Table I. These data are obtained on the pure homopolymers. In a homogeneous block copolymer each chain segment (regardless of its origin) exists in the same environment, which represents the ensemble average of all the components. The parameters listed in Table I then depend on the exact nature of the microscopic environment (thus the composition) of the copolymers. Values different from those of the homopolymers should, in principle, be used for block copolymers. However, the characteristic length and the number of monomeric units per submolecule are expected to be relatively insensitive to the block composition. Values cited for the pure homopolymers are adopted without further modification.

The monomeric frictional coefficient is a function not only of the structure of the segments but also of the matrix in which the segments are imbedded. Following this line of thought, the monomeric frictional coefficient associated with the more viscous component in the environment of a homogeneous block copolymer is expected to be smaller than that of the pure homopolymer. Conversely, the monomeric frictional coefficient associated with the less viscous block in the mixed environment now becomes greater than that of a homopolymer. Both these changes tend to decrease δ_r as the content of the less viscous block increases. Since there is no way to predict quantitatively the change in δ_r induced by composition variation, we can, in principle, employ the iso-free-volume analysis or other simple linear weighting schemes to evaluate the composition-dependent δ_r for block copolymers. However, as a first trial to fit experimental data, we will not incorporate such refinement into the model and will simply adhere to the value calculated by using data for the pure homopolymers. This is the most uncertain assumption of the present model since it ignores the influence of environment on the frictional force encountered when a given monomeric unit is displaced in the polymeric matrix. This uncertainty is shared by the earlier model for calculating the viscoelastic properties of block copolymers that do not form entanglements.[11,12] The main objective of the present model is to investigate the applicability of combining the unentangled block copolymer model and the transient network model for homopolymers in order to describe entangled block copolymers.

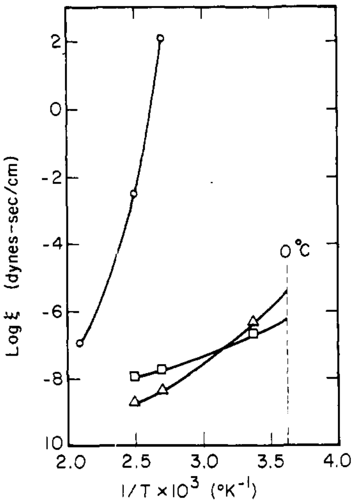

Figure 2. Logarithmic monomeric frictional coefficient[13] vs. $1/T$ for polystyrene (○), polybutadiene (□), and polyisoprene (△).

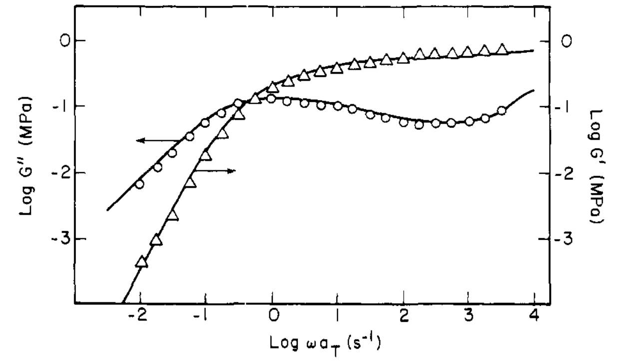

Figure 3. Dynamic storage moduli, $G'(\omega)$, and loss moduli, $G''(\omega)$, vs. frequency for diblock 2143. Solid curves are computed by the model, and symbols are experimental data.[16]

The monomeric frictional coefficients tabulated in Table I are estimated from values reported for a number of temperatures. Figure 2 shows the logarithmic of the reported monomeric frictional coefficients plotted against $1/T$. Note that data for all three polymers (polystyrene, polybutadiene, polyisoprene) follow fairly straight lines in the temperature range shown. This graph thus provides an easy means to interpolate and extrapolate data. The values estimated from this figure for polybutadiene and polyisoprene at 0 °C are given in Table I. The reported data for polystyrene are significantly higher than those of polybutadiene and polyisoprene over the indicated temperature range. When the temperature increases, this difference diminishes, and polystyrene has a monomeric frictional coefficient which is comparable to those of polybutadiene and polyisoprene. Indeed, at temperatures exceeding certain critical temperatures (which vary with molecular weights), the styrene–butadiene block copolymers become homogeneous,[5] and thus the present model could be applied to them too. The situation is very similar to block copolymers of butadiene and isoprene within the temperature range of Figure 2, where both blocks have comparable monomeric frictional coefficients. With the values given in Table I and eq 3, δ_r for the block copolymer of butadiene and isoprene is 6.2, with isoprene being the more viscous component. This number was used for all subsequent calculations.

The number of entanglements (N_e) in each block is determined by dividing the molecular weight of the block by the entanglement molecular weight for the particular block in the copolymer. This is assuming that the entanglement molecular weight of a given block is unaffected by the environment, which may appear to be rather unreasonable, since the number of backbone units (hence, the entanglement molecular weight) needed to form an entanglement depends not only on the flexibility of the chain but also on the surrounding molecules. In the present case, the entanglement molecular weights for polybutadiene and polyisoprene in their pure states are 6300 and 8500, respectively,[15] indicating that roughly the same number of backbone bonds are involved in forming an entanglement for either polymer. We conclude that these two polymers have similar chain flexibility, and the values quoted for the pure polymers are used to calculate the number of entanglements in the block copolymers.

The slippage parameter, α, should also depend on the block composition, since the elastic coupling force is transmitted via chains that are copolymers. Hence, some sort of weighting scheme should be devised to evaluate α for the copolymers. However, the optimal range of α lies near 0.1 for both polybutadiene and polyisoprene.[10] This value is adopted for the copolymers.

Once these parameters are fixed we can compare the calculated results with experimental data. Ramos and Cohen[16] have performed dynamic mechanical experiments on three butadiene–isoprene diblock copolymers. Their data will be compared with the calculated results of our model. The molecular characteristics and model parameters for these copolymers are summarized in Table II.

Figure 3 shows the computed curves and experimental data of dynamic storage moduli, $G'(\omega)$, and loss moduli, $G''(\omega)$, for diblock 2143, which is estimated to have 16 entanglements in the isoprene block and 17 in the butadiene block. The agreement between model prediction and experimental data is excellent. Figure 4 shows similar plots of $G'(\omega)$ and $G''(\omega)$ for diblock 2144, which has an estimated 25 entanglements in the butadiene block and 12 in the isoprene block. The calculated curve for $G'(\omega)$ agrees reasonably well with experimental data, whereas $G''(\omega)$ is predicted to have a slightly higher maximum near the onset of the flow region than the reported data. Note that the experimental $G''(\omega)$ curve shows a flat rubbery plateau and lacks the characteristic maximum at the onset of the flow region. Both of these observations are different from those expected for entangled homopolymers. The model indeed predicts the observed trend. The calculated $G''(\omega)$ curve has only a shallow minimum in the rubbery plateau region and an unusually small maximum at the onset of the flow region. Figure 5 shows similar plots of $G'(\omega)$ and $G''(\omega)$ for diblock 2148. This copolymer has an estimated 22 entanglements in the isoprene block and 12 in the butadiene block. It can be seen that the calculated $G''(\omega)$ curve is in reasonably good agreement with experimental data. Note that the reported data now have a prominent minimum in the rubbery region and a large maximum near the flow region. Both of these observations are predicted by the model. However, the $G'(\omega)$ reveals some discrepancy in the flow region. The reported data have a much gentler slope than the calculated curve. This may be due to the residual polydispersity of the sample, which generally tends to broaden the experimental data in the flow region.

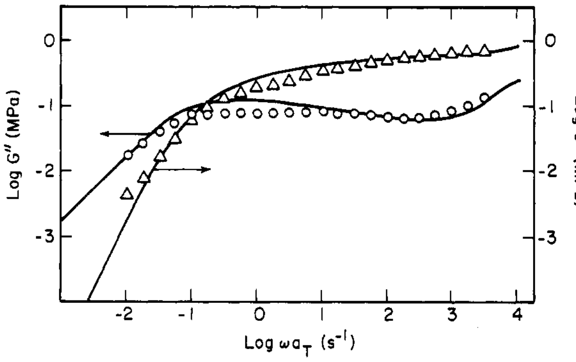

Figure 4. Dynamic storage moduli, $G'(\omega)$, and loss moduli, $G''(\omega)$, vs. frequency for diblock 2144. Solid curves are computed by the model, and symbols are experimental data.[16]

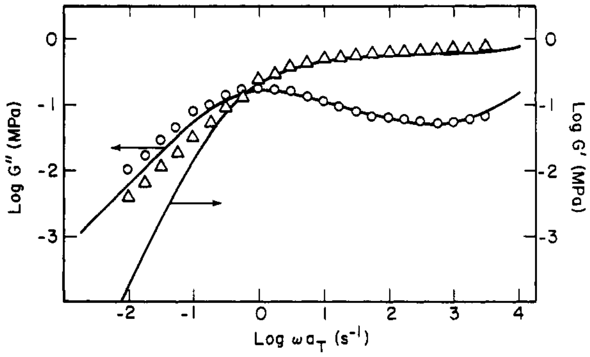

Figure 5. Dynamic storage moduli, $G'(\omega)$, and loss moduli, $G''(\omega)$, vs. frequency for diblock 2148. Solid curves are computed by the model, and symbols are experimental data.[16]

To observe the differences in predicted viscoelastic properties between a homogeneous entangled block copolymer and an entangled homopolymer (or random copolymer, which can be treated as a homopolymer), we performed the following model calculation. We computed $G'(\omega)$ and $G''(\omega)$ for a fictitious diblock copolymer AB which has 22 entanglements in the A block and 12 in the B block. The ratio of frictional coefficients, δ_r, is taken to be 50, and the slippage parameter, α, is 0.1. We also calculated the dynamic mechanical moduli for a random copolymer whose composition is identical with the diblock copolymer AB. Since the more viscous monomer A is randomly distributed along the chain, the copolymer es-

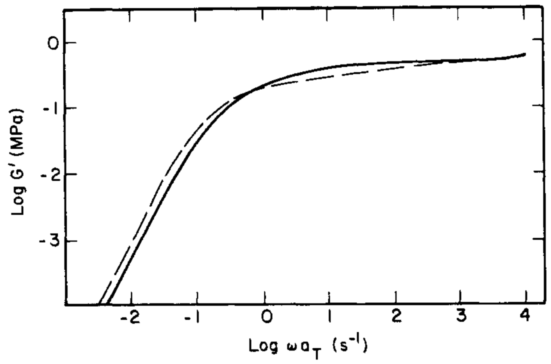

Figure 6. Calculated curves of dynamic storage moduli, $G'(\omega)$, for diblock copolymer (---) and random copolymer (—) having the same overall composition. Model parameters for the diblock copolymer are $N_{eA} = 22$, $N_{eB} = 12$, $f_A/f_B = 50$, and $\alpha = 0.1$. Model parameters for the random copolymer are $N_e = 34$, $f_r = 33$, and $\alpha = 0.1$.

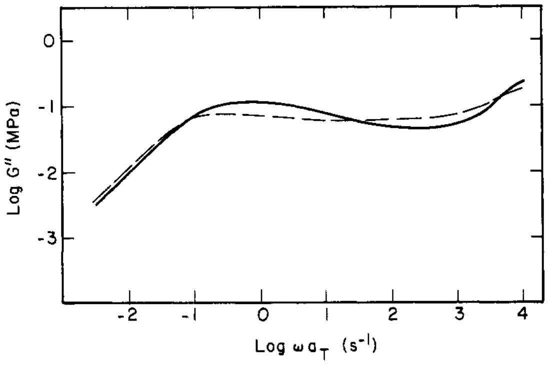

Figure 7. Calculated curves of dynamic loss moduli, $G''(\omega)$, for the same diblock copolymer (---) and random copolymer (—) described in the caption to Figure 6.

sentially behaves like an ordinary homopolymer. The frictional coefficients associated with all the unentangled beads for the random copolymer are the same. This value f_r is assumed to be given by a linear weighting scheme (eq 10). Thus the model parameters for the random copolymer are $N_e = 34$, $f_r = 33$, and $\alpha = 0.1$.

$$f_r = \frac{N_{eA}}{N_{eA} + N_{eB}} f_A + \frac{N_{eB}}{N_{eA} + N_{eB}} f_B \qquad (10)$$

Figure 6 shows the calculated $G'(\omega)$ for the diblock (dashed curve) and random (solid curve) copolymer. Little difference exists between the two curves, although the block molecule produces a mildly suppressed plateau and enhanced flow region. Figure 7 shows the calculated $G''(\omega)$ for the diblock (dashed curve) and random (solid curve) copolymer, and here significant differences are observed between the two curves. The diblock copolymer has a very flat rubbery plateau, lacking the characteristic maximum near the onset of the flow region. The random copolymer exhibits behavior expected for any ordinary homopolymer, i.e., a minimum in the rubbery plateau and a maximum at the onset of the flow region.

In summary, a simple molecular model has been developed to calculate the viscoelastic properties of homogeneous entangled block copolymers. Comparison of the predicted results with experimental data on a set of butadiene–isoprene diblock copolymers shows good agreement. It is also noted that for some block compositions the calculated $G''(\omega)$ curves are significantly different from those for homopolymers.

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