Viscoelastic Spectrum of Free-Draining Block Copolymers[1a]

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ABSTRACT: The continuous limit of the bead-spring model of chain dynamics is applied for free-draining (Rouse–Bueche) conditions to block copolymers, with illustrative calculations for diblock and symmetrical triblock structures. The basic mathematical problem is identical to that for heat flow in a nonuniform rod.

There is much current interest in the dynamic viscoelastic behavior of block copolymers,[2] and for this reason it would be useful to have an appropriate adaptation of the Rouse bead-spring model[3a] for the dynamics of flexible chain molecules. A treatment of the problem is presented here, with illustrative calculations for diblock and symmetric triblock copolymers of the types BA and ABA.

At the time our work was done, previous calculations relating to this question were apparently almost nonexistent. Some years ago DeWames, Hall, and Shen[3b] had considered a Rouse chain in which the central bead has a friction coefficient differing from those of all the other beads, but their result for this special case is not easily generalized. Our calculations are relatively simple because they are based on the continuous limit of the free-draining Rouse chain. This is known to be adequate[4–6] for treating the long-time portion of the relaxation spectrum and hence for discussing the viscoelastic response under most conditions of practical interest. The mathematical problem then closely resembles that of heat conduction in nonuniform rods.[7]

In the course of preparing our work for publication, we have learned of other related efforts. Shen and Hansen[8] have made numerical calculations for free-draining copolymers with finite but large numbers of submolecules. Where the results can be compared, agreement between their work and ours is good. More recently, we have found that Wang and DiMarzio[9] and Hall and DeWames[10] have also discussed the problem. Finally, Wang[11] has also treated block copolymers in the more difficult nondraining situation appropriate to dilute solutions.

Model and Method

The complex frequency-dependent intrinsic viscosity for a solution of Rouse or Zimm chains can be written in the form

$$[\eta] = (RT/M\eta_0) \sum_{p \geq 1} \tau_p/(1 + i\omega\tau_p) \quad (1)$$

in which M is the molecular weight, η_0 the solvent viscosity, ω the circular frequency, and τ_p the viscoelastic relaxation time for the pth normal mode of the chain. The corresponding relation[12] assumed for the viscosity η of an undiluted liquid polymer is

$$\eta = (\rho RT/M) \sum_{p \geq 1} \tau_p/(1 + i\omega\tau_p) \quad (2)$$

where ρ is the density. From the structure of the equations[3,4] for the model, it can be ascertained that these relations are unaffected by heterogeneity of chain composition, i.e., by variations in spring constants or friction coefficients among the elements of the model; only the eigenvalue problem associated with the relaxation times τ_p is altered in detail. Since the effective potential energy of the model is always quadratic, a set of normal coordinates always exists, and for the viscosity the relevant relaxations are always those of the quantities $\langle X_p Y_p \rangle$, where X_p and Y_p are Cartesian components of the pth normal mode displacement and the average refers to the nonequilibrium ensemble described by the Rouse diffusion equation. Thus, in the absence of a velocity gradient the above quantity relaxes exponentially from any initial value (subscript zero):

$$\langle X_p Y_p \rangle = (X_p Y_p)_0 \exp(-t/\tau_p) \quad (3)$$

Because of the separability in Cartesian coordinates, the above relation is equivalent to

$$\langle X_p \rangle/(X_p)_0 = \langle Y_p \rangle/(Y_p)_0 = \exp(-t/2\tau_p) \quad (4)$$

so that it suffices to consider only the time dependence of an *average* Cartesian component in order to arrive at the relaxation spectrum. This is a well-known result, and explains[13] the partial success of bead-spring treatments,[14,15] that do not explicitly consider the Brownian motion.

We may now proceed to treat the general heterogeneous chain. For the average x displacement x_j of the jth bead we have

$$\zeta_j(\mathrm{d}x_j/\mathrm{d}t) = -K_{j-1,j}(x_j - x_{j-1}) - K_{j,j+1}(x_j - x_{j+1}) \quad (5)$$

in which ζ_j is the friction coefficient of the bead and the K's are the force constants of its two contiguous Gaussian springs. In this and all subsequent equations the brackets denoting averages are suppressed but are always to be understood. As is easily shown,[13] eq 5 results from integration of the appropriate Rouse diffusion equation over the spatial coordinates.

In the interior of a given block within a block copolymer, or in a homopolymer chain, all friction coefficients and force constants are identical, and under these conditions eq 5 reduces to the standard Bueche[15] form

$$\zeta(\mathrm{d}x_j/\mathrm{d}t) = -K(2x_j - x_{j-1} - x_{j+1}) \quad (6)$$

Also, the force constant may be written[4]

$$K = 3kT/b^2 \quad (7)$$

where b^2 is the equilibrium mean square length of a spring.

In preparing to pass to the continuous limits of eq 5 and 6 it is well to recall the limited physical significance of the beads and the springs ("submolecules"), which has often been discussed. The slow part of the relaxation spectrum ($p \ll N$), which is of major interest for discussions of viscoelasticity, is independent of the number N of submolecules into which the chain is considered to be divided. For example, provided only that N is much larger than unity, the longest or "terminal" relaxation time for the homogeneous Rouse chain is given[2] by

$$\tau_1 = (N\zeta)(Nb^2)/6\pi^2 kT \quad (8)$$

where kT has its usual meaning. The quantities $N\zeta$ and Nb^2 describe the chain as a whole, and are of course each proportional to the true number n of links in the chain backbone, but the proportionality factor N/n can be varied at will, provided interest is confined to the modes with $p \ll N$. We may emphasize this assertion by recalling the free-draining expression for the translational diffusion coefficient of the chain, $D = kT/N\zeta$, and the expression for the

equilibrium mean square end-to-end distance, $\langle r^2 \rangle = Nb^2$; these permit eq 8 to be rewritten as

$$\tau_1 = \langle r^2 \rangle / 6\pi^2 D \qquad (8')$$

Moreover, the slow part of the free-draining relaxation spectrum follows the law

$$\tau_p = \tau_1 / p^2 \qquad (9)$$

whatever the value of N.

We may therefore pass to the limit of a continuous chain, letting N become indefinitely large while keeping fixed the true number of chain links and hence the quantities $\langle r^2 \rangle$, D, and τ_1. The numerical bead index j is replaced[4,5] by the continuous contour variable

$$s = (2j/N) - 1 \quad (-1 \leq s \leq +1) \qquad (10)$$

and eq 5 is expanded about any chosen point; that is, $x_j(t)$ is replaced by $x(s,t)$ and

$$x_{j+1} = x \pm 2N^{-1}(\partial x/\partial s) + 2N^{-2}(\partial^2 x/\partial s^2) + \ldots \qquad (11)$$

Making this substitution in eq 6 and using eq 8, we find the familiar "heat equation" or Fick equation

$$\partial x/\partial t = (2/\tau_1 \pi^2)\partial^2 x/\partial s^2 \qquad (12)$$

which holds for homopolymer chains, or for homogeneous sequences within block copolymers. In the latter case, τ_1 is to be interpreted as the terminal relaxation time for a homopolymer of the same chemical composition as the block but with the same number of links n as the entire block copolymer. In later equations we write τ_{1A} or τ_{1B}, the second subscript denoting the chemical nature of the block.

At a junction between two blocks a different equation obtains. Letting B and A denote the blocks at the left and right, respectively, of the junction bead j, we find by the foregoing procedure:

$$2\pi^2 N^{-1} K_B \tau_{1B}(\partial x/\partial t) = -K_B(\partial x_B/\partial s) + K_A(\partial x_A/\partial s) + 2N^{-1}[K_B(\partial^2 x_B/\partial s^2) + K_A(\partial^2 x_A/\partial s^2)] \qquad (13)$$

If A and B are identical, this reduces to eq 12. If they are different, we recall that each K is $O(1)$, so that passage to the limit then gives

$$K_A(\partial x_A/\partial s)_{s=\theta} = K_B(\partial x_B/\partial s)_{s=\theta} \quad \text{(any } t\text{)} \qquad (14a)$$

at the junction point $s = \theta$, where of course we also have

$$x_A(\theta, t) = x_B(\theta, t) \qquad (14b)$$

A familiar special case of eq 14a is found at a free chain end, where one of the K's is necessarily zero; then[4]

$$(\partial x/\partial s)_{end} = 0 \quad (s = \pm 1, \text{ any } t) \qquad (15)$$

Physically, the condition 14a states that the mean net force on the chain element at the junction point is zero, so that the displacements in the two regions ("springs") immediately adjacent to the junction adjust themselves in inverse ratio to the spring force constants. It is evident that the above considerations closely resemble those previously advanced by Zimm and Kilb[5] and by Ham[16] in treating the viscoelastic behavior of branched homopolymers.

The solution of eq 12 with the conditions 14 and 15 can now be pursued by standard methods,[7] e.g., separation of variables or Laplace transform. We proceed to do this for several examples.

Symmetric Triblock Polymers

Let a symmetric triblock ABA polymer be specified by a B region extending between $s = -\theta$ and $s = +\theta$; the A regions lie beyond. By symmetry, it is sufficient to confine attention to the half-chain with $s \geq 0$, and furthermore there must be either a node or an extremum in x_B at $s = 0$. By separation of variables, we then obtain for any normal mode

$$\begin{aligned} x_B &= \exp(-t/2\tau)(C_B \sin \beta s + D_B \cos \beta s) \\ x_A &= \exp(-t/2\tau)(C_A \sin \alpha s + D_A \cos \alpha s) \end{aligned} \qquad (16)$$

with

$$\tau = \tau_{1A}(\pi/2\alpha)^2 = \tau_{1B}(\pi/2\beta)^2 \qquad (17)$$

The condition at the middle of the chain ($s = 0$) further requires either $C_B = 0$ (even modes) or $D_B = 0$ (odd modes). Now upon application of conditions 14 and 15, the characteristic equations are found to be

$$\begin{aligned} \tan[\alpha(1-\theta)] &= -\lambda\mu \tan \alpha\lambda\theta \quad \text{(a) (even modes)} \\ &= +\lambda\mu \cot \alpha\lambda\theta \quad \text{(b) (odd modes)} \end{aligned} \qquad (18)$$

where we have abbreviated

$$\begin{aligned} \lambda &= \beta/\alpha = (\tau_{1B}/\tau_{1A})^{1/2} \\ \mu &= K_B/K_A = (b_A/b_B)^2 \end{aligned} \qquad (19)$$

In general, the transcendental eq 18 have, of course, to be solved numerically, but some limiting cases are easy to discuss analytically. If the B block shrinks to zero, $\theta = 0$, we obtain $\alpha = p\pi/2$ for both even and odd p, as for a homopolymer of type A. Similarly, for $\theta = 1$ we recover $\beta = p\pi/2$, appropriate to a B homopolymer. If the central block is small ($\theta \ll 1$), expansions lead to

$$\begin{aligned} 2\alpha/p\pi &= 1 + \theta(1 - \mu^{-1}) + \ldots \quad \text{(odd modes)} \\ &= 1 + \theta(1 - \lambda^2\mu) + \ldots \quad \text{(even modes)} \end{aligned} \qquad (20)$$

By use of eq 9, 17, and 19, these results can be transcribed to

$$\begin{aligned} \tau_p/\tau_{pA} &= 1 + 2\theta\gamma + \ldots \quad \text{(odd modes)} \\ &= 1 + 2\theta\delta + \ldots \quad \text{(even modes)} \end{aligned} \qquad (20')$$

where

$$\begin{aligned} \gamma &= (b_B^2 - b_A^2)/b_A^2 = \mu^{-1} - 1 \\ \delta &= (\zeta_B - \zeta_A)/\zeta_A = \lambda^2\mu - 1 \end{aligned}$$

At this point we can make contact with the special calculation of DeWames, Hall, and Shen[3] for a Rouse chain with all spring constants the same ($\gamma = 0$) but with the central bead having a different friction coefficient, thus corresponding to $\theta = 1/N$. As they worked with an approximation of a continuous distribution of eigenvalues, they could not distinguish between odd and even modes. The *average* of our relations (eq 20′) for their model gives $\tau_p/\tau_{pA} = 1 + (\delta/N)$, which corresponds exactly to their result.

Limiting forms of eq 18 can also be found when the dynamic flexibilities of the blocks differ greatly. If the central B block is far less mobile than the ends, $\lambda \gg 1$, and in this case we find (assuming θ to be noninfinitesimal)

$$\lim_{\lambda\to\infty} \alpha\lambda = \lim_{\lambda\to\infty} \beta = p\pi/2\theta \quad \text{(all modes)} \qquad (21)$$

This is just the Rouse spectrum for the central block alone, as would be predicted if the end blocks became ectoplasmic. In the other extreme, that of a highly mobile center block as compared to the wings ($\lambda \ll 1$), the limiting results are:

$$\begin{aligned} \alpha(1-\theta) &= \tan^{-1}(\mu/\alpha\theta) \quad \text{(odd modes)} \\ &= p\pi/2 \quad \text{(even modes)} \end{aligned} \qquad (22)$$

showing that the distribution of relaxation times in this case differs somewhat from Rouse behavior. However, the even modes alone are always distributed à la Rouse, as can again be understood physically when virtually all resistance is in the wings. For finite μ, each of the higher odd eigenvalues tends toward an adjacent even root, either the previous or subsequent one, depending on the value of θ. This produces a pairing of relaxation times, but a Rouse-like

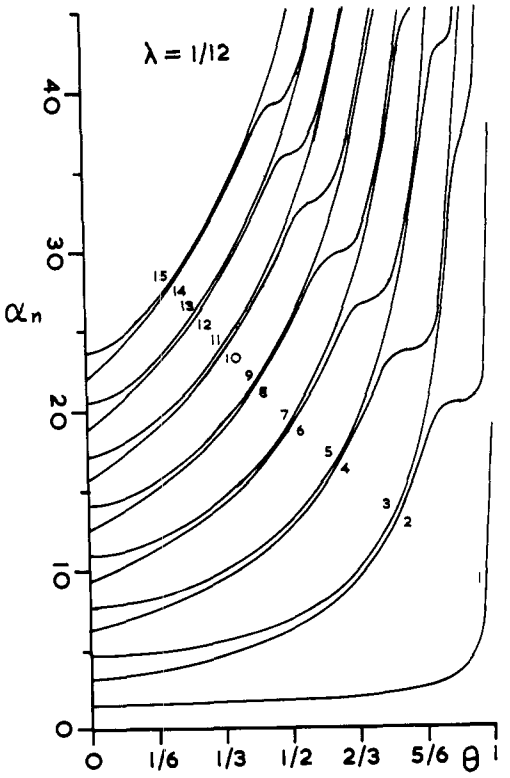

Figure 1. Roots α_n of eq 18 for symmetric triblock ABA copolymers with $\mu = 1$ and $\lambda = 1/12$, corresponding to a relatively mobile B block, plotted against the fractional length θ of the inner block. The corresponding relaxation times vary as α_n^{-2}. For even n, the same roots also apply to diblock BA copolymers.

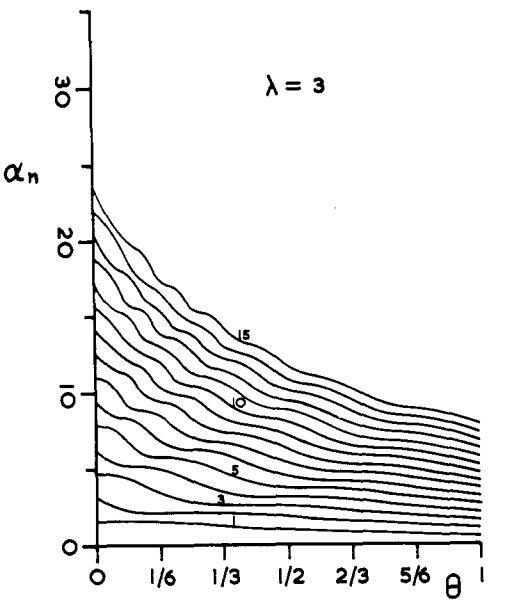

Figure 2. Roots α_n, as in Figure 1, for $\mu = 1$ and $\lambda = 3$, corresponding to moderately enhanced mobility in the terminal blocks.

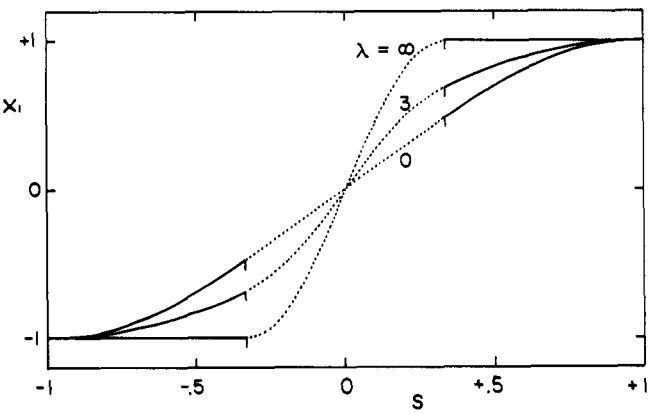

Figure 3. First normal relaxation mode of symmetric triblock ABA copolymers with three blocks of equal length ($\theta = 1/3$). The relative displacement is shown as a function of chain contour position, with dotted curves for the B block and full curves for the A blocks. Relative flexibility of the terminal blocks increases with λ.

spectrum at higher frequency in any case.

Computed roots from eq 18 are shown in Figures 1 and 2 for $\mu = 1$ and two different values of λ. In Figure 1 the pairing of eigenvalues for the case of a mobile inner block is clearly visible, while Figure 2 reveals an amusing oscillation of the roots about smooth curves. A check on these and our other computations (briefly described in the Appendix) is afforded by a sum rule

$$3\sum_{p\geq 1}\alpha_p^{-2} = 2J/(1 + \theta\delta) \qquad (23)$$

$$J = 1 + (3\theta/2)(\gamma + \delta) + 3\gamma\delta\theta^2 + \theta^3(\delta - \gamma + 2\delta^2 - 2\gamma\delta + 2\gamma\delta^2)/2$$

which can be obtained, independently of any direct appeal to eq 18, through an extension of Debye's[14] familiar calculation of the steady-flow free-draining intrinsic viscosity:

$$[\eta]_0 = \frac{N_A}{6M\eta_0}\sum_j \zeta_j\langle R_j^2\rangle = \frac{N_A N^2\zeta_A b_A^2 J}{36M\eta_0(1 + \theta\delta)} \qquad (24)$$

In this expression, N_A is Avogadro's number and $\langle R_j^2\rangle$ is the equilibrium mean-square distance of bead j from the molecular center of frictional resistance. Comparison of eq 24 with eq 1 for $\omega = 0$ leads to eq 23.

The shapes of the normal mode displacement amplitudes $x_n(s)$ are easily found from eq 16, and are shown in Figures 3 and 4 for the first two modes for the case $\mu = 1$ and $\theta = 1/3$, which means that all three blocks have the same length. For the terminal mode (Figure 3) the effect of high central-block mobility on the shape of the curve is very small; for example, the curve for $\lambda = 1$ (not shown, corresponding to a homopolymer) is only slightly displaced from that for $\lambda = 0$. On the other hand, when the terminal blocks become highly mobile (λ large), the central portion of the curve becomes dominant, in accord with eq 21.

It is important to ask whether the deviations from a pure Rouse spectrum produced by eq 18 will lead to observable effects on the frequency dependence of the viscoelastic properties. We made a number of calculations of the reduced storage and loss moduli[12] and found that in general the deviations are not large but possibly just detectable. A similar conclusion has been reached by Wang and DiMarzio.[9] In consequence, methods for extracting the terminal relaxation time τ_1 from experimental measurements need not be modified for block copolymers.

The remaining major question is then the dependence of τ_1 on the copolymer structure and composition. To illuminate this question, we define a reduced terminal relaxation time $\tilde{\tau}_1$ as follows:

$$\tilde{\tau}_1 = \tau_1/[(1 - \theta)\tau_{1A} + \theta\tau_{1B}] = (\pi/2\alpha_1)^2/[1 + (\lambda^2 - 1)\theta] \qquad (25)$$

This dimensionless quantity is seen to be just the ratio of τ_1 to a linear average value calculated from the relaxation times of the related homopolymers in the same medium. A few values of $\tilde{\tau}_1$ are shown in Figure 5, for selected values of λ, and it is seen that τ_1 can stray quite far from a simple linear average. For large λ, both eq 21 and Figure 3 show

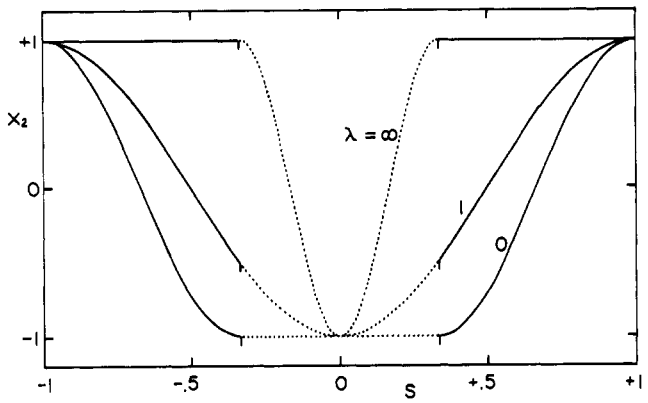

Figure 4. Displacement x_2 of second relaxation mode for symmetric triblock copolymers with $\theta = \frac{1}{3}$. The curves for positive contour variable r also describe the first mode for analogous diblock BA copolymers.

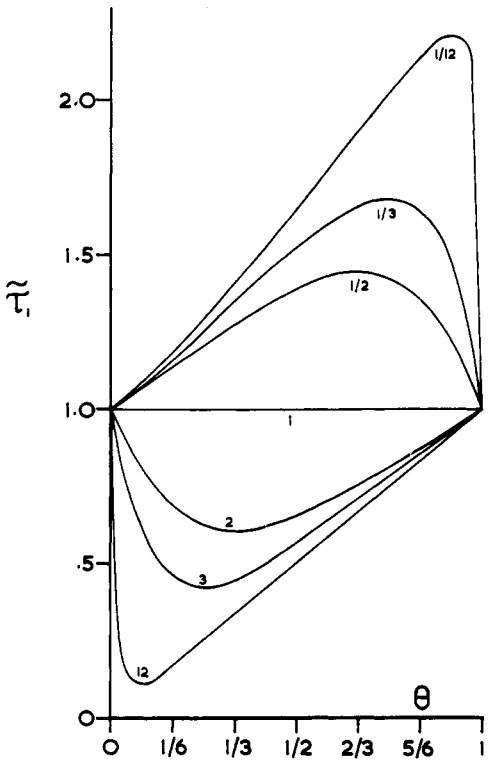

Figure 5. Reduced terminal relaxation time $\tilde{\tau}_1$ from eq 25 for symmetric triblock ABA copolymers as a function of θ for various values of λ, with $\mu = 1$.

that in fact for such cases τ_1 will vary as θ^2. On the other hand, for small λ the shape of the terminal mode is almost invariant (Figure 3) and $\tilde{\tau}_1$ should be more nearly constant.

An alternative quantity, inspired by the above observation for large λ, is defined by

$$\tilde{\tau}_1^* = \tau_1/[(1 - \theta)\tau_{1A}^{1/2} + \theta\tau_{1B}^{1/2}]^2 \qquad (26)$$

and indeed it is more nearly constant for large λ, but it is useless when λ is small. These remarks are illustrated in Figure 6, where both $\tilde{\tau}_1$ and $\tilde{\tau}_1^*$ are plotted as functions of log λ for $\theta = \frac{1}{3}$. On this graph we have also shown a reduced steady-flow viscosity, defined in accordance with eq 2 as

$$\tilde{\eta} = (\Sigma\tau_p)/[(1 - \theta)\Sigma\tau_{pA} + \theta\Sigma\tau_{pB}] \qquad (27)$$

and evaluated from eq 23. It is seen in Figure 5 that for small λ there is not too great a difference between $\tilde{\tau}_1$ and $\tilde{\eta}$, while in fact for $\lambda > 1$ the two curves are essentially indistinguishable. This emphasizes again that the deviations

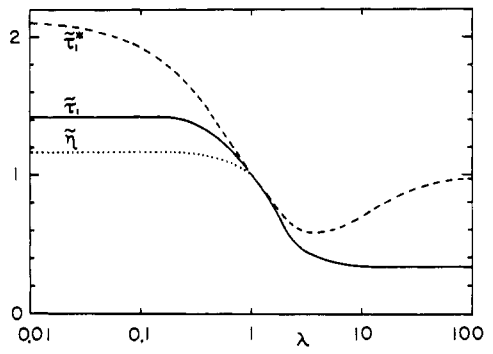

Figure 6. Reduced terminal relaxation times $\tilde{\tau}_1$ and $\tilde{\tau}_1^*$ and reduced viscosity $\tilde{\eta}$ for symmetric triblock ABA copolymers with $\mu = 1$ and $\theta = \frac{1}{3}$ (blocks of equal length) for various relative flexibilities λ. See eq 25–27.

from Rouse behavior in the eigenvalue spectrum are hard to detect.

Diblock Copolymers

Consider a two-piece block copolymer with the B block at the left. By a simple adjustment of scale, the previous calculations for the even modes of symmetrical triblock ABA polymers give the eigenvalues for the two-block case, because the extremum condition in the middle of the triblock chain is replaced by the free-end condition at the B end, which is mathematically identical. For the diblock chain, let the contour variable be redefined as

$$r = j/N \qquad (0 \leq r \leq 1) \qquad (28)$$

in place of eq 10, and let the B block correspond to the region $0 \leq r \leq \theta$. Repetition of the earlier procedure then gives, within each block

$$\partial x/\partial t = (1/2\pi^2\tau_1)\partial^2 x/\partial r^2 \qquad (29)$$

The appropriate solutions are found to be

$$x_B = \exp(-t/2\tau)C_B \cos \alpha\lambda r$$
$$x_A = \exp(-t/2\tau)C_A(\tan \alpha \sin \alpha r + \cos \alpha r) \qquad (30)$$

where the relaxation times are given by

$$\tau = \tau_{1A}\pi^2/\alpha^2 \qquad (31)$$

and

$$C_B/C_A = (\sin \alpha\theta - \tan \alpha \cos \alpha\theta)/\lambda\mu \sin \alpha\lambda\theta = (\tan \alpha \sin \alpha\theta + \cos \alpha\theta)/\cos \alpha\lambda\theta \qquad (32)$$

The two last equalities lead to

$$\tan(\alpha - \alpha\theta) = -\lambda\mu \tan \alpha\lambda\theta \qquad (18a)$$

which, as expected, is identical to that for the even modes of the symmetric diblock polymer.

Some values of the reduced terminal relaxation time τ_1 for diblock polymers, defined as in eq 25, are shown in Figure 7. As in the triblock case, there is no simple algebraic formula for relating τ_1 to copolymer composition.

Discussion

The foregoing theory and calculations are restricted to free-draining hydrodynamic conditions, and therefore are expected to apply only to molten copolymers or to sufficiently concentrated solutions. Fortunately, these are also the conditions for minimizing excluded volume effects. In practice, a further consideration relates to the values of the friction coefficients and chain dimensions to be assigned to the elements of the blocks. If the extent of microphase segregation is large, it would be natural to choose the model parameters for an A block as identical to those for a pure homopolymer of type A under the same conditions of tem-

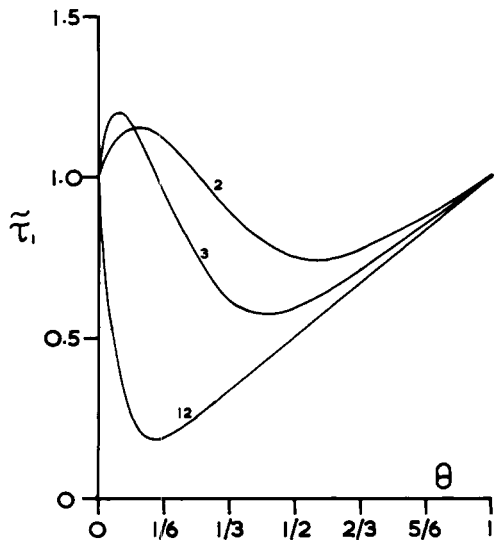

Figure 7. Reduced terminal relaxation time τ_1 for diblock BA copolymers with $\mu = 1$. Curves are shown only for $\lambda > 1$, since for this case $\tilde{\tau}_1(\lambda, \theta) = \tilde{\tau}_1(\lambda^{-1}, 1 - \theta)$.

perature, pressure, and concentration. If, on the other hand, the melt is essentially homogeneous in composition, the model parameters would have to be evaluated in a different way. A recent study of dielectric relaxation in concentrated polymer solutions[18] suggests that a combination of the free-volume approach[12] with a theory of polymer solutions such as that of Flory[19] can be used to make useful approximate predictions of frictional coefficients in binary mixtures from those of the pure components. This procedure will be discussed elsewhere.[18] Its extension to the case of well-mixed block copolymers would be straightforward.

Although our calculations have been restricted to simple tractable examples, the basic relations are in principle applicable to flexible linear block copolymers of arbitrary structure. It would also be perfectly feasible to perform calculations for model graft copolymers under free-draining conditions, making contact with the appropriate theory for branched homopolymers.[5]

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Appendix

The roots of eq 18 were found numerically by the following simple algorithm based on the Newton–Raphson technique

$$\alpha^{(i+1)} = \alpha^{(i)} - \Delta\alpha^{(i)}$$
$$\Delta\alpha^{(i)} \equiv F^{(i)}/(\partial F/\partial\alpha)^{(i)} \quad \text{(A1)}$$

where $\alpha^{(i)}$ is the ith approximant to a given root, and

$$F(\alpha) = \cos(\alpha\lambda\theta)\sin\alpha(1-\theta) + \lambda\mu\cos\alpha(1-\theta)\sin(\alpha\lambda\theta) = 0 \quad \text{(A2)}$$

for the even modes, and

$$F(\alpha) = \sin(\alpha\lambda\theta)\sin\alpha(1-\theta) - \lambda\mu\cos\alpha(1-\theta)\cos(\alpha\lambda\theta) = 0 \quad \text{(A3)}$$

for the odd modes, as can easily be established by rearrangement of eq 18. Further details of these and the other calculations can be furnished on request.

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