Analytic Relations for Block Copolymer Relaxation Times in the Rouse Model

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ABSTRACT: The simplest relevant model of polymer viscoelasticity is used to predict the relaxation spectrum of block copolymers. A procedure is outlined for obtaining an analytic expression for the condition determining the relaxation spectrum for arbitrary multiblock copolymers. The results of this procedure for the symmetrical triblock copolymer are given, and the behavior of the two longest relaxation times is illustrated for this case.

Recently, there has been considerable interest in the viscoelastic properties of polymeric systems in which more than one type of monomer appears in the same molecule, especially where each monomeric type appears in long "strings" or blocks.[1] Such a copolymeric system can easily be described within the Rouse submolecule picture, and relationships among the viscoelastic properties of the copolymers and those of their constituent homopolymers can then be derived.[2-4]

The viscoelastic relaxation time spectrum (τ_j) of a copolymer composed of different homopolymeric blocks is determined in this model[5,7] by the eigenvalues $\lambda_j = (2\tau_j)^{-1}$ of the equations describing the collective motion of the N submolecules into which one conceptually divides the polymer chain

$$K_i(u_i - u_{i-1}) - K_{i+1}(u_{i+1} - u_i) = \lambda f_i u_i \qquad (1)$$

$$i = 1, \ldots, N; \quad u_0 = u_1; \quad u_{N+1} = u_N$$

In the interior of a homopolymeric block of type μ the entropic spring constant $K_i = 3kT/l_\mu^2$, where l_μ^2 is the mean-square end-to-end distance $\langle r_\mu^2\rangle$ for the whole block, divided by the number N_μ of submolecules making up the block. At the junction between two blocks μ and ν of differing composition one cannot say within this model what the connecting spring constant should be, so we shall simply denote it by $K_{\mu\nu}$, leaving it a free parameter. Each submolecule will be regarded as belonging to a definite homopolymeric block, so its friction factor f_i will be the total friction factor F_μ for the appropriate block, divided by N_μ.

In the case of a homopolymer, one can find the eigenspectrum for N submolecules by elementary techniques and verify that the longest relaxation times, on which most observable viscoelastic properties depend, are independent of the exact number of submolecules into which the polymer has been divided. In the case of a block copolymer, dependence of the submolecule properties on its position within the chain prevents a direct application of these techniques. However, within each homopolymeric block these properties remain constant, so that it is possible to partition the equations of motion into as many simple submatrices as there are such blocks, with only elements at the ends of each block differing from those for a free-floating homopolymer. If one denotes the nearest-neighbor matrix of size N_μ by A^μ, and the ratio f_μ/K_μ by d_μ, then these equations in matrix form may be written as

$$[A^\mu - \lambda \mathbf{I}^\mu d_\mu]\mathbf{X}^\mu + \delta_{i,1}\left(\frac{K_{\mu,\mu-1}}{K_\mu}\right)[-X_{N_{\mu-1}}{}^{\mu-1} + X_1{}^\mu] + \delta_{i,N_\mu}\left(\frac{K_{\mu,\mu+1}}{K_\mu}\right)[X_{N_\mu}{}^\mu - X_1{}^{\mu+1}] = 0 \qquad (2)$$

$$(i = 1, \ldots, N_\mu)\ (\mu = 1, \ldots, M)$$

where $\mathbf{X}^\mu$ is the vector of displacements $\{u_i\}$ within the μth block, $\mathbf{I}^\mu$ denotes the identity matrix of size N_μ, and M is the number of distinct blocks in the copolymer.

The inverse of $A^\mu - \lambda\mathbf{I}^\mu d_\mu$, which we shall call $G^\mu(\lambda d_\mu)$, can be used to greatly simplify the determination of the eigenspectrum for the copolymer. Multiplying each block of N_μ equations by the appropriate G^μ reduces eq 2 to the nearly diagonal form

$$\mathbf{I}^\mu\mathbf{X}^\mu + \left(\frac{K_{\mu,\mu-1}}{K_\mu}\right)G_{i,1}{}^\mu[-X_{N_{\mu-1}}{}^{\mu-1} + X_1{}^\mu] + \left(\frac{K_{\mu,\mu+1}}{K_\mu}\right)G_{i,N\mu}{}^\mu[X_{N_\mu}{}^\mu - X_1{}^{\mu+1}] = 0 \qquad (3)$$

$$(i = 1, \ldots, N_\mu) \quad (\mu = 1, \ldots, M)$$

For $i \neq 1$ or N_μ, these equations determine $X_i{}^\mu$ in terms of the displacements of the submolecules adjoining either end of the μth block, $X_{N_\mu}{}^\mu$ and $X_1{}^\mu$. The remaining $2(M - 1)$ equations involve only $X_{N_\mu}{}^\mu$ and $X_1{}^\mu$, so the requirement that the determinant of their coefficients vanish yields a single equation for the eigenvalues λ in terms of the functions $G_{1,1}{}^\mu$, $G_{1,N_\mu}{}^\mu$, $G_{N_\mu,1}{}^\mu$, and $G_{N_\mu,N_\mu}{}^\mu$, and the parameters $(K_{\mu,\mu\pm1}/K_\mu)$ and d_μ.

The required elements of $G = (A - \xi)^{-1}$ can be expressed analytically[6] in the form

$$G_{1,1} = G_{N,N} = \frac{-\cos{(N - 0.5)\theta}}{2\sin{(\theta/2)}\sin{N\theta}}$$

$$G_{1,N} = G_{N,1} = \frac{-\cos{(\theta/2)}}{2\sin{(\theta/2)}\sin{N\theta}} \qquad (4)$$

where $\theta = \cos^{-1}(1 - \xi/2)$. As the degree of subdivision N is increased, d decreases as N^{-2} and θ approach $(\lambda d)^{1/2}$ for fixed λ. Thus, that part of the relaxation spectrum which is independent of N can be found by replacing $\theta_\mu G_{1,1}{}^\mu$ by $-\cot \pi(\tau_\mu/\tau)^{1/2}$, and $\theta_\mu G_{1,N_\mu}{}^\mu$ by $-\operatorname{cosec} \pi(\tau_\mu/\tau)^{1/2}$, where $\tau_\mu = \langle r_\mu^2\rangle F_\mu/6\pi^2kT$ is the longest relaxation time for a free-floating segment of the μth composition and molecular weight.

For the symmetrical triblock copolymer a–b–a, this procedure yields the condition

$$\frac{(\cos \pi\sqrt{\tau_b/\tau} \pm 1)}{\sin \pi\sqrt{\tau_b/\tau}}\tan \pi\sqrt{\tau_a/\tau} = -\frac{K_b}{K_a}\frac{d_b}{d_a} = -\sqrt{\frac{F_b\langle r_a^2\rangle}{F_a\langle r_b^2\rangle}} \qquad (5)$$

where we have assumed that the springs connecting b to a at either end are equally strong, i.e., $K_{ab} = K_{ba}$. The roots of (5) corresponding to the two different signs interlace, with the longest relaxation time being obtained for the lower sign. The appropriate condition for the diblock a–b is obtained from (5) by dropping the ±1 altogether. These conditions are also derivable by a direct argument which treats the chain as a continuum, as Stockmayer and Kennedy[3] have shown.

One limiting case of practical interest is $\tau_b/\tau_a \rightarrow 0$, corresponding to a "b" segment much shorter than the surrounding "a's". In this case, the longest relaxation time τ_1 approaches $4\tau_a$ (appropriate to a molecule consisting of two "a" segments only), while the next longest, τ_2, approaches τ_a. Expanding the arguments of the trigonometric functions in (5) about these values, one finds that the relaxation times approach their limits in the following way:

$$\begin{aligned} \tau_1 &\sim 4\tau_a(1 + \langle r_b^2\rangle/\langle r_a^2\rangle) \\ \tau_2 &\sim \tau_a(1 + (F_b/F_a)) \end{aligned} \tag{6}$$

The surprising result that τ_1 is to first order independent of the "b" segment friction factor follows from the fact that the displacement of the center of the polymer from equilibrium is zero for the lowest frequency eigenmode; the "b" segment does not move against the surrounding medium in this limit. Similarly, the fact that the derivative of the displacement vanishes at the center of the polymer for the second-lowest eigenmode implies that τ_2 in this limit will be independent of the "b" spring constant, $3KT/\langle r_b^2\rangle$. Thus, the slope of the initial departure of τ_1 and τ_2 from their pure "a" values gives a direct measure of F_b and $\langle r_b^2\rangle$ at low molecular weight for the "b" segment.

These results can be compared with the estimate derived in our earlier work[5] for a single "b" bead in between two long strings of "a"

$$\tau_p' - \tau_p \simeq [(f_b - f_a)/Nf_a]\tau_p \tag{7}$$

where τ_p is the pth relaxation time for a pure "a" polymer of the same length. Clearly, this estimate is in error for τ_1, which does not shift when two systems of the same length are compared. In fact, our derivation of (7) assumed that $G_{\nu\nu}(\zeta)$ for $\nu = (N + 1)/2$ could be approximated by $[N(\lambda_p - \lambda)]^{-1}$ for λ near λ_p, which is only true for the even eigenmodes. The odd eigenmodes are not present in the spectral representation of $G_{\nu\nu}$, and hence they are not shifted by the change in friction factor of the central bead.

A more detailed picture of the consequences of forming a symmetrical triblock copolymer on the two longest relaxation times is given in Figures 1 and 2. The parameter R in these plots is the right-hand side of (5), $[F_b\langle r_a^2\rangle/F_a\langle r_b^2\rangle]^{1/2}$. When R is unity, the square roots of the relaxation times for the individual segments add, exactly as though only one type of segment were present; this is represented by the straight line in each figure. For small R, τ_1 rapidly increases with τ_b, while for large R it is initially insensitive; eventually, for sufficiently large τ_b, $\tau_1 \sim \tau_b$ + constant. The behavior of τ_2 is somewhat different. For small R, τ_2 is at first insensitive to τ_b; it crosses over the homopolymeric line at $\tau_b = 4\tau_a$ and eventually becomes asymptotic to $\tau_b/4$ + constant. For large R, the initial behavior is reversed, with τ_1 crossing under the homopolymeric line at $\tau_b = 4\tau_a$.

The quantitative significance of this behavior for copolymers in solution or in bulk is not immediately clear, for several reasons. Most restrictive is our assumption that every block is free draining, i.e., that the Rouse model applies. This restriction can be removed for copolymers in dilute solution by including an appropriate hydrodynamic interaction matrix **H** (after the fashion of Zimm[7]), chosen for each block to match the properties of the homopolymer. However, the arguments leading to eq 3 can no longer be carried through, because elements in one block will have a hydrodynamic interaction with all the elements of a neighboring block. Thus, to find the relaxation spectrum one must resort to computer diagonalization of the complete matrix as Wang[4] has done. For copolymers in bulk, where the Rouse model may be justified, one must acknowledge that the total friction factor for each block and its mean-square end-to-end distance depend strongly upon the composition of its environment, which may vary with the degree of microphase separation; also, the details of this dependence are not known.

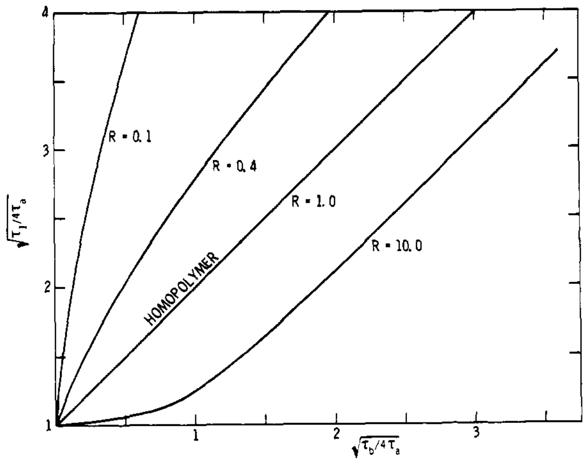

Figure 1. Longest relaxation time τ_1 for the symmetrical triblock copolymer a–b–a as a function of τ_b, the longest relaxation time for the "b" segment alone.

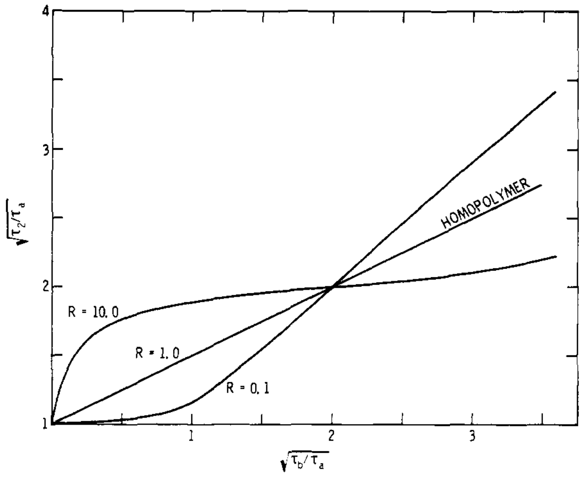

Figure 2. Second-longest relaxation time τ_2 for the symmetrical triblock copolymer a–b–a as a function of τ_b.

The qualitative behavior of the relaxation spectrum can nonetheless be deduced from this simple model and compared with bulk and solution viscosity measurements. Where the Rouse model is found to fit, useful information should be derivable concerning the parameters which characterize the interaction of the individual segments with their environment.

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References and Notes

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