

The Dynamics of Block-Copolymer Molecules in Solution. The Free-Draining Limit

F. W. Wang* and E. A. DiMarzio

*Institute for Materials Research, National Bureau of Standards, Washington, D.C. 20234.
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ABSTRACT: A theory for the viscoelasticity of block-copolymer molecule solutions in the free-draining limit has been developed by modifying the bead-spring model theory of Rouse to take into account the existence of dissimilar segments in block copolymers. The eigenvalue problem encountered in the theory has been solved numerically by matrix computations. Furthermore, for the case of a diblock copolymer, a simple form of the secular equation which is useful for extracting the eigenvalues has been obtained. The applications of the theory have been illustrated with calculations for the viscoelastic properties of poly(styrene-*b*-*cis*-1,4-isoprene) solutions. It is found that the calculated properties for the diblock copolymer are nearly the same as those for the Rouse theory while the calculated properties for the symmetric triblock copolymers deviate from those of the Rouse theory.

I. Introduction

In a previous paper¹ hereafter referred to as paper I, one of us has developed a theory for the dynamics of block-copolymer molecules in dilute solution by modifying the bead-spring model theory of Zimm² to take into account the existence of dissimilar segments in block copolymers. In the case of homopolymer molecules in solution, it has been observed³ that the spectrum of viscoelastic response is that of a free-draining chain at higher concentrations and becomes more nearly nonfree-draining as the concentration is decreased. These observations could be explained by the concept of foreign molecules interfering with the hydrodynamic interactions between parts of one chain. Wang and Zimm⁴ have introduced such interference in a simplified form and have found that it does, in fact, produce the expected change in viscoelastic spectrum with concentration. The theory of paper I can be further extended by similarly taking into account such interference from foreign molecules. We discuss in this paper the viscoelasticity of block-copolymer solution in the free-draining limit in which the hydrodynamic interactions between parts of one chain are completely screened out by such interference. Shen and Hansen⁵ have recently treated the free-draining diblock copolymer numerically. Stockmayer and Kennedy⁶ have recently solved the large molecular weight case exactly in the continuum limit.

II. Characteristic Value Problem

The representation of the A-B-C type linear block-copolymer molecule by a bead-spring model has been discussed in detail in paper I. Here, we describe briefly the bead-spring model in order to introduce the notations. The block-copolymer molecule is represented as a chain of N Hookean springs joining $N + 1$ beads with complete flexibility at each bead. The A block is represented by a chain of $(N_a - 1)$ springs joining N_a beads, each of which is characterized by the translational friction constant ρ_a . The force constant of each of the springs is $3kT/b_a^2$, where b_a^2 is its mean-square length, and k and T are the Boltzmann constant and the absolute temperature. The symbols N_b , N_c , ρ_b , ρ_c , b_b , and b_c are similarly defined. The beads of the model for the A block are enumerated serially from 0 to $(N_a - 1)$, correspondingly from N_a to $(N_a + N_b - 1)$ for the B block, and from $(N_a + N_b)$ to N for the C block. The $(N_a - 1)$ th bead of the A block and the N_a th bead of the B block are connected by free joints to the ends of a spring whose mean-square length b_{ab}^2 is given by the arithmetic mean of b_a^2 and b_b^2 . Finally, the bead-spring model for the block-copolymer molecule as a whole is formed by connect-

ing with free joints the $(N_a + N_b - 1)$ th bead of the B block and the $(N_a + N_b)$ th bead of the C block to the ends of a spring of mean-square length b_{bc}^2 which is defined in the same manner as b_{ab}^2 .

As is known¹⁻³ the dynamic properties of interest are determined by the eigenvalues λ_k ($k = 1, 2, \dots, N$) of the matrix \mathbf{B} of order N defined by eq 28 of ref 1. In the limit of negligible hydrodynamic interaction (the so-called free-draining case^{2,3}), the off-diagonal terms of the matrix \mathbf{H} (defined by eq 16 of ref 1) vanish and hence the matrix \mathbf{B} becomes tridiagonal with nonzero elements given as follows:

$$B_{jk} = (b^2\rho/b_a^2\rho_a)(-\delta_{j+1,k} + 2\delta_{jk} - \delta_{j-1,k}) \quad (1a)$$

for

$$1 \leq k \leq N_a - 1$$

$$B_{jk} = (b^2\rho/b_{ab}^2)\left[-\frac{\delta_{j+1,k}}{\rho_a} - \left(\frac{1}{\rho_a} + \frac{1}{\rho_b}\right)\delta_{jk} - \frac{\delta_{j-1,k}}{\rho_b}\right] \quad (1b)$$

for

$$k = N_a$$

$$B_{jk} = (b^2\rho/b_b^2\rho_b)(-\delta_{j+1,k} + 2\delta_{jk} - \delta_{j-1,k}) \quad (1c)$$

for

$$N_a + 1 \leq k \leq N_a + N_b - 1$$

$$B_{jk} = (b^2\rho/b_{bc}^2)\left(\frac{-\delta_{j+1,k}}{\rho_b} + \left(\frac{1}{\rho_b} + \frac{1}{\rho_c}\right)\delta_{jk} - \frac{\delta_{j-1,k}}{\rho_c}\right) \quad (1d)$$

for

$$k = N_a + N_b$$

$$B_{jk} = (b^2\rho/b_c^2\rho_c)(-\delta_{j+1,k} + 2\delta_{jk} - \delta_{j-1,k}) \quad (1e)$$

for

$$N_a + N_b + 1 \leq k \leq N$$

where ρ is an arbitrary friction constant and b is the root-mean-square length of an arbitrary spring. For the case of a homopolymer molecule with $\rho_a = \rho_b = \rho_c = \rho$ and $b_a = b_b = b_c = b$, the matrix \mathbf{B} reduces to the \mathbf{A} matrix that Rouse uses.⁷

For the case of an A-B type block-copolymer molecule with $\rho_c = \rho_b$ and $b_c = b_b$, we can reduce the characteristic determinant of the matrix \mathbf{B} given by eq 1 to a simple expression. The nonzero elements of the characteristic determinant $\det \mathbf{W}$, where \mathbf{W} is tridiagonal, are given in eq 2 and 3. We can find an explicit form for the characteristic determinant by reducing the above $N \times N$ determinant to an $(N$

$$\det W = \begin{bmatrix} W_a & 1 & \dots & & & & & & & \\ & 1 & W_a & 1 & \dots & & & & & \\ & & 1 & W_a & \dots & & & & & \\ & & & 1 & \dots & & & & & \\ & & & & \dots & & & & & \\ & & & & & W_a & 1 & & & \\ & & & & & 1 & W_a & (b_a^2/b_{ab}^2) & & \\ & & & & & & 1 & W_{ab} & (b_a^2\rho_a/b_b^2\rho_b) & \\ & & & & & & & (b_b^2/b_{ab}^2) & W_b & \\ & & & & & & & & 1 & \\ & & & & & & & & & 1 & W_b & 1 & \dots & \\ & & & & & & & & & & 1 & W_b & \dots & 1 & \\ & & & & & & & & & & & \dots & 1 & W_b & 1 & \\ & & & & & & & & & & & & \dots & 1 & W_b & \end{bmatrix} \quad (2)$$

where

$$W_a = (\lambda b_a^2 \rho_a / b^2 \rho) - 2 \quad (3a)$$

$$W_b = (\lambda b_b^2 \rho_b / b^2 \rho) - 2 \quad (3b)$$

and

$$W_{ab} = (\lambda b_a^2 \rho_a / b^2 \rho) - (b_a^2 / b_{ab}^2)(1 + \rho_a / \rho_b) \quad (3c)$$

$-1) \times (N-1)$ determinant, and then reducing this to an $(N-2) \times (N-2)$ determinant and so on. To reduce $\det W$ to an $(N-1) \times (N-1)$ determinant we first multiply the second column by W_a and then subtract the first column from it

$$\det W = \frac{1}{W_a} \begin{bmatrix} W_a & W_a & & & \\ 1 & W_a^2 & 1 & & \\ & W_a & W_a & 1 & \dots \\ & & 1 & \dots & \\ & & & \dots & \end{bmatrix} = \frac{1}{W_a} \begin{bmatrix} W_a & 0 & & & \\ 1 & (W_a^2 - 1) & 1 & & \\ & W_a & W_a & \dots & \\ & & 1 & \dots & \end{bmatrix} \quad (4)$$

$$\begin{aligned} f(0) &= 1 \\ f(1) &= W_a \\ f(2) &= W_a f(1) - 1 \\ f(3) &= W_a f(2) - f(1) \\ f(4) &= W_a f(3) - f(2) \\ &\vdots \\ f(j) &= W_a f(j-1) - f(j-2) \end{aligned} \quad (7)$$

After $(N_a - 2)$ such reductions we obtain eq 8, where the $N \times N$ determinant now has been reduced to an $(N - (N_a - 2)) \times (N - (N_a - 2))$ determinant. In a like manner we can work up from the bottom right to obtain eq 9-11:

$$\det W = \begin{bmatrix} f(N_a - 1) & (b_a^2/b_{ab}^2) & & & & & & & & \\ f(N_a - 2) & W_{ab} & (b_a^2\rho_a/b_b^2\rho_b) & & & & & & & \\ & (b_b^2/b_{ab}^2) & W_b & & & & & & & \\ & & 1 & & & & & & & \\ & & & W_b & 1 & & & & & \\ & & & 1 & W_b & 1 & \dots & & & \\ & & & & \dots & & & & & \\ & & & & \dots & 1 & W_b & 1 & & \\ & & & & & \dots & 1 & W_b & \end{bmatrix} \quad (8)$$

We now expand along the first column to obtain

$$\det W = \begin{bmatrix} (W_a^2 - 1) & 1 & & & \\ W_a & W_a & 1 & \dots & \\ & 1 & W_a & \dots & \\ & & \dots & & \end{bmatrix} \quad (5)$$

Thus we have reduced the order of the determinant by 1. To reduce it again by one we multiply the second column by $(W_a^2 - 1)$ and subtract the first column from the second. Expanding along the first column we obtain

$$\det W = \begin{bmatrix} [W_a(W_a^2 - 1) - W_a] & 1 & & & \\ (W_a^2 - 1) & W_a & \dots & & \\ & 1 & \dots & & \end{bmatrix} \quad (6)$$

which is of order $(N-2) \times (N-2)$. Note that in this procedure the second column of the new determinant is always 1, W_a , 1 while the first column is $f(j)$, $f(j-1)$. The prescription for determining $f(j)$ is $f(j) = W_a f(j-1) - f(j-2)$. Thus we have

$$\det W = \begin{bmatrix} f(N_a - 1) & (b_a^2/b_{ab}^2) & 0 & & \\ f(N_a - 2) & W_{ab} & (b_a^2\rho_a/b_b^2\rho_b) & & \\ 0 & (b_b^2/b_{ab}^2)g(N_b^* - 2) & g(N_b^* - 1) & & \end{bmatrix} \quad (9)$$

where

$$N_b^* = N_b + N_c = (N + 1) - N_a \quad (10)$$

and

$$\begin{aligned} g(0) &= 1 \\ g(1) &= W_b \\ g(2) &= W_b g(1) - 1 \\ g(3) &= W_b g(2) - g(1) \\ &\vdots \\ g(l) &= W_b g(l-1) - g(l-2) \end{aligned} \quad (11)$$

The secular equation can now be written explicitly

$$\det W = W_{ab}f(N_a - 1)g(N_b^* - 1) - (b_a^2\rho_a/b_{ab}^2\rho_b)f(N_a - 1)g(N_b^* - 2) - (b_a^2/b_{ab}^2)g(N_b^* - 1)f(N_a - 2) = 0 \quad (12)$$

It can be shown⁸ that the recurrence relations (eq 7) give

$$f(k) = (r_2^{k+1} - r_1^{k+1})/(r_2 - r_1) \quad (13)$$

where the distinct roots r_1 and r_2 are given by

$$r_1 = [W_a + (W_a^2 - 4)^{1/2}]/2 \quad (14a)$$

$$r_2 = [W_a - (W_a^2 - 4)^{1/2}]/2 \quad (14b)$$

When r_1 and r_2 are complex, we have

$$f(k) = \sin[(k + 1)\Theta_a]/\sin \Theta_a \quad (15)$$

where

$$\cos \Theta_a = \frac{1}{2}W_a \quad (16)$$

When $W_a = 2$

$$f(k) = 1 + k \quad (17)$$

The expressions for $g(k)$ are identical in form to the above with W_b and Θ_b replacing W_a and Θ_a .

The viscoelastic properties and parameters of interest are given^{2,3} in terms of the eigenvalues λ_k of \mathbf{B} as follows:

$$G_R' = \sum_{k=1}^N \frac{(\omega\tau_1)^2(\lambda_1/\lambda_k)^2}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_k)^2} \quad (18)$$

$$(G'' - \omega\eta)_R = \sum_{k=1}^N \frac{(\omega\tau_1)(\lambda_1/\lambda_k)}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_k)^2} \quad (19)$$

$$S_1 = \sum_{k=1}^N (\lambda_1/\lambda_k) \quad (20)$$

and

$$J_{eR} = \sum_{k=1}^N (\lambda_1/\lambda_k)^2/S_1^2 \quad (21)$$

Here G_R' and $(G'' - \omega\eta)_R$ are the reduced shear moduli³ when the strain varies sinusoidally with the angular frequency ω , τ_1 is the longest relaxation time of the chain molecule, and J_{eR} is the reduced steady state compliance.³

In order to illustrate the applications of the theory, we shall present in the next section the viscoelastic properties predicted by our theory for some block copolymer solutions. The procedure for the evaluation of the parameters that appear in our theory is identical to that described in paper I, so we may write down the results with a minimum of comment.

We shall use the symbols St and Ip to designate respectively the polystyrene block and the *cis*-1,4-polyisoprene block. For example, ABA poly(styrene-*b*-*cis*-1,4-isoprene), a block copolymer consisting of one block of *cis*-1,4-polyisoprene in between two blocks of polystyrene, will be designated as St-*Ip*-St. The contour lengths of the blocks, L_{cv} ($v = a, b, c$), for each of the block copolymers under consideration are given in Table I. These polymers are chosen to have the same number of skeletal carbon atoms.

Table II gives the bead-spring model parameters for poly(styrene-*b*-*cis*-1,4-isoprene) of Table I in methyl isobutyl ketone at 35°. Methyl isobutyl ketone at 35° is nearly a Θ solvent for polystyrene and *cis*-1,4-polyisoprene.⁹ We have therefore used, in the evaluation of these parameters for block copolymers, the homopolymer properties at Θ temperatures that are given in Table I of ref 1.

III. Results and Discussion

Table III gives the calculated values of the reduced steady state compliance J_{eR} and the constants S_1 , λ_1 , and λ_k/λ_1 for the block copolymers listed in Table I. In the preparation of Table III as well as Figures 1 and 2 to be

Table I
Contour Lengths of the Blocks, L_{ca} , L_{cb} , and L_{cc} , for Polymers Whose Viscoelastic Properties Are Calculated from the Present Theory

Polymers	$L_{ca} \times 10^{-3}$, Å	$L_{cb} \times 10^{-3}$, Å	$L_{cc} \times 10^{-3}$, Å
St- <i>Ip</i> - <i>Ip</i>	10.4	5.3	5.3
<i>Ip</i> -St- <i>Ip</i>	5.2	10.4	5.4
St- <i>Ip</i> -St	5.2	10.6	5.2

Table II
Bead-Spring Model Parameters Calculated for Poly(styrene-*b*-*cis*-1,4-isoprene) of Table I in Methyl Isobutyl Ketone at 35°^a

Polymers	N_a	N_b	N_c	ρ/ρ_a	ρ/ρ_b	ρ/ρ_c	b^2/b_a^2	b^2/b_b^2	b^2/b_c^2
St- <i>Ip</i> - <i>Ip</i>	40	42	42	1.00	1.97	1.97	1.00	4.25	4.25
<i>Ip</i> -St- <i>Ip</i>	42	40	42	1.97	1.00	1.97	4.25	1.00	4.25
St- <i>Ip</i> -St	20	84	20	1.00	1.97	1.00	1.00	4.25	1.00

^a The values of N , ρ/η , and b are 123, 380 Å, and 70 Å, respectively. Symbols employed are defined in the text.

Table III
Calculated Values of the Reduced Steady State Compliance J_{eR} and the Constants S_1 , λ_1 , and λ_k/λ_1 for the Poly(styrene-*b*-*cis*-1,4-isoprene) of Table I in Methyl Isobutyl Ketone at 35° when N is Taken to be 123^a

	St- <i>Ip</i> -St	<i>Ip</i> -St- <i>Ip</i>	St- <i>Ip</i> - <i>Ip</i>	Free-draining case, homopolymer
S_1	1.83	1.51	1.60	1.64
J_{eR}	0.342	0.464	0.418	0.400
$\lambda_1 \times 10^3$	2.58	1.61	1.96	
λ_2/λ_1	3.03	4.86	4.46	4
λ_3/λ_1	6.78	12.3	9.14	9
λ_4/λ_1	13.5	21.6	17.4	16
λ_5/λ_1	20.3	31.6	26.0	25
λ_6/λ_1	27.6	44.4	38.1	36
λ_7/λ_1	39.3	62.4	52.0	49
λ_8/λ_1	52.3	84.0	66.6	64
λ_9/λ_1	63.3	105.2	86.1	81
λ_{10}/λ_1	78.3	125.8	103.7	100

^a Equations 20 and 21 express S_1 and J_{eR} in terms of the eigenvalues λ_k of \mathbf{B} .

considered in the next paragraph, the eigenvalues of \mathbf{B} have been calculated by using a routine¹⁰ which is based on the Q-R algorithm. Table III shows that, for the block copolymers *Ip*-St-*Ip* and St-*Ip*-*Ip*, the values of S_1 are smaller than the values of S_1 for the homopolymer in the free-draining limit (the Rouse theory), while the values of J_{eR} and λ_k/λ_1 , the spacings of eigenvalues, are larger than the corresponding values for the Rouse theory. However, the deviation from the predictions of the Rouse theory is rather small in the case of the diblock copolymer St-*Ip*-*Ip*. For the block copolymer St-*Ip*-St, there is also a departure from the predictions of the Rouse theory. However, the deviations are in the opposite directions; for St-*Ip*-St, the value of S_1 is larger than that for the Rouse theory while the values of J_{eR} and λ_k/λ_1 are smaller than those for the Rouse theory.

In Figures 1 and 2, the calculated values of the reduced

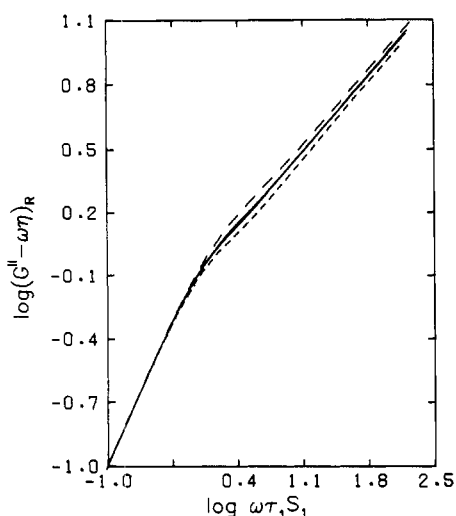


Figure 1. Log-log plots of the reduced loss modulus $(G'' - \omega\eta)_R$ against the dimensionless frequency $\omega\tau_1S_1$ calculated with $N = 123$ for the poly(styrene-*b*-*cis*-1,4-isoprene) of Table I, where τ_1 is the longest relaxation time of the chain and ω is the angular frequency. $(G'' - \omega\eta)_R$ and S_1 are given by eq 19 and 20 of the text. The curve of long dashes and the curve of short dashes represent respectively the predictions of the present theory for the block copolymers St-Ip-St and Ip-St-Ip. The solid curve represents the prediction of the free-draining case for a homopolymer and the prediction of the present theory for the block copolymer St-Ip-Ip. The difference in the value of $\log(G'' - \omega\eta)_R$ obtained for the last two polymers is less than the width of the solid curve.

shear moduli $(G'' - \omega\eta)_R$ and G_R' for the block copolymers of Table I are compared with those predicted by the Rouse theory. We observe in Figures 1 and 2 that the curves for St-Ip-Ip are nearly coincident with those for the Rouse theory. The curves for the block copolymers St-Ip-St and Ip-St-Ip both deviate from those for the Rouse theory, but the deviation exhibited by St-Ip-St is in opposite direction to that exhibited by Ip-St-Ip. However, even with the aforementioned deviations, the curves for the block copolymers in the limit of vanishing hydrodynamic interaction resemble the predictions of the Rouse theory more than they resemble the predictions for a homopolymer in the non-free-draining limit.

An application of eq 12 is illustrated in Table IV where some values of the secular determinant for the diblock copolymer St-Ip-Ip of Table I are given. We observe in Table IV that the value of $\det \mathbf{W}$ at λ equal to λ_k , the k th eigenvalue from the matrix computation previously described, is negligibly small in comparison with the value of $\det \mathbf{W}$ at λ which deviates slightly from λ_k toward the next eigenvalue. Equation 12 is therefore very useful for checking the precision of the eigenvalues obtained by matrix computation. Alternatively, the eigenvalues for a diblock copolymer in the limit of vanishing hydrodynamic interaction may be obtained from eq 12 by numerically determining the roots of the equation.

The close resemblance shown in Figures 1 and 2 between the reduced shear moduli for St-Ip-Ip and the reduced shear moduli for the Rouse theory suggests that it might be useful to represent a diblock copolymer by an equivalent bead-spring model consisting of identical springs with effective mean-square length b_e^2 and identical beads with effective friction constant ρ_e . The eigenvalues λ_k for the equivalent bead-spring model are of course determined by solving eq 12 with the conditions $\rho_a = \rho_b = \rho_e$ and $b_a = b_b = b_e$. They are given by the expression

$$\lambda_k = 4(b_e^2\rho_e/2N) \sin^2[\pi k/(2N + 2)] \quad (22)$$

Table IV
Values of the Secular Determinant, $\det \mathbf{W}$, for the Diblock Copolymer St-Ip-Ip of Table I^a

k	λ	$\det \mathbf{W}$
1	1.95×10^{-3}	-1.9×10^{-2}
	2.02×10^{-3}	4.7
	2.09×10^{-3}	9.1
2	8.71×10^{-3}	3.5×10^{-3}
	30	3.6×10^{-4}
	1.676	-0.1
31	1.677	-0.2
	1.678	-4.0 $\times 10^{-4}$
	1.775	-2.2 $\times 10^{-2}$
57	3.9760	3.7
	3.9935	2.1
	3.9937	9.2×10^{-2}
58	3.9939	

^a A number k is used to indicate that the assumed value in the next column is the k th eigenvalue obtained for St-Ip-Ip by the matrix computation described in the text.

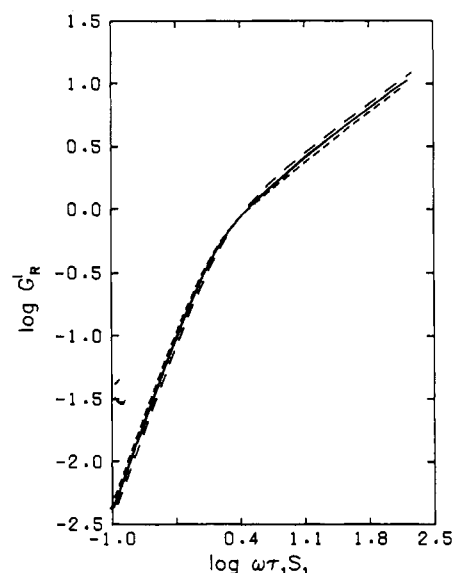


Figure 2. Log-log plots of the reduced storage modulus G_R' against the dimensionless frequency $\omega\tau_1S_1$ calculated with $N = 123$ for the poly(styrene-*b*-*cis*-1,4-isoprene) of Table I, where τ_1 is the longest relaxation time of the chain and ω is the angular frequency. G_R' and S_1 are given by eq 18 and 20 of the text. The curve labels are the same as for Figure 1. The difference in the value of G_R' obtained for the homopolymer in the free-draining limit and for the block copolymer St-Ip-Ip is less than the width of the solid curve.

which becomes identical to that given by Rouse⁷ when the arbitrary constants b and ρ are chosen to be b_e and ρ_e , respectively. An approximate additive rule for the calculation of $b_e^2\rho_e$ is suggested by the form of eq 12.

$$b_e^2\rho_e = N^{-2}[N_a(b_a^2\rho_a)^{1/2} + N_b(b_b^2\rho_b)^{1/2}]^2 \quad (23)$$

In Table V, the values of λ_1 obtained for four-block copolymers by applying eq 22 and 23 are compared with the values obtained by calculating the eigenvalues of the matrix \mathbf{B} . With the exception of λ_1 for the last copolymer, the values of λ_1 obtained by the two methods described above differ by less than 6%. In Figures 3 and 4, the reduced shear moduli calculated for the last copolymer of Table V by use of the eigenvalues from eq 22 and 23 are compared with those calculated for the same copolymer by use of the eigenvalues of the matrix \mathbf{B} . Since $(\tau_1\lambda_1)$ is given by²

$$\tau_1\lambda_1 = \rho b^2/6kT \quad (24)$$

Table V
Bead-Spring Model Parameters and the First Eigenvalues for Diblock Copolymers^a

Copolymer	N_a	N_b^*	ρ/ρ_a	ρ/ρ_b	b^2/b_a^2	b^2/b_b^2	$b^2\rho/b_a^2\rho_a$	$\lambda_1 \times 10^4$, from B	$\lambda_1 \times 10^4$, from eq 22
I	40	84	1.00	1.97	1.00	1.00	1.54	9.3	9.9
II	62	62	1.00	1.97	1.00	1.00	1.37	9.2	8.8
III	40	84	1.00	1.97	1.00	4.25	3.23	19.6	20.7
IV	62	62	1.00	1.97	1.00	4.25	2.21	12.5	14.2

^a The values of N , ρ/η , and b are 123, 380 Å, and 70 Å, respectively. Symbols employed are defined in the text.

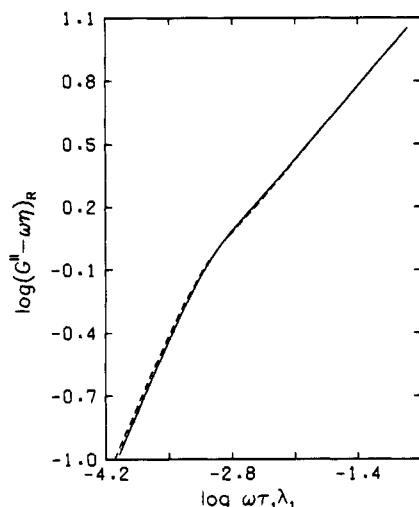


Figure 3. Log-log plots of the reduced loss modulus $(G'' - \omega\eta)_R$ against $\omega\tau_1\lambda_1$ calculated for copolymer IV of Table V. The solid curve represents the prediction obtained by using the eigenvalues from eq 22 and 23. The dashed curve represents the prediction obtained by using the eigenvalues of **B** from matrix computations. Symbols employed are defined in the text.

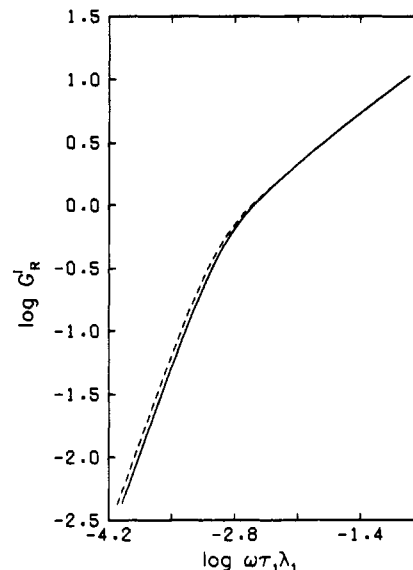


Figure 4. Log-log plots of the reduced storage modulus G'_R against $\omega\tau_1\lambda_1$ calculated for copolymer IV of Table V. The curve labels are the same as in Figure 3. Symbols employed are defined in the text.

$(\omega\tau_1\lambda_1)$ is proportional to ω when ρ , b , and T are kept constant as in the preparation of Figures 3 and 4. It is seen in Figures 3 and 4 that the reduced shear moduli calculated by the aforementioned two methods differ from each other only slightly. We have also calculated the reduced shear moduli for the first three diblock copolymers of Table V. For each of these copolymers, the curves for $(G'' - \omega\eta)_R$ or G'_R obtained by the two methods are practically coincident. Therefore, eq 22 and 23 may turn out to be useful for estimating the viscoelastic properties of diblock copolymers in the limit of vanishing hydrodynamic interaction.

IV. Concluding Remarks

We have calculated the viscoelastic properties of some styrene-*cis*-1,4-isoprene block copolymers by applying the previously described theory¹ in the limit of vanishing hydrodynamic interaction. It is found that the calculated properties for the diblock copolymer are nearly the same as those for the Rouse theory while the calculated properties for the symmetric triblock copolymers deviate from those for the Rouse theory. For the case of a diblock copolymer, we have obtained a simple form of the secular equation which is useful for extracting the eigenvalues as well as for checking the precision of the eigenvalues which may be obtained by matrix computations. Although the predicted deviations from the Rouse theory are not very pronounced, it is hopeful that some of them, those involving $(G'' - \omega\eta)_R$

and J_{eR} , for example, may be observed experimentally at higher concentrations where the present treatment is applicable and measurements are easier than at very high dilution.

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