motions are independent of local rearrangements in polystyrene, the data obtained for the methyl derivative might provide a better test of the high-frequency limitations of the Peterlin theory than the polystyrene studies since the chain backbone motions should then be detectable. Such information might provide considerable insight into configurational dynamics on spatial scales of importance in the glassy state. A future paper will report on more extensive studies of the high-frequency regime for both polystyrene and poly(α-methylstyrene).

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Dynamics of Block-Copolymer Molecules in Dilute Solution

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ABSTRACT: A theory for the dynamics of block-copolymer molecules in dilute solution has been developed by modifying the bead-spring model theory of Zimm to take into account the existence of dissimilar segments in block copolymers. The eigenvalue equation encountered in the theory has been solved numerically by extending the method of Lodge and Wu. The applications of the theory have been illustrated with calculations for the viscoelastic properties of poly(styrene-*b*-methyl methacrylate) solutions and poly(styrene-*b*-*cis*-1,4-isoprene) solutions. It is found that, for some block copolymers in solution, the calculated values of the viscoelastic properties deviate significantly from the values for the parent homopolymers toward the values predicted by the free-draining case.

I. Introduction

The conformation of block-copolymer molecules in dilute solution still remains ambiguous. There are two conformations often discussed as plausible: one in which dissimilar segments are interpenetrating, and one in which the segregation of unlike segments occurs. Although there have been a large number of measurements[1] on the solution properties of block copolymers, the experimentalists have not been able to argue conclusively in favor of one of the plausible conformations. Considerable uncertainties are introduced in the conclusions obtained from viscometry, because these conclusions are invariably arrived at by extending, with the use of some additive rules, theories and procedures developed strictly for homopolymer solutions. In this work, a step toward the removal of these uncertainties has been made by generalizing the bead-spring model theory of Zimm[2] to make the generalized theory applicable to the viscoelasticity of block-copolymer solutions. The eigenvalue equation encountered in the Zimm theory[2] has been solved numerically by Lodge and Wu[3] and by Thurston.[4] We have numerically solved the eigenvalue problem from the present theory by extending the method of Lodge and Wu.[3] Our theory in the present form is strictly useful only to block-copolymer solutions in which the excluded-volume effect is negligible. However, if our theory is further modified to take into account the excluded-volume effect, we can use the theory thus obtained to determine whether the viscoelastic properties of block-copolymer molecules in non-Θ solvents can be interpreted without invoking the segregated conformation.

Work of a similar nature but in the free-draining limit is being communicated by Shen and Hansen,[5] by Stockmayer and Kennedy,[6] and by Wang and DiMarzio.[7]

II. Formulation of the Problem

We derive in this section the equation of motion of a block-copolymer molecule in dilute solution under the condition characteristic of the Θ temperature.[8] We shall restrict our treatment to A–B–C type linear block copolymers which consist of a B block of homopolymer B flanked by an A block of homopolymer A and a C block of homopolymer C. The extension of our treatment to linear block copolymers of more than three blocks is straightforward and should become evident as our discussion progresses.

Our model of the block-copolymer molecule in dilute solution is similar to the bead-spring model of Rouse[9] and of Zimm.[2] In our model, the chain molecule is represented as a chain of N Hookean springs joining $N + 1$ beads with complete flexibility at each bead. The solvent is treated as a hydrodynamic continuum with a viscosity η. The jth bead, characterized by the translational friction constant ρ_j ($j = 0, 1, 2, \ldots, N$), offers hydrodynamic resistance to the flow of solvent, but the springs do not. The force constant of the jth spring is $3kT/b_j^2$ ($j = 1, 2, \ldots, N$), where b_j^2 is its mean-square length, and k and T are the Boltzman constant and the absolute temperature.

The representation of a block-copolymer molecule by a bead-spring model is similar to that of our previous paper.[10] We divide the V block ($V = A, B, C$) into N_v equal segments of contour length L_{cv}^* ($v = a, b, c$), and replace each segment, as far as its hydrodynamic properties are concerned, by a bead located at its center. These beads are then connected by $(N_v - 1)$ springs which represent the elastic properties of the V block. The root-mean-square length of a spring must then equal the root-mean-square length of the V block between neighboring segment centers, which is two half segments or one whole segment, and is denoted by b_v. If the V block has a finite degree of flexibility and the contour length L_{cv}^* of each segment is chosen to be sufficiently large, the springs may be considered to be connected by free joints at the beads.[11] The mean-square length of the equivalent bead-spring model for the V block is then $(N_v - 1)b_v^2$, while the mean-square length of the V block as a whole, L_v^2, is given by

$$L_v^2 = N_v b_v^2 \tag{1}$$

since the V block contains N_v segments. 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 last bead of the A block ($j = N_a - 1$) and the first bead of the B block ($j = N_a$) are connected by free joints to the ends of a spring whose root-mean-square length is denoted by b_{ab}. The mean-square length b_{ab}^2 of the spring separating these two beads is equal to mean-square length of a linear segment formed by joining one half-segment from the A block and one half-segment from the B block. Thus, we have

$$b_{ab}^2 = (b_a^2 + b_b^2)/2 \tag{2}$$

Finally, the bead-spring model for the block-copolymer molecule as a whole is formed by connecting with free joints the last bead of the B block ($j = N_a + N_b - 1$) and the first bead of the C block ($j = N_a + N_b$) to the ends of a spring of root-mean-square length b_{bc} which is defined in the same manner as b_{ab}. Thus, we have

$$b_{bc}^2 = (b_b^2 + b_c^2)/2 \tag{3}$$

The mean-square length of the equivalent bead-spring model for the block-copolymer molecule is then given by

$$L_{bs}^2 = (N_a - \tfrac{1}{2})b_a^2 + N_b b_b^2 + (N_c - \tfrac{1}{2})b_c^2 \tag{4}$$

while the mean-square length of the block-copolymer molecule as a whole is

$$L^2 = N_a b_a^2 + N_b b_b^2 + N_c b_c^2 \tag{5}$$

The difference in mean-square length arises because two half-segments at the ends of the block-copolymer molecule do not contribute to the length of the bead-spring model.

The friction constant ρ_v of a bead from the model for the V block must be equal to the friction constant of the segment represented by the bead. The latter friction constant is calculated in this work by the Yamakawa-Fujii formula[12] for wormlike chains of contour length L_{cv}^*. Their formula, which is given by eq 49 to 52 of ref 12, expresses the friction constant of a wormlike chain as a function of its contour length, its Kuhn statistical segment length b_{kv}, its cross sectional diameter d_{pv}, and the solvent viscosity.

The formulation of the dynamical problem is similar to that discussed in detail by Zimm[2] and by Zimm and Kilb,[13] so we may write down the results with a minimum of comment. The force F_{xj} acting in the x direction on the jth bead located at (x_j, y_j, z_j) is

$$F_{xj} = -kT\partial \ln \psi/\partial x_j - (3kT/b^2)[k_j(x_j - x_{j-1}) + k_{j+1}(x_j - x_{j+1})] \tag{6}$$

where $\psi(x_0, y_0, \ldots, z_N)$ is the distribution function for the beads, $(3kT/b^2)$ is an arbitrary spring constant, and the dimensionless spring constants k_j for the springs are as follows

$$k_j = 0 \quad \text{for } j = 0 \text{ or } (N + 1) \tag{7a}$$

$$k_j = k_a \equiv b^2/b_a^2 \quad \text{for } 1 \leq j \leq (N_a - 1) \tag{7b}$$

$$k_j = k_{ab} \equiv b^2/b_{ab}^2 \quad \text{for } j = N_a \tag{7c}$$

$$k_j = k_b \equiv b^2/b_b^2 \quad \text{for } (N_a + 1) \leq j \leq (N_a + N_b - 1) \tag{7d}$$

$$k_j = k_{bc} \equiv b^2/b_{bc}^2 \quad \text{for } j = (N_a + N_b) \tag{7e}$$

$$k_j = k_c \equiv b^2/b_c^2 \quad \text{for } (N_a + N_b + 1) \leq j \leq N \tag{7f}$$

Similar equations can be written for motion in the y and z directions.

The force on the jth bead is balanced by a friction force

$$F_{xj} = \rho_j(\dot{x}_j - v_{xj}') \tag{8}$$

where $\dot{x}_j$ is the x component of the velocity of the jth bead, v_{xj}' is the x component of the velocity that the fluid would have at the position of j if the bead were absent, and the friction constant ρ_j of the jth bead is given by

$$\rho_j = \rho_a \quad \text{for } 0 \leq j \leq (N_a - 1) \tag{9a}$$

$$\rho_j = \rho_b \quad \text{for } N_a \leq j \leq (N_a + N_b - 1) \tag{9b}$$

$$\rho_j = \rho_c \quad \text{for } (N_a + N_b) \leq j \leq N \tag{9c}$$

According to the treatment of Kirkwood and Riseman[14]

$$v_{xj}' = v_{xj} + \sum_{k \neq j} T_{jk} F_{xk} \tag{10}$$

where v_{xj} is the x component of the velocity that the fluid would have in the absence of the chain, and the interaction coefficients T_{jk} are given by

$$T_{jk} = 1/[(6\pi^3)^{1/2}\eta\langle R_{jk}^2\rangle^{1/2}] \tag{11}$$

with $\langle R_{jk}^2\rangle$ the mean-square distance between the jth and the kth beads. The expressions for $\langle R_{jk}^2\rangle$ are given for example by

$$\langle R_{jk}^2\rangle = b_a^2|j - k| \tag{12}$$

when both beads are from the A block

$$\langle R_{jk}^2\rangle = b_a^2(N_a - j + \tfrac{1}{2}) + b_b^2(k - N_a - \tfrac{1}{2}) \tag{13}$$

when jth bead and kth bead are respectively from the A block and the B block, and

$$\langle R_{jk}^2 \rangle = b_a^2(N_a - j + \tfrac{1}{2}) + b_b^2(N_b - N_a) + b_c^2(k - N_b - \tfrac{1}{2}) \tag{14}$$

when jth bead and the kth bead are respectively from the A block and the C block.

It is convenient to cast the equations of motion into matrix form. We define the $(N + 1)$-dimensional column vector $\mathbf{x}$ as

$$\mathbf{x} = (x_0, x_1, \ldots, x_N)^T \tag{15}$$

with similar definitions for $\mathbf{v}_x$ and $\mathbf{F}_x$. We also introduce the matrices $\mathbf{A}$ and $\mathbf{H}$ of order $(N + 1)$. The elements of $\mathbf{H}$ are given by

$$H_{jj} = \rho/\rho_j \tag{16a}$$

$$H_{jk} = \rho T_{jk} \qquad j \neq k \tag{16b}$$

where ρ is an arbitrary friction constant. The nonzero elements of the tridiagonal matrix $\mathbf{A}$ are defined as follows:

$$(A_{00}; A_{01}) = (k_1; -k_1) \tag{17a}$$

$$(A_{j,j-1}; A_{jj}; A_{j,j+1}) = (-k_j; k_j + k_{j+1}; -k_{j+1}) \quad \text{for } 1 \leq j \leq (N-1) \tag{17b}$$

$$(A_{N,N-1}; A_{NN}) = (-k_N; k_N) \tag{17c}$$

Combining eq 6, 8, and 10, we can write the equation of motion in the x direction in matrix notation

$$\mathrm{d}\mathbf{x}/\mathrm{d}t = \mathbf{v}_x + (1/\rho)\mathbf{H}\cdot\mathbf{F}_x = \mathbf{v}_x - D\mathbf{H}\cdot(\partial/\partial\mathbf{x}) \ln \psi - \sigma\mathbf{H}\cdot\mathbf{A}\cdot\mathbf{x} \tag{18}$$

where

$$\partial/\partial\mathbf{x} = (\partial/\partial x_0, \partial/\partial x_1, \ldots, \partial/\partial x_N)^T \tag{19}$$

$D = kT/\rho$, and $\sigma = 3kT/b^2\rho$. Corresponding equations can be written for the y and z velocities.

III. Eigenvalue Problem and Viscoelastic Properties

Equation 18 is identical in form to the equation of motion obtained by Zimm.[2] Zimm[2] has shown that, if the matrices $\mathbf{A}$ and $\mathbf{H}$ are symmetric and the eigenvalues λ_k of the eigenvalue equation

$$\mathbf{H}\cdot\mathbf{A}\cdot\alpha = \lambda\alpha \tag{20}$$

are distinct, the viscoelastic properties are determined by λ_k. Since the matrices $\mathbf{H}$ and $\mathbf{A}$, defined respectively by eq 16 and 17, are symmetric and the eigenvalues λ_k turn out to be distinct, Zimm's results[2] are directly applicable to the viscoelasticity of block-copolymer solutions.

The eigenvalues of eq 20 may be calculated numerically in a manner similar to that described by Lodge and Wu.[15] Since $\mathbf{A}$ is singular, it is convenient to treat $\mathbf{A}$ as the limit, as ϵ approaches zero, of the matrix $\mathbf{A}_\epsilon$ which is obtained by replacing the element A_{00} of $\mathbf{A}$ with $(k_a + \epsilon^2)$; that is

$$(A_\epsilon)_{00} = k_a + \epsilon^2 \tag{21a}$$

$$(A_\epsilon)_{jk} = A_{jk} \tag{21b}$$

for j and k not both zero. $\mathbf{A}_\epsilon$ can be expressed as the product

$$\mathbf{A}_\epsilon = \widetilde{\mathbf{C}}_\epsilon \cdot \mathbf{C}_\epsilon \tag{22}$$

where the matrix $\mathbf{C}_\epsilon$ of order $(N + 1)$ is defined by the equation

$$\mathbf{C}_\epsilon = \begin{bmatrix} \epsilon & 0 & 0 & \ldots & 0 & 0 \\ -1 & 1 & 0 & \ldots & 0 & 0 \\ 0 & -1 & 1 & \ldots & 0 & 0 \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot & \cdot \\ 0 & 0 & 0 & \ldots & 1 & 0 \\ 0 & 0 & 0 & \ldots & -1 & 1 \end{bmatrix} \tag{23}$$

and the only nonzero elements of the $(N + 1)$th order matrix $\tilde{\mathbf{C}}_\epsilon$ are either on the principal diagonal or on the diagonal next above the principal diagonal, and are defined as follows:

$$\widetilde{C}_{\epsilon,00} = \epsilon \tag{24a}$$

$$(\widetilde{C}_{\epsilon,jj}; \widetilde{C}_{\epsilon,j-1,j}) = (k_j; -k_j) \qquad \text{for } 1 \leq j \leq N \tag{24b}$$

Since det $\mathbf{C}_\epsilon = \epsilon$ and det $\tilde{\mathbf{C}}_\epsilon = \epsilon\, \Pi_{j=1}{}^{N}\, \mathrm{k}_\mathrm{j}$, it follows that $\mathbf{C}_\epsilon$ and $\tilde{\mathbf{C}}_\epsilon$, and hence also $\mathbf{A}_\epsilon$, are nonsingular provided that $\epsilon \neq 0$. Thus $\mathbf{C}_\epsilon$ possesses an inverse $\mathbf{C}_\epsilon^{-1}$, and hence

$$\det(\mathbf{H}\cdot\mathbf{A}_\epsilon - \mathbf{I}\lambda) = \det\mathbf{C}_\epsilon \det(\mathbf{H}\cdot\widetilde{\mathbf{C}}_\epsilon\cdot\mathbf{C}_\epsilon - \mathbf{I}\lambda) \det\mathbf{C}_\epsilon^{-1} = \det(\mathbf{B}_\epsilon' - \mathbf{I}\lambda) \tag{25}$$

where

$$\mathbf{B}_\epsilon' = \mathbf{C}_\epsilon\cdot\mathbf{H}\cdot\widetilde{\mathbf{C}}_\epsilon \tag{26}$$

and $\mathbf{I}$ denotes the unit matrix of order $(N + 1)$. Thus, $\mathbf{H}\cdot\mathbf{A}_\epsilon$ and $\mathbf{B}_\epsilon'$ have the same characteristic values provided that $\epsilon \neq 0$.

From a theorem of Ostrowski[16] on the continuity of eigenvalues, it follows that, as ϵ approaches zero, the eigenvalues of $\mathbf{H}\cdot\mathbf{A}_\epsilon$ approach the eigenvalues of $\mathbf{H}\cdot\mathbf{A}$, and also the eigenvalues of $\mathbf{B}_\epsilon'$ approach the eigenvalues of $\mathbf{B}'$, where

$$\mathbf{B}' = \lim_{\epsilon\to 0} \mathbf{B}_\epsilon' = \begin{bmatrix} 0 & 0 & 0 & \ldots & 0 \\ 0 & B_{11} & B_{12} & \ldots & B_{1N} \\ 0 & B_{21} & B_{22} & \ldots & B_{2N} \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ 0 & B_{N1} & B_{N2} & \ldots & B_{NN} \end{bmatrix} \tag{27}$$

Here, B_{jk}, the elements of the matrix $\mathbf{B}$ of order N, are given by

$$B_{jk} = k_k(H_{j,k} - H_{j,k-1} - H_{j-1,k} + H_{j-1,k-1}) \tag{28}$$

It follows that $\mathbf{H}\cdot\mathbf{A}$ has the same eigenvalues as $\mathbf{B}'$, namely 0, $\lambda_1, \lambda_2, \ldots, \lambda_N$, where $\lambda_1, \lambda_2, \ldots, \lambda_N$ are the eigenvalues of $\mathbf{B}$. The eigenvalues of $\mathbf{B}$ were calculated in this work on a computer by using a routine[17] which first reduces the matrix $\mathbf{B}$ to upper Hessenberg form by elementary similarity transformations and then applies the Q–R algorithm to the resulting Hessenberg matrix.

The viscoelastic properties and parameters of interest are given[2,18] in terms of the eigenvalues λ_k as follows:

$$G_R' = \sum_{k=1}^{N} \frac{(\omega\tau_1)^2(\lambda_1/\lambda_k)^2}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_k)^2} \tag{29}$$

$$(G'' - \omega\eta)_R = \sum_{k=1}^{N} \frac{(\omega\tau_1)(\lambda_1/\lambda_k)}{1 + (\omega\tau_1)^2(\lambda_1/\lambda_k)^2} \tag{30}$$

$$\Phi = (\pi^3/3)^{1/2} N_0 h N^{-2} \left[\sum_{k=1}^{N} (1/\lambda_k)\right] \left[\sum_{j=a}^{c} (N_j/Nk_j)\right]^{-3/2} \tag{31}$$

$$S_1 = \sum_{k=1}^{N} (\lambda_1/\lambda_k) \tag{32}$$

and

$$J_{eR} = \sum_{k=1}^{N} (\lambda_1/\lambda_k)^2/S_1^{\,2} \qquad (33)$$

Here G_R' and $(G'' - \omega\eta)_R$ are the reduced shear moduli[18] when the strain varies sinusoidally with the angular frequency ω, τ_1 is the longest relaxation time of the chain molecule, N_0 is the Avogadro number, and J_{eR} is the reduced steady state compliance.[18,19] The quantity h is defined as

$$h = N^{1/2}\rho/\{(12\pi^3)^{1/2} b\eta\} \qquad (34)$$

and the Flory–Fox constant Φ is defined by the relation

$$[\eta] = \Phi(L^3/M) \qquad (35)$$

where M and L are the molecular weight and the root-mean-square length of the chain molecule, and $[\eta]$ is the limiting viscosity number.

IV. Evaluation of Parameters

In order to illustrate the applications of our theory, we shall present in the next section the viscoelastic properties predicted by our theory for some block-copolymer solutions. We describe in this section the evaluation of parameters that appear in our theory. The procedure for evaluation is similar to that described in our previous papers[10,20] so we may write down the procedure with a minimum of comment.

In the calculation of the parameters, we have assumed that the properties of homopolymers in their respective Θ solvents are as given in Table I. In this table, the symbols L_c, b_k, and d_p denote respectively the contour length, the Kuhn statistical segment length, and the cross-sectional diameter of a homopolymer molecule, and the symbols L, R_g, and M denote respectively the root-mean-square length, the root-mean-square radius, and the molecular weight of a whole polymer molecule, homopolymer, or block copolymer. In the calculation of (L_c/M) for polystyrene and poly(methyl methacrylate), the distance between alternate carbon atoms has been assumed to be 2.53 Å. This assumption is in agreement with the conclusion derived by Maeda and coworkers[21] from a comparison of the broken and wormlike chains. In the calculation of (L_c/M) for *cis*-1,4-polyisoprene, the contour length per repeating unit is assumed to be 5.13 Å. The cross-sectional diameters d_p have been estimated from the crystallographic data for isotactic polystyrene,[22] for isotactic poly(methyl methacrylate),[23] and for *cis*-1,4-polyisoprene.[24] The relation $L^2 = 6R_g^{\,2}$, which should be valid for chains of sufficient length and flexibility, has been used to calculate (L^2/M) from $(R_g^{\,2}/M)$, and vice versa. The Kuhn statistical segment lengths have been calculated from the formula[25]

$$L^2 = L_c b_k - (b_k^{\,2}/2)[1 - \exp(-2L_c/b_k)] \qquad (36)$$

We shall use the symbols St, MM, and Ip to designate respectively the polystyrene block, the poly(methyl methacrylate) 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 as well as the contour lengths L_c of the homopolymers to be considered are given in Table II. These polymers are chosen to have the same number of skeletal carbon atoms.

Table I
Properties of Polystyrene, Poly(methyl methacrylate), and *cis*-1,4-Polyisoprene in Θ Solvents[a]

Polymer	Polystyrene	Poly-(methyl methacrylate)	*cis*-1,4-Polyisoprene
Solvent	Cyclohexane	Cyclohexanol	*n*-Propyl ketone
θ temp, °C	34.8[b]	78.8[c]	14.3[d]
$(R_g^{\,2}/M) \times 10^{18}$, cm^2/dalton	7.6[b]	5.44[c]	11.5
$(L^2/M) \times 10^{18}$, cm^2/dalton	46	32.6	69[d]
$(L_c/M) \times 10^2$, Å/dalton	2.43	2.43	7.5
b_k, Å	19	13	9.1
d_p, Å	9.4	9.0	5.9

[a] Symbols employed and the calculations of the derived quantities are described in the section on the evaluation of parameters. [b] G. C. Berry, *J. Chem. Phys.*, 44, 4550 (1966). [c] Reference 26. [d] H. L. Wagner and P. J. Flory, *J. Am. Chem. Soc.*, 74, 195 (1952).

Table II
Contour Lengths of the blocks, L_{ca}, L_{cb}, L_{cc}, and Contour Lengths of the Homopolymer L_c 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	$L_c \times 10^{-3}$, Å
St-MM-MM	10.4	5.2	5.2	
MM-St-MM	5.2	10.4	5.2	
St-MM-St	5.2	10.4	5.2	
St-Ip-Ip	10.4	5.3	5.3	
Ip-St-Ip	5.2	10.4	5.4	
St-Ip-St	5.2	10.6	5.2	
Polystyrene				20.8
Poly(methyl methacrylate)				20.8
cis-1,4-Polyisoprene				21.2

Tables III and IV give respectively the bead-spring model parameters for poly(stryene-*b*-methyl methacrylate) of Table II in cyclohexanol at 81.0° and the bead-spring-model parameters for poly(styrene-*b*-*cis*-1,4-isoprene) of Table II in methyl isobutyl ketone at 35°. Cyclohexanol at 81.0° is nearly a Θ solvent for polystyrene and poly(methyl methacrylate),[26] and so is methyl isobutyl ketone at 35° for polystyrene and *cis*-1,4-polyisoprene.[27] 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.

In our previous papers[10,20] on the viscoelasticity of homopolymer solutions, we have discussed the selection of N, the number of springs in the bead-spring model for a homopolymer molecule, and have concluded[20] that for N sufficiently large, approximately above 100, the viscoelastic properties of long chain molecule solutions predicted by the bead-spring model theory of Zimm[2] are rather insensitive to the exact choice of N. We expect the viscoelastic properties of block-copolymer solutions predicted by the present theory to be similarly insensitive to N, the total number of springs in the model for a block-copolymer molecule, and have chosen N to be 107 or 123. However, in the case of block-copolymer solutions, we are confronted with another problem; that is, how to distribute $(N + 1)$ beads among the models for the blocks in a block-copolymer molecule. In this work, we have distributed $(N + 1)$ beads by imposing the condition that the values of L_{cv}^{*}/b_{kv} ($v = a, b, c$) for different blocks are nearly the same. This condition

Table III
Bead-Spring Model Parameters Calculated for Poly(styrene-*b*-methyl methacrylate) of Table II in Cyclohexanol at 81.0°[a]

Polymers	N_a	N_b	N_c	ρ/ρ_a	ρ/ρ_b	ρ/ρ_c	k_a	k_b	k_c
St-MM-MM	44	32	32	1.00	1.36	1.36	1.00	2.11	2.11
MM-St-MM	32	44	32	1.36	1.00	1.36	2.11	1.00	2.11
St-MM-St	22	64	22	1.00	1.36	1.00	1.00	2.11	1.00

[a] Symbols employed are defined in the text: $N = 107$, $h/N^{1/2} = 0.28$, $\rho/\eta = 360$ Å, $b = 67$ Å.

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

Polymers	N_a	N_b	N_c	ρ/ρ_a	ρ/ρ_b	ρ/ρ_c	k_a	k_b	k_c
St-Ip-Ip	35	36	37	1.00	1.97	1.97	1.00	4.22	4.22
Ip-St-Ip	36	35	37	1.97	1.00	1.97	4.22	1.00	4.22
St-Ip-St	18	73	17	1.00	1.97	1.00	1.00	4.22	1.00
St-Ip-Ip	40	42	42	1.00	1.97	1.97	1.00	4.25	4.25
Ip-St-Ip	42	40	42	1.97	1.00	1.97	4.25	1.00	4.25
St-Ip-St	20	84	20	1.00	1.97	1.00	1.00	4.25	1.00

[a] For the first three polymers, the values of N, $h/N^{1/2}$, ρ/η, and b are 107, 0.28, 410 Å, and 75 Å, respectively. For the last three polymers, the values of N, $h/N^{1/2}$, ρ/η, and b are 123, 0.28, 380 Å, and 70 Å, respectively. Symbols employed are defined in the text.

Table V
Calculated Values of the Flory–Fox Constant, Φ, the Reduced Steady State Compliance, J_{eR}, and the Constants λ_1 and λ_k/λ_1 for the Polystyrene, the Poly(methyl methacrylate), and the Poly(styrene-*b*-methyl methacrylate) of Table II in Cyclohexanol at 81° when N is Taken to be 107[a]

	Poly(methyl methacrylate)	Polystyrene	St-MM-St	MM-St-MM	St-MM-MM	Free-draining case
Φ, 10^{23}ml/g	2.99	2.93	2.90	3.08	3.10	
S_1	2.36	2.33	2.43	2.22	2.20	1.64
J_{eR}	0.209	0.213	0.202	0.230	0.233	0.400
$\lambda_1 \times 10^3$	4.07	3.93	7.16	6.19	6.07	
λ_2/λ_1	3.13	3.14	2.85	3.34	3.59	4
λ_3/λ_1	5.86	5.89	5.44	6.64	6.30	9
λ_4/λ_1	9.08	9.15	8.88	10.2	10.1	16
λ_5/λ_1	12.7	12.8	12.0	13.8	14.3	25
λ_6/λ_1	16.6	16.8	15.5	17.9	18.3	36
λ_7/λ_1	20.9	21.1	20.1	22.9	23.7	49
λ_8/λ_1	25.4	25.8	24.4	28.4	28.1	64
λ_9/λ_1	30.1	30.6	28.4	33.5	33.8	81
λ_{10}/λ_1	35.1	35.7	33.4	38.5	39.4	100

[a] Equations 31–33 express Φ, S_1, and J_{eR} in terms of the eigenvalues λ_k of eq 20.

may seem rather arbitrary; however, in using b_{kv}, which reflects the stiffness of a block, as a reducing factor we are guided by the following consideration. In order to represent each segment connecting two beads as a Hookean spring with the force constant $3kT/b_v^2$, each segment must be sufficiently long to render negligible the influence of one segment on the direction of the next.[28] Thus, the segment contour length L_{cv}^* must be larger the stiffer the block. In other words, L_{cv}^* must be approximately proportional to b_{kv}.

Having selected the number of beads for each block, and hence the segment contour length for each block, we can fix the values for b_v and ρ_v by using eq 1 and the Yamakawa–Fujii formula,[12] respectively. The value of h may be calculated from eq 34 after arbitrarily choosing the values of (ρ/η) and b to be those for a polystyrene block. Although, at first sight, it appears that the parameter Φ depends on the choices of ρ and b, it can be shown that all the properties given by eq 29 to 33 are independent of ρ and b. (To avoid misunderstanding, we like to point out that the arbitrary constants ρ and b are to be distinguished from ρ_v and b_v which are related to the assumed value of N and the distribution of $(N + 1)$ beads among the models for the blocks.) The relaxation times, τ_k, are given by[2]

$$\tau_k = (2\sigma\lambda_k)^{-1} = b^2\rho/6kT\lambda_k \qquad (37)$$

Since the elements of **A** and **H** have the factor b^2 and the factor ρ, respectively, the eigenvalues λ_k of $\mathbf{A} \cdot \mathbf{H}$ must vary as $b^2\rho$. The relaxation times τ_k and the ratios (λ_1/λ_k) must therefore be independent of b^2 and ρ. Consequently, the viscoelastic properties G_R', $(G'' - \omega\eta)_R$, S_1, and J_{eR}, all expressible in terms of (λ_1/λ_k) and τ_1, must be independent of b^2 and ρ. In the expression for Φ, the factors h, $(1/\lambda_k)$, and $k_j^{3/2}$ vary as (ρ/b), $(\rho b^2)^{-1}$, and b^3, respectively. The product of the last three factors is unity, hence Φ must be independent of the choice of ρ and b. In the following section,

Table VI
Calculated Values of the Flory–Fox Constant, Φ, the Reduced Steady State Compliance, J_{eR}, and the Constants λ_1 and λ_k/λ_1 for the Polystyrene, the *cis*-1,4-Polyisoprene, and the Poly(styrene-*b*-*cis*-1,4-isoprene) of Table II in Methyl Isobutyl Ketone at 35° when N is taken to be 107[a]

	cis-1,4-Polyisoprene	Polystyrene	St-Ip-St	Ip-St-Ip	St-Ip-Ip	Free-draining case
Φ, 10^{23} ml/g	2.95	2.93	3.01	3.25	3.36	
S_1	2.34	2.33	2.31	2.13	2.02	1.64
J_{eR}	0.212	0.213	0.220	0.250	0.270	0.400
$\lambda_1 \times 10^3$	3.97	3.93	11.1	9.48	8.68	
λ_2/λ_1	3.13	3.14	2.95	3.28	3.96	4
λ_3/λ_1	5.88	5.89	5.98	7.08	7.67	9
λ_4/λ_1	9.13	9.15	9.12	11.2	11.1	16
λ_5/λ_1	12.8	12.8	12.9	15.4	16.4	25
λ_6/λ_1	16.8	16.8	17.1	19.7	22.0	36
λ_7/λ_1	21.1	21.1	21.1	23.9	26.3	49
λ_8/λ_1	25.6	25.8	26.0	29.5	32.8	64
λ_9/λ_1	30.4	30.6	30.9	35.9	39.7	81
λ_{10}/λ_1	35.5	35.7	35.3	42.6	44.8	100

[a] Equations 31–33 express Φ, S_1, and J_{eR} in terms of the eigenvalues λ_k of eq 20.

Table VII
Calculated Values of the Flory–Fox Constant Φ, the Reduced Steady State Compliance, J_{eR}, and the Constants λ_1 and λ_k/λ_1 for the Polystyrene and the Poly(styrene-*b*-*cis*-1,4-isoprene) of Table II in Methyl Isobutyl Ketone at 35° when N is taken to be 123[a]

	Polystyrene	St-Ip-St	Ip-St-Ip	St-Ip-Ip	Free-draining case
Φ, 10^{23} ml/g	2.93	3.01	3.25	3.37	
S_1	2.34	2.33	2.14	2.02	1.64
J_{eR}	0.212	0.216	0.247	0.268	0.400
$\lambda_1 \times 10^3$	3.21	9.20	7.82	7.12	
λ_2/λ_1	3.14	2.88	3.27	3.96	4
λ_3/λ_1	5.90	5.93	7.06	7.70	9
λ_4/λ_1	9.16	9.21	11.2	11.1	16
λ_5/λ_1	12.8	12.6	15.4	16.5	25
λ_6/λ_1	16.7	17.0	19.7	22.1	36
λ_7/λ_1	21.2	21.3	24.0	26.5	49
λ_8/λ_1	25.8	25.5	29.6	33.1	64
λ_9/λ_1	30.7	31.0	36.1	40.1	81
λ_{10}/λ_1	35.9	35.7	42.8	45.2	100

[a] Equations 31–33 express Φ, S_1, and J_{eR} in terms of the eigenvalues λ_k of eq 20.

we give the results calculated by using the eigenvalues λ_k and eq 29 to 33.

It seems worthwhile to dispel now some confusion that could arise as a result of our effort to cast the equation of motion in the same form as the one obtained by Zimm.[2] We must point out that the symbols h, D, and σ used in this work are different in meaning from the very same symbols used in Zimm's paper.[2] In his paper, these symbols are defined in terms of the friction constant ρ of each bead and the root-mean-square length b of each spring; while, in this work, these symbols are defined in terms of an arbitrary friction constant and an arbitrary root-mean-square length denoted also by ρ and b, respectively. For the special case of a homopolymer, all the beads and the springs are characterized by the same friction constant, ρ_a, say, and the same root-mean-square length, b_a, say, respectively. In this case, using the definitions of this work, we may calculate the viscoelastic properties by arbitrarily setting ρ identical to ρ_a and b identical to b_a. Only when ρ and b are chosen in the manner described above do the symbols h, D, and σ, as well as $\mathbf{A}$ and $\mathbf{H}$, have the same meanings as those in Zimm's paper.

V. Results and Discussion

Tables V, VI, and VII give the calculated values of the Flory–Fox constant Φ, the reduced steady state compliance J_{eR}, and the constants S_1, λ_1, and λ_k/λ_1 for the polymers listed in Table II. In these tables, the values for the homopolymers are calculated from the Zimm theory in the manner previously described.[20] For the cases with $N = 107$, the values of the hydrodynamic interaction parameter $(h/N^{1/2})$ for the polystyrene, the poly(methyl methacrylate), and the poly(*cis*-1,4-isoprene) are 0.29, 0.30, and 0.29, respectively. For the polystyrene, the value of $(h/N^{1/2})$ is 0.29, when $N = 123$.

Tables V and VI show that, with the exception of St-MM-St, the effect of the presence of dissimilar blocks is to shift the values of S_1 and J_{eR} toward those described by the free-draining case or the Rouse theory. In other words, in comparison with homopolymers, the block copolymers have smaller values of S_1 and larger values of J_{eR}. Similarly, a shift toward free-draining behavior is seen in λ_k/λ_1, the spacings of eigenvalues, for block copolymers MM-St-MM, St-MM-MM, Ip-St-Ip, and St-Ip-Ip; that is, for these

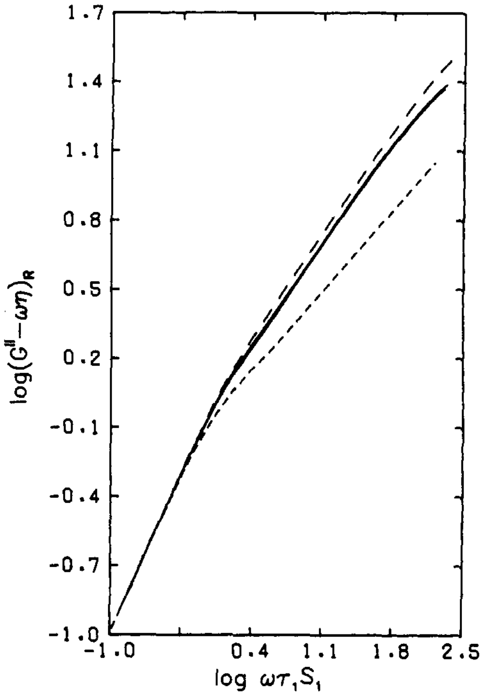

Figure 1. Log–log plots of the reduced loss modulus $(G'' - \omega\eta)_R$ against the dimensionless frequency $\omega\tau_1 S_1$ calculated with $N = 107$ for the poly-*cis*-1,4-isoprene and the poly(styrene-*b*-*cis*-1,4-isoprene) of Table II, where τ_1 is the longest relaxation time of the chain and ω is the angular frequency. $(G'' - \omega\eta)_R$ and S_1 are given by eq 30 and 32 of the text. The curve of short dashes represents the free-draining case or the Rouse theory. The curve of long dashes represents the predictions of the Zimm theory with $N = 107$ and $h/N^{1/2} = 0.29$ for the poly-*cis*-1,4-isoprene of Table II. The solid curve represents the predictions of the present theory for the block copolymers St-Ip-Ip and Ip-St-Ip. The difference in the values of log $(G'' - \omega\eta)_R$ obtained for St-Ip-Ip and for Ip-St-Ip is less than the width of the solid curve.

block copolymers, the values of λ_k/λ_1 are larger than those for homopolymer. However, the values of λ_k/λ_1 for St-MM-St are slightly smaller than those for homopolymers and the values of λ_k/λ_1 for St-Ip-St are nearly the same as those for homopolymers.

We also observe in Tables V and VI that, with the exception of St-MM-St, the presence of dissimilar blocks increases the calculated values of Φ, the Flory–Fox constant, above those for homopolymers. The increase in the values of Φ as well as the shift toward the free-draining behavior is more noticeable in the block copolymers of styrene and isoprene than in the block copolymers of styrene and methyl methacrylate, since the dissimilarity between the blocks is more pronounced in the former than in the latter.

Tables V and VI also show that, for a given composition, the effect of the presence of dissimilar blocks, i.e., the shift toward the free-draining behavior and the increase in the Flory–Fox constant, is most pronounced in a diblock copolymer and least pronounced or nearly absent in a triblock copolymer in which the friction constant ρ_b and the root-mean-square spring length b_b of the central block are smaller than the corresponding quantities for the flanking blocks. However, we have not ascertained the applicability of this conclusion to triblock copolymers whose flanking blocks are different in contour length.

A comparison of Tables VI and VII shows that the calculated results for the viscoelastic properties of the poly(styrene-*b*-*cis*-1,4-isoprene) remain essentially unchanged when the value of N is changed from 107 to 123. Thus, as in the case for homopolymers, the predicted viscoelastic properties are rather insensitive to the exact choice of N.

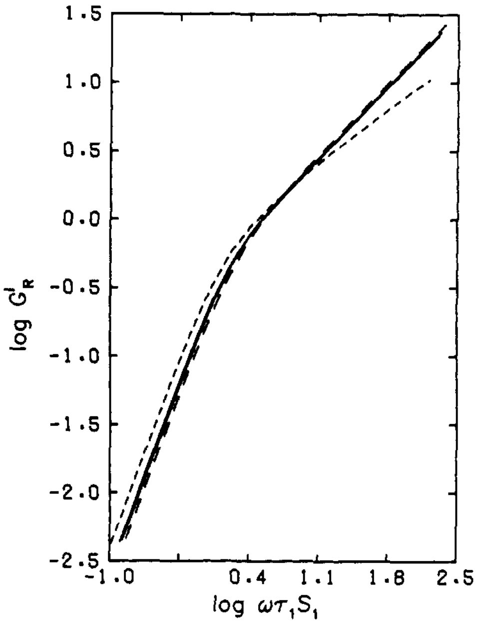

Figure 2. Log–log plots of the reduced storage modulus G_R' against the dimensionless frequency $\omega\tau_1 S_1$ calculated with $N = 107$ for poly-*cis*-1,4-isoprene and the poly(styrene-*b*-*cis*-1,4-isoprene) of Table II, where τ_1 is the longest relaxation time of the chain and ω is the angular frequency. G_R' and S_1 are given by eq 29 and 32 of the text. The curve labels are the same as for Figure 1. The difference in the values of log G_R' obtained for St-Ip-Ip and Ip-St-Ip is less than the width of the solid curve.

In Figures 1 and 2, the calculated values of the reduced shear moduli $(G'' - \omega\eta)_R$ and G_R' for St-Ip-Ip and Ip-St-Ip of Table II are compared with those predicted by the free-draining case as well as those calculated for the poly-*cis*-1,4-isoprene of Table II by using the Zimm theory. The curve for the block copolymer St-Ip-St of Table II, which would lie between the curve for the homopolymer and the curve for Ip-St-Ip, has been omitted to avoid crowding. We observe in Figures 1 and 2 that the curves for the block copolymers deviate from those for the homopolymer toward those for the free-draining case. This is consistent with the observation of Sakanishi and Tanaka[29] that the experimental values of the reduced shear moduli for styrene–butadiene block copolymers in toluene at 30° lie between the curve for the nonfree-draining case and the curve for the free-draining case, while those for a styrene–butadiene random copolymer in the same good solvent lie closely on the curve for the nonfree-draining case.

VI. Concluding Remarks

We have extended the bead-spring model theory of Zimm to take into account the existence of dissimilar segments in block copolymers. We have illustrated the applications of our theory with some examples and have found that, for some block copolymers, the calculated values of the viscoelastic properties deviate significantly from the values for the homopolymer toward the values predicted by the free-draining case. The usefulness of our theory can be further increased by taking into account the excluded-volume effect. However, it might be more fruitful, for the understanding of block copolymer solutions, to check the conclusions of this work with carefully selected experiments. For this purpose, the block copolymers of styrene and isoprene or the block copolymers of styrene and butadiene seem to be better subjects than those of styrene and methyl methacrylate, if proper poor solvents can be found, since the effects of dissimilar segments are more pronounced in the former than in the latter. The present model is expect-ed to be inadequate when the contour length of any of the blocks is not sufficiently long in comparison with its Kuhn length. We are developing a theory, based on a more appropriate model, for the dynamics of such block copolymers in solution.

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Notes

On the Narrow Miscibility Gap in Polymer 1–Polymer 2–Solvent Ternary Systems

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Koningsveld, *et al.*,[1] reported in 1970 on the very narrow one-phase temperature region between the lower and upper two-phase regions in the ternary mixture of isotactic polypropylene, polyethylene, and diphenyl ether. They suggested that this occurrence was caused by some effect from the tacticity of the polypropylene molecule, since this occurrence was not found in the atactic polypropylene system with similar components. Recently the author found quite a similar phenomenon in other ternary systems containing two polymers and one solvent: the polystyrene (PS)–polydimethylsiloxane (PDMS)–ethyl acetate system (Figure 1) and the PS–PDMS–methyl acetate system (Figure 2). As seen in the figures the narrow miscibility gap appears close to the cloud point curve of one of the corresponding binary polymer solvent systems. The fact that a similar phenomenon was observed in the three different ternary systems and not in the binary system suggests the existence of certain special features which are common in ternary (or multicomponent) systems. One of the noteworthy features common to these three systems is that the critical solution temperatures of the two binary polymer–solvent systems corresponding to each ternary system are close. On this basis, the PDMS–polyisobutene–phenetole system was also examined, since the Flory temperatures of the two corresponding binary systems lay within 83 to 86°,[2,3] and gave the results illustrated in Figure 3. Although this system did not show the narrow miscibility gap, it would appear that the cloud point curve suggests the interpenetration of the lower and upper cloud point curves.

A similar behavior of the spinodal curve on the temperature was found (Figure 4a) from the computer analysis of the Scott theory[4] on condition that the values of the interaction parameters between the solvent and the two polymers (χ_{01}, χ_{02}) are the same and decrease with increasing temperature, and that the polymer–polymer interaction parameter χ_{12}, which is very small, increases with increasing temperature (Figure 4b). The analysis under many different conditions was tried, but the very small value (around 0.02) and the positive temperature dependence of χ_{12} seem to be essential in order to obtain the narrow miscibility gap.[5]

The necessity of considering the positive temperature dependence of χ had been suggested already by Koningsveld, *et al.*,[1] and cases of positive temperature dependence of χ parameters have been found in many polymer–solvent or polymer–polymer binary systems, and are well interpreted by means of the concept of the free volume dissimilarity between the components.[6] Our particular binary mixture of styrene and dimethylsiloxane oligomers (both approximately hexamers) has, however, an "upper" critical solution temperature which we noticed to be above 35°. This indicates that the χ_{12} value of this system which is higher than 0.3 decreases with increasing temperature. This fact seems to indicate that, as solvent is added as a third component to a binary mixture of two polymers, the magnitude of χ_{12} decreases drastically and the temperature dependence is reversed from negative to positive.

At the lower polymer concentration, the polymer molecules form segment clouds around the center of gravity of the molecules. This behavior prevents the occurrence of intermolecular segment–segment contacts. The probability of making this contact must be reflected in the apparent value of the polymer–polymer interaction parameter χ_{12} in dilute ternary systems, and this apparent value must be far

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