EDITOR'S NOTE: The history of science is full of simultaneous discoveries, but the quadruple near-coincidence shown by this and the following three papers is probably a rather rare occurrence. All of these papers had their origin in the experimental work on molten styrene-α-methylstyrene block copolymers done in Mitchel Shen's group at Berkeley, and two of them were directly inspired by Shen's lecture at the 1974 Gordon Conference on Polymer Physics in July of that year. However, each group solved the same general problem independently and by methods differing considerably in detail. By mutual agreement among all the authors, the four papers are printed together in this issue of *Macromolecules* as a microsymposium on the dynamics of block-polymer chains.

Viscoelastic Retardation Time Computations for Homogeneous Block Copolymers

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ABSTRACT: The Rouse–Bueche–Zimm molecular theory of viscoelasticity has been extended to compute the retardation time spectra of block copolymers of various configurations and compositions. The basic assumption of the block copolymer model is that the effect of the presence of foreign blocks on the retardation spectrum is due exclusively to the difference in the friction coefficients. Mathematically this modification is accomplished by introducing into the equations of motion a frictional coefficient matrix. Retardation spectra can then be obtained by numerically solving for the eigenvalue spectrum on a computer. Results show that the viscoelastic retardation spectra and maximum retardation times of the block copolymers vary as a function of the block configurations, block composition, and the friction coefficient ratio of the blocks. The model is restricted to bulk homogeneous block copolymers, or block copolymers dissolved in appropriate solvents without microphase separation.

Block copolymers, along with graft copolymers, exhibit some interesting viscoelastic properties. Many of these unique properties are a consequence of the heterophase structure, since it is now well known that the free energy of mixing for many polymeric blocks is positive. However, some of the block copolymers are homogeneous, even in bulk, e.g., the block copolymers of styrene and α-methylstyrene.[1,2] Block copolymers in appropriate solvents also show no microphase separation.[3-5] The viscoelastic properties of these homogeneous block copolymers are amenable to theoretical treatment by the bead-and-spring model enunciated by Rouse,[6] Bueche,[7] and Zimm.[8] Previously, this theory was applied to block copolymers containing a very small copolymeric block.[9,10] The aim of that treatment was to test the limit of the RBZ theory by introducing the foreign block as a perturbation to the system and predict the consequence of this perturbation. In this work, we shall extend the model to cover the whole range of block composition and a variety of block configurations. Viscoelastic retardation spectra and maximum retardation times are computed numerically for all of these block copolymers.

Theory

In the previous treatment for the viscoelastic behavior of macromolecules containing a small copolymeric block, a rigorous mathematical derivation was given.[9] In this work, however, we shall follow a simplified procedure first proposed by Peticolas.[11] The free-draining case of Rouse[6] and Bueche[7] will be used for our calculations.

The RBZ model represents the polymer molecule by replacing the N submolecules with $N + 1$ beads held together with N entropy springs. When the polymer coil is disturbed by a velocity gradient, the springs are stretched. The restoring force of these entropy springs is proportional to displacement, the spring constant being given by $3kT/b^2$ where b^2 is the average end-to-end distance of the submolecule. As the beads move through the medium, a viscous drag is exerted on them whose magnitude is determined by the friction coefficient f. As the flow ceases, the recovery of the polymer chain is effected without acceleration, so that the viscous and the elastic forces are exactly equal to each other. The equations of motion for the string of identical beads can be represented in matrix notation as[11]

$$\dot{\mathbf{x}} = -\sigma \mathbf{Z}\mathbf{x} \qquad (1)$$

where $\mathbf{x}$ and $\dot{\mathbf{x}}$ are column vectors of bead positions and bead velocities respectively, $\mathbf{Z}$ is the nearest neighbor matrix and $\sigma = 3kT/b^2f$.

Equation 1 was written for homopolymers. For block copolymers, the equation must be revised to take into account the fact that not all beads are the same. We shall assume, for simplicity, that the submolecular spring constants are the same for the copolymeric blocks, and that only the frictional coefficients of the beads are different.[9] For a block copolymer consisting of copolymeric blocks A, B, C, . . ., their frictional coefficients can be designated by f_A, f_B, f_C, ... Thus the equations of motion for this block copolymer become

$$\dot{\mathbf{x}} = \sigma_B \mathbf{D}^{-1}\mathbf{Z}\mathbf{x} \qquad (2)$$

where $\sigma_B = 3kT/b^2f_B$. $\mathbf{D}^{-1}$ is the inverse of a diagonal matrix whose elements are the frictional coefficients of the re-

Table I
Structures and Maximum Retardation Times of Various Block Copolymers

Polymer	Block configuration	Log $\tau_{\max}$[a] 10% A	Log $\tau_{\max}$[a] 50% A
I. Diblock copolymer	A_xB_y ($x + y = 50$)	−0.42	0.65
II. Triblock copolymers	(a) $A_xB_yA_x$ ($2x + y = 50$)	0.64	1.22
	(b) $B_xA_yB_x$ ($2x + y = 50$)	−0.62	0.65
	(c) $A_xB_xC_x$ ($x = 16$, total 48 beads)		
III. Alternating (segmented) block copolymers	(a) $A_xB_xA_xB_x\ldots$ ($x = 1, 5, 10$, total 50 beads)		0.97
	(b) $A_xB_yA_xB_y\ldots$ $(x, y) = (1, 9); (1, 4); (1, 2); (2, 1); (4, 1); (9, 1)$ (total 50 beads)	0.26	0.97
IV. Multiblock copolymers	(a) $B_xA_yB_z$ ($x + y + z = 50$, center of A block fixed at 13th position)	−0.60	0.65
	(b) $B_xA_yB_zA_yB_x$ ($2x + 2y + z = 50$, centers of A blocks fixed at 13th and 38th positions)	0.34	1.01
	(c) B_xAB_yA ($x + y = 48$)		
	(d) $B_xAB_yAB_x$ ($x + 2y = 48$, A's equidistant from center of chain)		

[a] Computed for $f_A/f_B = 185$, except for IIc.

spective beads divided by those of B beads. For example,

$$\mathbf{D} = \begin{bmatrix} 1 & & & & & & & & \\ & 1 & & & & & & & \\ & & \ddots & & & & & & \\ & & & \delta_A & & & & & \\ & & & & \delta_A & & & & \\ & & & & & \ddots & & & \\ & & & & & & \delta_C & & \\ & & & & & & & \delta_C & \\ & & & & & & & & \ddots \end{bmatrix} \tag{3}$$

where $\delta_A = f_A/f_B$, $\delta_C = f_C/f_B, \ldots$

To solve eq 3, we define a new set of coordinates **r** related to **x** through

$$\mathbf{r} = \mathbf{A}\mathbf{x} \tag{4}$$

where the **A** matrix is defined by $\mathbf{Z} = \mathbf{A}^T\mathbf{A}$. Operating on both sides of eq 2 with **A**, we get

$$\dot{\mathbf{r}} = -\sigma_B\mathbf{A}\mathbf{D}^{-1}\mathbf{A}^T\mathbf{A}\mathbf{x} = -\sigma_B\mathbf{S}\mathbf{r} \tag{5}$$

where

$$\mathbf{S} = \mathbf{A}\mathbf{D}^{-1}\mathbf{A}^T \tag{6}$$

is a symmetrical tridiagonal $N \times N$ matrix which differs from the well-known Rouse matrix[6] ($\mathbf{R} = \mathbf{A}\mathbf{A}^T$) by the extra operation $\mathbf{D}^{-1}$. For a homopolymer, all of the elements in our **D** matrix (eq 3) are unity, and the **S** matrix is reduced to the **R** matrix. In this instance, the Rouse model predicts a discrete retardation spectrum given by[11]

$$\tau_p = 1/\sigma\lambda_p = fb^2/3kT\lambda_p \tag{7}$$

where λ_p's are the N eigenvalues of the **R** matrix.[6]

$$\lambda_p = 4\sin^2[p\pi/2(N + 1)] \tag{8}$$
$$p = 1, 2, \ldots, N$$

For our block copolymers, the eigenvalue spectrum of the **S** matrix is more readily obtained numerically on a computer. Computations are particularly expedited by the availability of a subroutine[12] at the University of California Computer Center for determining the eigenvalues and eigenvectors of symmetric matrices. Using the computed eigenvalues, the corresponding retardation times are given by eq 7. The relaxation times are just half of the corresponding retardation times.[11]

The introduction of our **D** matrix into the equation of motion is mathematically analogous to the operation by the **H** matrix for hydrodynamic interaction. It has been shown that the essential effect of that modification is on the eigenvalue spectrum.[13] Thus it is believed that, since we are mainly interested in the viscoelastic retardation (or relaxation) behavior of the block copolymers in comparison to that of the homopolymers, our simplified analysis is valid and the main results of the Rouse theory other than the eigenvalue spectrum remain unchanged.

In presenting our data, we shall use a normalized retardation time defined by

$$\tau_p(\text{normalized}) = 1/(N + 1)^2\lambda_p \tag{9}$$

The use of the normalized retardation time removes the arbitrariness of the choice of the value of N in the computation of maximum retardation times. We arrived at eq 9 by noting that $f = m\xi$, where m is the number of monomers per submolecule and ξ is the monomeric friction coefficient. In addition, $b^2 \propto ml^2$ where l is the length of the monomeric segment. For a fixed molecular weight M, $m = M/(N + 1)$. Therefore the retardation time (eq 7) would be expected to be inversely proportional to $(N + 1)^2$. The use of τ_p(normalized) does not eliminate the dependance on N of shorter retardation times, as evidenced by eq 8 for the case of homopolymers.

In carrying out our computations. We must first determine an optimum size for the **S** matrix. We arrived at this number by carrying out the computations for values of $N + 1$ varying from 6 to 146 for several cases of different block structures and different values of δ's. It was found that for $N + 1 > 20$, no significant changes in computed maximum retardation times can be observed. Thus in all other computations, a fixed value of $N + 1 = 50$ was used unless otherwise specified.

Results and Discussion

Table I summarizes the ten different types of block copolymers that we have investigated in this work. These are various diblock, triblock, alternating block, and multiblock copolymers. Their structures are indicated in column 2. The maximum retardation times (normalized) for two block compositions (10 and 50% of A) are included in columns 3 and 4 for the sake of comparison. In all instances, except for case IIc, 50 beads were used in the computations and δ_A was chosen to be 185. The latter value is the ratio of

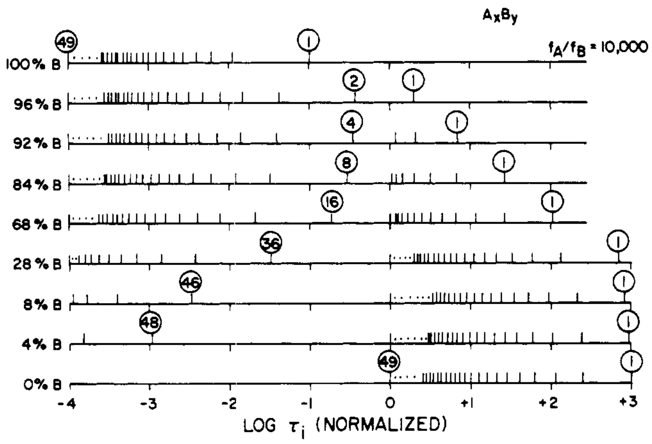

Figure 1. Distribution of retardation times for the diblock copolymer A_xB_y (case I) computed on the basis of 50 beads (f_A = 10,000, f_B = 1).

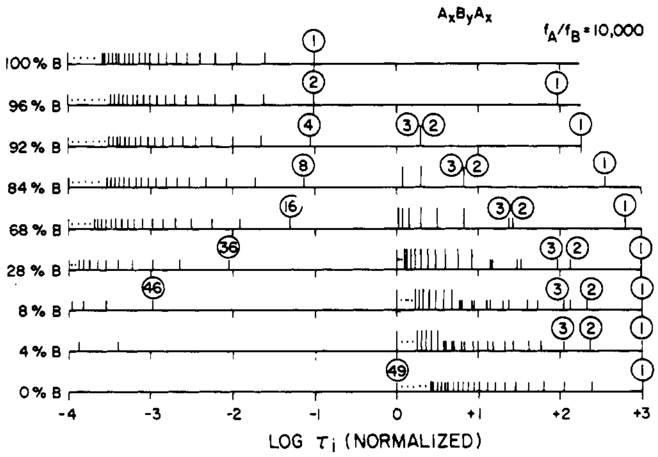

Figure 2. Distribution of retardation times for the triblock copolymer $A_xB_yA_x$ (case IIa) computed on the basis of 50 beads (f_A = 10,000, f_B = 1).

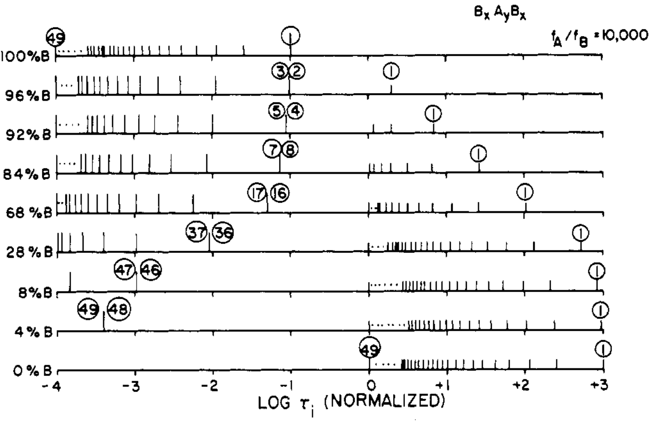

Figure 3. Distribution of retardation times for the triblock copolymer $B_xA_yB_x$ (case IIb) computed on the basis of 50 beads (f_A = 10,000, f_B = 1).

monomeric friction coefficients of polystyrene and poly(α-methylstyrene) and was selected for the ease of subsequent comparison with experimental data in a following paper.[1]

1. Viscoelastic Retardation Spectra. Although most of our computations were carried out for δ_A = 185, it is instructive to first consider the retardation spectra for a more extreme case of δ_A = 10,000. Figure 1 shows the distribution of retardation times for diblock copolymers (A_xB_y, case I) over the entire range of block composition. Distributions for 100% A's and B's (A and B homopolymers) are also included for the sake of comparison. At 96% B (48 B beads and 2 A beads), we note that the maximum normalized retardation time (τ_m) of the copolymer is shifted to a much longer time. However, from the τ_2 on until τ_{49} (minimum retardation time) the distribution is very similar to that of a homopolymer, except that they are all proportionally shifted to longer times. The 49th retardation time is τ_N, since for $N + 1$ beads in the model N retardation times are expected. Now at 92% B (46 B's, 4 A's), the first three retardation times seem to have formed a spectrum of their own and the next 46 formed another. The trend persists for all the subsequent compositions. The spectra for A beads, because of their higher friction coefficient, are all shifted to longer times. The number of retardation times in the A spectrum is always $x - 1$, where x is the number of A beads in the model ($x + y = N + 1$). At low B content, we see that the B spectra in the shorter time regions clearly consist of y retardation times, e.g., there are four short retardation times for 8% B (4 B's, 46 A's) and two short retardation times for 4% B (2 B's, 48 A's).

For the triblock copolymer $A_xB_yA_x$, we again note the shift of τ_m to longer times for the composition of 2 A beads and 48 B beads (96% B). The shift is more than three orders of magnitude, much greater than in the case A_xB_y (a little over one decade). Beginning with 92% B, there is not only the clear splitting of the A spectra from the B spectra, but also the occurrence of degeneracy in the A spectra. In this case there are two equivalent A blocks separated by a B block each giving rise to its own spectrum. However, this degeneracy turns into doublets for the longer retardation times as the content of A increases, such as τ_2, τ_3 for 68% B, etc. Since there is only one B block, neither degeneracy nor doublet formation can be seen in the B spectrum. Again as in the diblock case, for all compositons of $A_xB_yA_x$ the number of retardation times in the A spectrum is always equal to total number of A beads minus one.

Now in the case of $B_xA_yB_x$, as one might expect, the splitting of the A and B spectra and the formation of degeneracy are also observed. For this block copolymer the degeneracy occurs in the shorter time region, since now there are two equivalent B blocks separated by an A block. However, the presence of degeneracy seems to persist throughout the entire range of block composition. The exact cause for the absence of doublet formation is not apparent. In both $A_xB_yA_x$ and $B_xA_yB_x$, two presumably equivalent blocks are connected to each other through one foreign block. The presence of the sluggish (high friction coefficient) end blocks in the chain seems to play a significant role.

Figures 4 through 6 are for cases I, IIa, and IIb (A_xB_y, $A_xB_yA_x$, and $B_xA_yB_x$) with δ_A = 185. Here the splitting of A spectra and B spectra is only apparent for lower B content. For these compositions, the presence of degeneracy and doublets are also observable for the triblock copolymers. At high B content (small number of A beads), there seems to be some doublet formation for all three cases. This is in contrast to the cases for δ_A = 10,000, where only the A spectra of the $A_xB_yA_x$ system at low B content exhibit this phenomenon. The doublets in Figures 4–6 are apparently due to the lack of clean separation between the A and B spectra, rather than the presence of equivalent chains.

To further scrutinize this problem, we show in Figure 7 the retardation spectra for the tricomponent triblock polymers ($A_xB_xC_x$, case IIc) for three different sequences and three different values of friction factors. Here x was fixed at 16 for all systems. The first three spectra are for f_A =

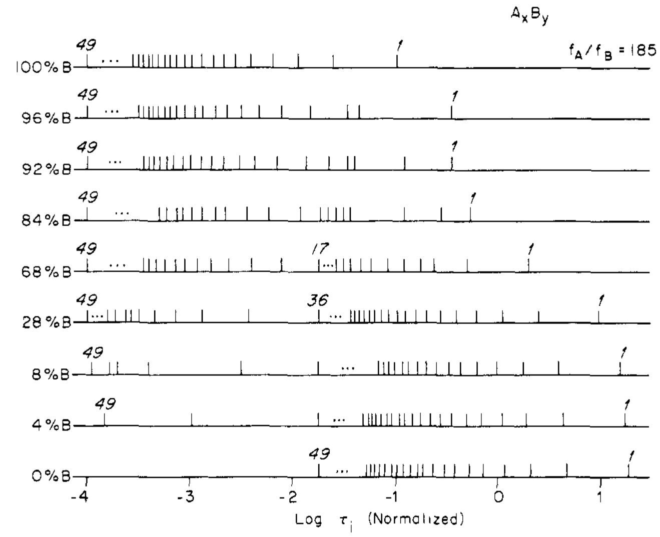

Figure 4. Distribution of retardation times for the diblock copolymer A_xB_y (case I) computed on the basis of 50 beads ($f_A = 185, f_B = 1$).

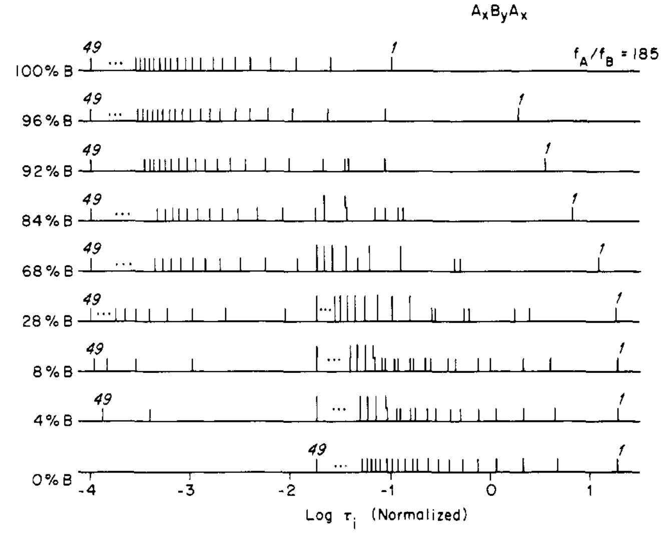

Figure 5. Distribution of retardation times for the triblock copolymer $A_xB_yA_x$ (case IIa) computed on the basis of 50 beads ($f_A = 185, f_B = 1$).

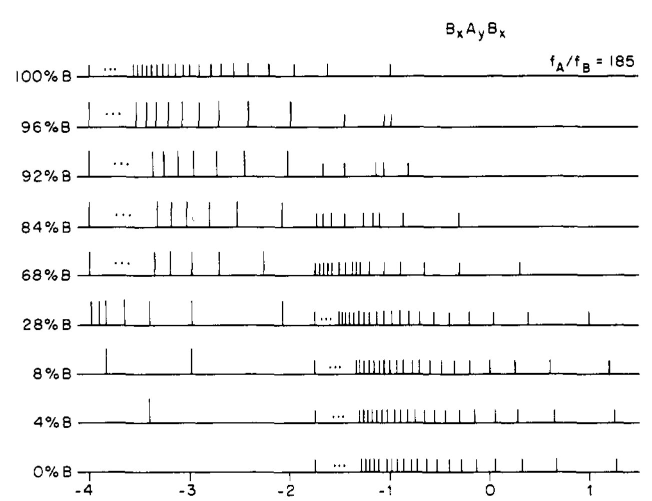

Figure 6. Distribution of retardation times for the triblock copolymer $B_xA_yB_x$ (case IIb) computed on the basis of 50 beads ($f_A = 185, f_B = 1$).

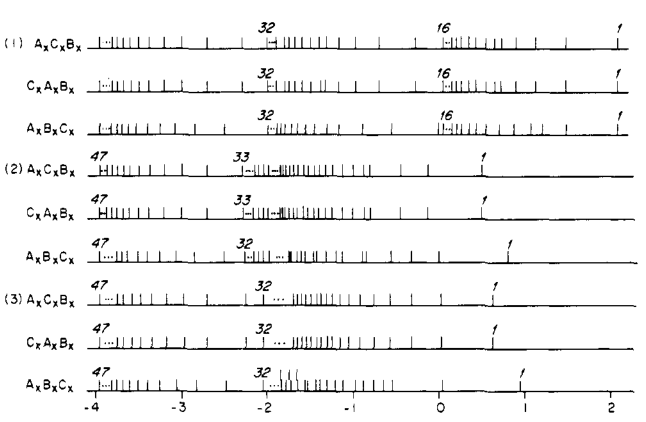

Figure 7. Distribution of retardation times for the tricomponent triblock copolymers $A_xB_yC_x$, $C_xA_xB_x$ and $A_xC_xB_x$ (case IIc) computed on the basis of 48 beads ($x = 16$) and: (1) $f_A = 10{,}000, f_B = 1, f_C = 100$; (2) $f_A = 100, f_b = 1, f_C = 50$; (3) $f_A = 100, f_B = 1, f_C = 80$.

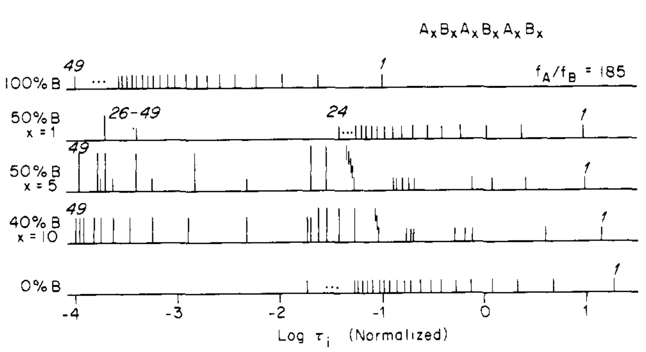

Figure 8. Distribution of retardation times for the evenly alternating block copolymer $A_xB_xA_xB_xA_xB_x$ . . . (case IIIa) computed on the basis of 50 beads ($x = 1, 5, 10$) ($f_A = 185, f_B = 1$).

10,000, $f_B = 1$, and $f_C = 100$. Here because of the wide differences in values of f, three distinct spectra can be observed. The second three spectra are for $f_A = 100$, $f_B = 1$, and $f_C = 50$. Since there is only a factor of 2 difference in friction factor between A and B blocks, their spectra become merged and difficult to distinguish. For the final three spectra, values of f's for A beads and C beads were made nearly the same (100 and 80, respectively). Now the $A_xC_xB_x$ and $C_xA_xB_x$ cases approach that of the diblock, and there are only two separated spectra. The $A_xB_xC_x$ case is similar to the triblock $A_xB_yA_x$, complete with the doublet formation. These spectra again demonstrate the fact that for block copolymers with widely different friction factors, distinct splitting of the spectra can be expected. As values of f's become closer, these spectra are superposed onto each other. The appearance of the superposed spectra depends on the block configurations.

Retardation spectra for the alternating block copolymers $A_xB_xA_xB_xA_xB_x$ . . . (case IIIa in Table I) are shown in Figure 8. These polymers contain blocks of A's and B's of equal size (x = 1, 5, and 10). Only one composition (50% B) is possible here, except for x = 10, in which case the polymer contains three A blocks and two B blocks (40% B). For the x = 1 case, the A spectrum is almost unperturbed, as if the presence of the lower friction coefficient B beads is all but ignored by the A beads in the chain. The B spectrum on the shorter time scale, on the other hand, is split from the A spectrum and contains one retardation time plus another one with 24-fold degeneracy. It seems that the alternating single B beads separated by the high friction coefficient A beads are acting as single beads. Now when the lengths of the alternating blocks are extended to five each,

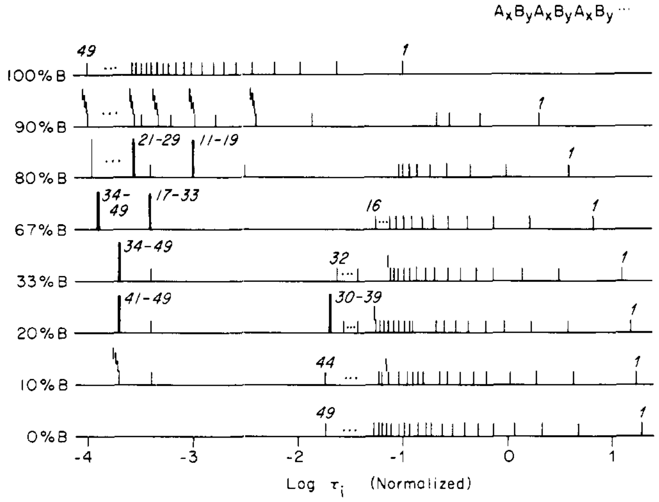

Figure 9. Distribution of retardation times for the unevenly alternating block copolymer $A_xB_yA_xB_yA_xB_y$ . . . (case IIIb) computed on the basis of 50 beads (f_A = 185, f_B = 1).

both A and B spectra take on a more complex appearance. Quinteplets and retardation times with fivefold degeneracies are seen, reflecting the presence of five equivalent A and B blocks. Finally, for the case of $x = 10$, triplets and threefold degeneracies are found in the A spectrum as a consequence of the existence of three equivalent A blocks, and twofold degeneracies are observed in the B spectrum because of the two equivalent B blocks.

Figure 9 shows the retardation spectra for the other alternating block copolymer $A_xB_yA_xB_yA_xB_y$ . . . (case IIIb). The 90% B chain consists of five B blocks of nine beads each and five A blocks of one bead each. We note that the A spectrum consists of four retardation times, and the B spectrum contains a number of quadruplets. The trend is continued with increasing A content. Generally the number of retardation times in the A spectra is related to the number of A beads. The fact that the B spectra appears as a series of groupings of a singlet and a quadruplet may be due to the fact that the chain is not symmetric.

2. Maximum Retardation Times. In Figure 10 we show the normalized maximum retardation times (τ_m) for various block copolymers as a function of block composition. Three values for δ_A, namely 10,000, 185, and 10, were chosen for these computations. First we consider the intermediate case of δ_A = 185. As we start to interchange A beads for B beads in the $A_xB_yA_x$ chain, there is an immediate increase in τ_m. The increase is very large at the high end of B content. At 50% of B in the chain, the maximum retardation time has reached a plateau. Further addition of the high friction coefficient A beads produced no more change in the value of τ_m. By contrast, in the case of $B_xA_yB_x$ the presence of the initial 5% of A beads has little effect. Subsequent addition of A beads, however, brought about a steady rise in the value of τ_m throughout the entire range of composition. This observed difference is due solely to the block configuration. Apparently the presence of high friction coefficient blocks on the ends is more effective in inhibiting the retardation behavior of the block copolymer than if they are in the chain middle.

The curve for the A_xB_y diblock copolymer is a composite of the $A_xB_yA_x$ and $B_xA_yB_x$. At high B content, it follows the former curve. However, after the initial steep rise in τ_m the curve levels off and undergoes a "transition" to the $B_xA_yB_x$ curve. The same is true for the uneven triblock copolymer $B_xA_yB_z$ (case IVa), but the "transition" occurs more rapidly. By placing the "slow-moving" A blocks on one end of the chain (diblock), or even near one end (uneven triblock), there is an immediate effect in slowing down the retardation behavior, although its effectiveness does not increase at the same rate as the $A_xB_yA_x$ case with increasing A content.

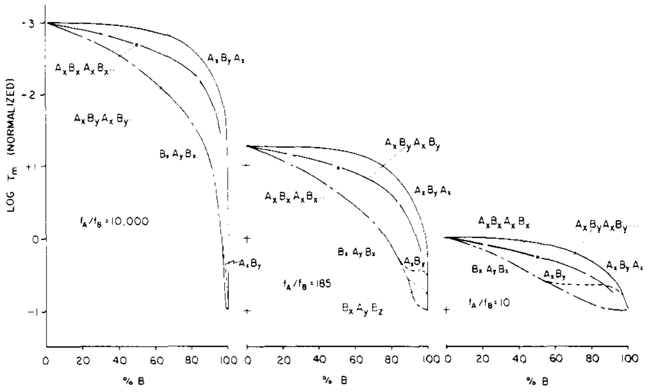

Figure 10. Maximum retardation times of diblock, triblock, and alternating block copolymers (cases I, IIa, IIb, IIIa, IIIb, IVa, and IVb) as a function of copolymer composition computed for δ_A = 10,000, 185, and 10 and f_B = 1.

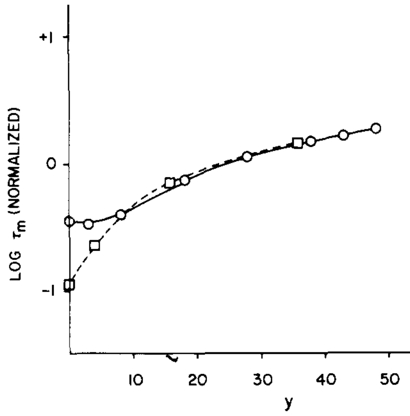

Figure 11. Maximum retardation times of multiblock copolymers B_xAB_yA (case IVc) and $B_xAB_yAB_x$ (case IVd) containing 2 A beads and 48 B beads as a function of the number of B beads between A beads (y) (f_A = 185, f_B = 1): circles, B_xAB_yA; squares, $B_xAB_yAB_x$.

The unevenly alternating block copolymer $A_xB_yA_xB_yA_xB_y$ . . . (case IIIb) has an intermediate behavior between $A_xB_yA_x$ and $B_xA_yB_x$. The unevenly alternating block copolymer $A_xB_xA_xB_xA_xB_x$ . . . (case IIIa) falls on the same curve at 50% point, as expected. Another kind of unevenly alternating block copolymer is $B_xA_yB_zA_yB_x$ (case IVc). The initial A beads were positioned in the 13th and 38th positions of a B chain, further additions of A beads were accomplished by simultaneously placing new A-bead neighbors to the initial A beads. The resulting curve closely follows, though it is not completely identical to, the case IIIb curve.

All of the above discussed behavior applies to the curves for δ_A = 10,000 and δ_A = 10. However, in the former case the trends are further enhanced in magnitude, but diminished in the latter case. In particular the "transition" for the diblock copolymer is delayed with an extended plateau, when the friction coefficient ratio is low. The plateau is however almost nonexistent when the ratio is very high.

Finally to further demonstrate the difference in retardation behavior due to the position of A beads, we show in Figure 11 the computed τ_m's for cases IVc and IVd (see Table I). In both instances, only 2 A beads were used along with 48 B beads. For case IVc, one of the A beads was fixed

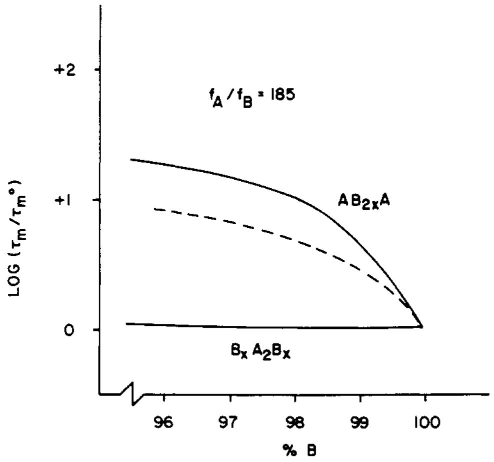

Figure 12. Comparison of the ratio of retardation times of block copolymer and homopolymer as a function of percent B. Dotted line, eq 10; solid lines, computed by the methods of this work by varying x ($25 < x < 76$) for $B_xA_2B_x$ and $AB_{2x}A$ ($f_A = 185, f_B = 1$).

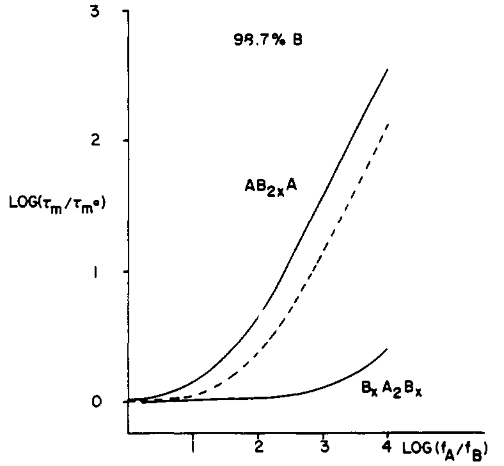

Figure 13. Comparison of the ratio of retardation times of block copolymer and homopolymer as a function of log (f_A/f_B). Dotted line, eq 10; solid lines, computed by the methods of this work for $B_xA_2B_x$ and $AB_{2x}A$ by fixing the percent of A beads at 1.3% ($2x = 76$) and varying the ratio of friction coefficients ($1 < \delta_A < 10{,}000$, $f_B = 1$).

at one end, and the other one was permitted to move farther and farther away. The formula for this case is B_xAB_yA, and y varies from 0 to 48. As the second A bead moves away from the initial one at the end (y increases), the retardation time first takes a very slight drop then increases monatomically with increasing y. For case IVb, two A beads are initially positioned in the chain middle and then permitted to move away from each other. Thus for this polymer $B_xAB_yAB_x$, and y varies again from 0 to 48. Here as y increases, there is a steady increase in τ_m. This differs from case IVa only because of the initial position of the A beads. At $y \geq 8$, there is very little difference between these two cases. At $y = 48$, of course, they are identical.

3. Comparison with Previous Work. In the previous work, the dynamics of a block copolymer chain containing only one foreign bead was treated by a more elaborate mathematical derivation. The main result from this treatment was[9]

$$\tau_m = \tau_m°(1 + \Delta/N) \qquad (10)$$

where

$$\Delta = (f_A - f_B)/f_B \qquad (11)$$

and $\tau_m°$ is the maximum retardation time of the homopolymer B. In order to compare eq 10 with results from the present computation, we first note that the model for this treatment is $B_xA_2B_x$. We choose an arbitrary value of δ_A, say 185, and then let x vary between 25 and 76. For the sake of comparison, we also compute for $AB_{2x}A$. The results are shown in Figure 12. The curve for eq 10 is seen to deviate from that for $B_xA_2B_x$, but approaches the $AB_{2x}A$ curve.

Another method to compare with eq 10 is to fix the total number of beads at a constant percent of A, and vary δ_A. Figure 13 shows the results obtained by fixing the A content at 1.3%, and $1 < \delta_A < 10{,}000$. Again similar deviations can be seen. It should be noted that although eq 10 was derived by a more rigorous mathematical treatment, a number of approximations were used because of the very low copolymeric block in the model. Thus for a more meaningful comparison, our numerical computation should be compared with analytical results from a rigorous derivation without approximations.[14,15]

Acknowledgment. This work was supported by the Office of Naval Research and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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