It is expected that the observed shape of the loss curve will be explained by taking account of an appropriate correlation among dipoles in the near future.

Conclusion

Dielectric dispersion of poly(*p*-chlorostyrene) in dilute solution can be attributed to a local conformational transition of the chain backbone, which is either a crankshaft transition or a transition in which rotation of a few monomer units between two simultaneously rotating bonds is accompanied by a slight translation of one of the two bonds relative to the other. The relaxation process can be interpreted by the Kramers theory of the rate constant for the transition and evidence is presented which shows that Stokes law is applicable to the friction for the chain motion. The theory gives an adequate explanation not only to the dependence of the relaxation time observed on solvent viscosity and temperature, but also to the magnitude of the relaxation time.

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References and Notes

(1) W. H. Stockmayer, *Pure Appl. Chem.*, **15**, 539 (1967).
(2) W. H. Stockmayer and K. Matsuo, *Macromolecules*, **5**, 766 (1972).
(3) W. H. Stockmayer, *Suppl. Pure Appl. Chem. Macromol. Chem.* **8**, 379 (1973).
(4) A. M. North and P. J. Phillips, *Trans. Faraday Soc.*, **64**, 3235 (1968).
(5) S. Mashimo and A. Chiba, *Polym. J.*, **5**, 41 (1973).
(6) H. A. Kramers, *Physica*, **7**, 284 (1940).
(7) E. Helfand, *J. Chem. Phys.*, **54**, 4651 (1971).
(8) A. Kotera, T. Saito, H. Matsuda, and R. Kamata, *Rep. Prog. Polym. Phys. Jpn.*, **3**, 51 (1960).
(9) M. Nozaki, K. Shimada, and S. Okamoto, *Jpn. J. Appl. Phys.*, **10**, 179 (1971).
(10) S. Mashimo and K. Shinohara, *J. Phys. Soc. Jpn.*, **34**, 1141 (1973).
(11) S. Mashimo, A. Chiba, and K. Shinohara, *Polym. J.*, **6**, 170 (1974).
(12) J. G. Kirkwood and R. M. Fuoss, *J. Chem. Phys.*, **9**, 329 (1941).
(13) L. Onsager, *J. Am. Chem. Soc.*, **58**, 1486 (1936).
(14) E. W. Washburn et al., Ed., "International Critical Tables of Numerical Data, Physics, Chemistry and Technology", Vol. VII, McGraw-Hill, New York, N.Y., 1930.
(15) W. G. Parks, I. M. LeBaron, and E. Molloy, *J. Am. Chem. Soc.*, **63**, 3331 (1941); J. A. Geddes, *ibid.*, **55**, 4832 (1933).
(16) A. Kotera, *Nippon Kagaku Zasshi*, **70**, 118 (1949).
(17) P. Debye and F. Bueche, *J. Chem. Phys.*, **19**, 589 (1951).
(18) L. L. Burshtein and T. P. Stepanova, *Polym. Sci. USSR* (*Engl. Transl.*), **11**, 2885 (1969).
(19) J. E. Mark, *J. Chem. Phys.*, **56**, 458 (1972).
(20) B. Baysal, B. A. Lowry, H. Yu, and W. H. Stockmayer, "Dielectric Properties of Polymers", F. E. Karasz, Ed., Plenum Press, New York, N.Y., 1972, pp 329–341.
(21) G. P. Mikhailov, A. M. Lobanov, and M. P. Platonov, *Polym. Sci. USSR* (*Engl. Transl.*), **9**, 2565 (1967).
(22) G. Natta, P. Corradini, and I. W. Bassi, *Nuovo Cimento*, **15**, 68 (1960).
(23) G. Natta, *Makromol. Chem.*, **35**, 94 (1960).
(24) G. Natta, P. Corradini, and I. W. Bassi, *Gazz. Chim. Ital.*, **89**, 784 (1959).
(25) H. Nomura, S. Kato, and Y. Miyahara, *Nippon Kagaku Zasshi*, **90**, 1218 (1969); **91**, 837 (1970); **91**, 1042 (1970).
(26) M. T. Vala, Jr., and S. A. Rice, *J. Chem. Phys.*, **39**, 2348 (1963).
(27) M. Kobayashi, K. Tsumura, and H. Tadokoro, *J. Polym. Sci., Part A-2*, **6**, 1493 (1968).
(28) H. A. Pohl and H. H. Zabusky, *J. Phys. Chem.*, **66**, 1390 (1962).
(29) J. D. Hoffman and H. G. Pfeiffer, *J. Chem. Phys.*, **22**, 132 (1954); J. D. Hoffman, *ibid.*, **23**, 1331 (1955).
(30) H. J. Bauer, H. Hässler, and M. Immendörfer, *Discuss. Faraday Soc.*, **49**, 238 (1970).
(31) H. Lamb, "Physical Accoustics IIA", W. P. Mason, Ed., Academic Press, New York, N.Y., 1965, Chapter 4.
(32) E. Paul and R. M. Mazo, *Macromolecules*, **4**, 424 (1971).
(33) Yu. Ya. Gotlib, *J. Polym. Sci., Part C*, **16**, 3365 (1968).
(34) M. B. Clark, ref 17, pp 73–97.
(35) H. Morawetz, *Acc. Chem. Res.*, **3**, 354 (1970).
(36) R. H. Boyd and S. M. Breitling, *Macromolecules*, **7**, 855 (1974).
(37) R. N. Work and S. Fujita, *J. Chem. Phys.*, **43**, 3779 (1966).
(38) J. E. Anderson, *J. Chem. Phys.*, **52**, 2821 (1970).
(39) D. J. Isbister and D. A. McQuarrie, *J. Chem. Phys.*, **60**, 1937 (1974).
(40) G. Williams and D. C. Watts, *Trans. Faraday Soc.*, **66**, 80 (1970); G. Williams, D. C. Watts, S. B. Dev, and A. M. North, *ibid.*, **67**, 1323 (1971).
(41) B. Valeur, J. P. Jarry, F. Gény, and L. Monnerie, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 667 (1975); B. Valeur, L. Monnerie, and J. P. Jarry, *ibid.*, **13**, 675 (1975).

Frictional Properties of Dilute Block-Copolymer Solutions and Homopolymer Solutions. Application to Molecular Weight Determination

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ABSTRACT: An equation for the translational diffusion coefficient of block copolymers in dilute solution has been obtained by modifying Zimm's equation for homopolymers to take into account the existence of dissimilar segments in block copolymers. Illustrative calculations for homopolymers and block copolymers have been made and the results for homopolymers have been compared with experiments and with the calculations of Yamakawa and Fujii. A procedure has been proposed to determine the molecular weight of a block copolymer from measurements of its limiting viscosity number and its sedimentation coefficient or translational diffusion coefficient.

I. Introduction

There has been much interest in the dynamics of block copolymers. For example, Hall and DeWames,[1] Shen and Hansen,[2] Stockmayer and Kennedy,[3] and Wang and DiMarzio[4] have all discussed the dynamics of free-draining block copolymers. In a previous paper[5] hereafter referred to as paper I, we have discussed the viscoelasticity of block copolymers in dilute solution. In this work, we generalize the bead-spring model theory of Zimm[6] to obtain an equation for the translational diffusion coefficient of block copolymers in dilute solution. Applications of the equation thus obtained to homopolymers and block copolymers in dilute solution are then presented. Finally, we discuss the application of the Mandelkern–Flory–Scheraga equation[7,8] to the determination of the molecular weight of block copolymers.

II. Theory and Method of Calculation

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 solvent is treated as a hydrodynamic continuum with a viscosity η. 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 Boltzman constant and the absolute temperature. The symbols N_b, N_c, ρ_b, ρ_c, b_b, and b_c are similarly defined for the B and C blocks. The beads of the model for the A block are numbered 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 b_{ab} is given by $b_{ab}^2 = (b_a^2 + b_b^2)/2$. 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}.

In paper I, we have introduced the matrices **A** and **H** of order $(N + 1)$ and have shown that the viscoelastic properties of block-copolymer molecules in dilute solution are determined by the nonzero eigenvalues λ_k ($k = 1, 2, \ldots, N$) of the matrix **H·A**. The elements of **H** are given by

$$H_{jj} = \rho/\rho_j \tag{1a}$$

$$H_{jk} = \rho T_{jk} \qquad j \neq k \tag{1b}$$

where ρ is an arbitrary friction constant, ρ_j is the translational friction consatant of the jth bead, and the interaction coefficients T_{jk} are given by

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

with $\langle R_{jk}^2\rangle$ the mean-square distance between the jth and the kth beads. The nonzero elements of the tridiagonal matrix **A** are defined for $j = 0, 1, 2, \ldots, N$ as follows:

$$A_{0k} = k_1\delta_{0k} - k_1\delta_{1k} \tag{3a}$$

$$A_{jk} = -k_j\delta_{j-1,k} + (k_j + k_{j+1})\delta_{jk} - k_{j+1}\delta_{j+1,k} \tag{3b}$$

$$\text{for } 1 \leqslant j \leqslant (N - 1)$$

$$A_{Nk} = -k_N\delta_{N-1,k} + k_N\delta_{N,k} \tag{3c}$$

where k_j is given by

$$k_j = b^2/b_j^2 \tag{4}$$

Here, b_j^2 is the mean-square length of the spring between the $(j - 1)$th and the jth beads, and b^2 is the mean-square length of an arbitrary spring. For the case of a homopolymer with $\rho_a = \rho_b = \rho_c = \rho$ and $b_a = b_b = b_c = b$, the matrices **A** and **H** reintroduced here become identical with **A** and **H** given by Zimm.[6] It is shown in paper I that the limiting viscosity number $[\eta]$ for a block copolymer is given by

$$[\eta] = \Phi(L^3/M) \tag{5}$$

with

$$\Phi = (\pi^3/3)^{1/2}N_0hN^{-2}\left[\sum_{k=1}^{N}(1/\lambda_k)\right]\left[\sum_{j=\mathrm{a,b,c}}(N_j/Nk_j)\right]^{-3/2} \tag{6}$$

where M and L are the molecular weight and the root-mean-square length of the block copolymer, N_0 is Avogadro's number, and h is defined as

$$h = N^{1/2}\rho[(12\pi^3)^{1/2}b\eta]^{-1} \tag{7}$$

In paper I, we have shown that the equations of motion of a block copolymer are identical in form with the equations obtained by Zimm[6] for a homopolymer, with **H**, **A**, b, and ρ defined in paper I and here replacing the very same symbols (**H**, **A**, b, and ρ) defined differently by Zimm. Since the diffusion equation for the distribution function of the coordinates of the beads is obtained[6] by combining the equations of motion and the equation of continuity, the diffusion equation for a block copolymer is again identical in form with the diffusion equation for a homopolymer. Thus, in the manner described by Zimm[6] for a homopolymer, we can show that the translational diffusion coefficient for a block copolymer is given by

$$D_t = kT(P\eta L)^{-1} \tag{8}$$

with

$$P^{-1} = N\left[\sum_{j=\mathrm{a,b,c}}(N_j/Nk_j)\right]^{1/2} \times \left[(12\pi^3)^{1/2}h\sum_i\sum_j(H^{-1})_{ij}\right]^{-1} \tag{9}$$

where $(H^{-1})_{ij}$ are the elements of the inverse of **H**.

Eliminating L from eq 5 and 8 we obtain the Mandelkern–Flory–Scheraga constant[7] for a block copolymer as

$$\Phi^{1/3}P^{-1} = D_t[\eta]^{1/3}M^{1/3}\eta/kT \tag{10}$$

Alternatively, $\Phi^{1/3}P^{-1}$ may be determined from the relation[8]

$$\Phi^{1/3}P^{-1} = N_0s_0[\eta]^{1/3}M^{-2/3}(1 - \bar{v}\rho^*)^{-1}\eta \tag{11}$$

where ρ^* is the density of the solvent, s_0 is the sedimentation coefficient of the block copolymer at infinite dilution and under 1 atm, and $\bar{v}$ is the partial specific volume of the block copolymer.

III. Evaluation of Parameters

The procedure for the evaluation of the parameters that appear in our theory is identical with that described in paper I, so we shall write down the procedure with a minimum of comment. We shall use the subscript v (v = a, b, c) to designate the properties associated with the V block (V = A, B, C).

We divide the V block whose contour length is L_{cv} into N_v equal segments of contour length L_{cv}^*, 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. 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

$$L_v^2 = N_vb_v^2 \tag{12}$$

Table I

Values of the Coefficient P^{-1}, the Flory–Fox Constant Φ, and the Mandelkern–Flory–Scheraga Constant $\Phi^{1/3}P^{-1}$ Calculated from the Zimm Theory[a]

d_p/b_k	L_c/b_k	L_c^*/b_k	N	$h/N^{1/2}$	P^{-1} from eq 9	P^{-1} from ref 9	Φ, 10^{23} ml/g from eq 6	$\Phi^{1/3}P^{-1}$, 10^7 cm/g$^{1/3}$ from eq 6 and 9
0.022	114	5.72	19	0.16	0.217	0.223	1.81	1.23
0.022	476	4.76	99	0.16	0.204	0.209	2.20	1.23
0.022	510	5.10	99	0.16	0.204	0.208	2.21	1.23
0.022	9080	90.8	99	0.23	0.194	0.198	2.64	1.24
0.03	100	1.00	99	0.12	0.215	0.222	1.90	1.23
0.03	400	4.00	99	0.16	0.204	0.208	2.21	1.23
0.03	400	8.00	49	0.18	0.204	0.208	2.20	1.23
0.03	10000	100.0	99	0.23	0.187	0.192	2.66	1.20
0.60	400	4.00	99	0.31	0.193	0.198	3.07	1.30

[a] Symbols employed are defined in the text.

Table II

Values of the Coefficient P^{-1}, the Flory–Fox Constant Φ, and the Mandelkern–Flory–Scheraga Constant $\Phi^{1/3}P^{-1}$ Calculated from the Zimm Theory[a]

Polymer	$M \times 10^{-3}$	L_c/b_k	L_c^*/b_k	N	$h/N^{1/2}$	P^{-1} from eq 9	Φ, 10^{23} ml/g from eq 6	$\Phi^{1/3}P^{-1}$, 10^7 cm/g$^{1/3}$ from eq 6 and 9
cis-1,4-Polyisoprene	281	2320	21.4	107	0.29	0.189	2.95	1.26
Polystyrene	860	1110	10.3	107	0.29	0.189	2.93	1.26
	265	343	3.4	100	0.30	0.188	3.00	1.26
	77	100	1.0	99	0.34	0.186	3.19	1.27
	39	50	1.0	49	0.34	0.183	3.26	1.26

[a] Symbols employed are defined in the text. The values of d_p/b_k for polystyrene and polyisoprene are 0.50 and 0.65, respectively. The values of d_p/b_k, L_c/b_k, L_c^*/b_k, and $h/N^{1/2}$ have been calculated with the use of the homopolymer properties at theta temperature that are given in Table I of paper I.

since the V block contains N_v segments.

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[9] for wormlike chains of contour length L_{cv}^*. Their formula, which is given by eq 49 to 52 of ref 9, 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.

As in paper I, we have distributed $(N + 1)$ beads among the models for the blocks by imposing the condition that the values of L_{cv}^*/b_{kv} for different blocks are nearly the same. 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 12 and the Yamakawa-Fujii formula,[9] respectively.

IV. Results and Discussion

In order to illustrate the applications of our theory, we present in this section the frictional properties predicted by our theory for some homopolymers and block copolymers in dilute solution. The eigenvalues λ_k have been calculated numerically in the manner described in paper I. The inverse of **H** has been calculated numerically by using a routine[10] which first applies triangular decomposition to **H**.

1. Homopolymer. For the special case of a homopolymer, all the beads and the springs are characterized by the same friction constant and the same root-mean-square length. In this case, our theory reduces to the Zimm theory[6] and we may drop the subscripts v altogether. Tables I and II give, for some homopolymers, the values of P^{-1}, Φ, and $\Phi^{1/3}P^{-1}$ calculated from the Zimm theory. In the preparation of Table II, we have taken from Table I of paper I the properties of polystyrene and *cis*-1,4-polyisoprene in theta solvents.

In our previous work[11] on the evaluation of hydrodynamic interaction, we have shown that the values of the Flory–Fox constant predicted by the Zimm theory agree well with those predicted by the Yamakawa–Fujii[12] theory of the limiting viscosity number of wormlike chains. We see in Table I that the values of P^{-1} calculated from the Zimm theory differ by less than 3% from those calculated from the Yamakawa–Fujii theory[9] of the translational friction constant of wormlike chains. Thus, for the limiting viscosity number and the translational friction constant at the very least, we have demonstrated the reasonableness of the way we apply the Zimm theory to wormlike chains whose value of $h/N^{1/2}$ are not necessarily near 0.25.

For the chain in Table I with $d_p = 0.03b_k$ and $L_c = 400b_k$, we have calculated P^{-1} from eq 9 by assuming two values of N. It is seen here that the value of P^{-1} predicted by the Zimm theory is not sensitive to the exact choice of N. For the chains with $d_p = 0.03b_k$, Table I shows that the value of $\Phi^{1/3}P^{-1}$ changes only slightly when the length of the chain, L_c, increases by a factor of 100, although there is a dependence of P^{-1} and Φ on the chain length. Table I also shows that the increase in d_p/b_k from 0.03 to 0.60 has only a small effect on the value of $\Phi^{1/3}P^{-1}$.

Yamakawa and Fujii[9] have obtained estimates of b_k = 1300 Å and d_p = 25 Å for deoxyribonucleic acid (DNA) in 0.2 *M* aqueous solution of NaCl by an analysis of the molecular weight dependence of its sedimentation coefficient. If we use their estimates, the value of d_p for DNA is $0.022b_k$. We see in the first four rows of Table I that a representative value of $\Phi^{1/3}P^{-1}$ calculated from the Zimm theory for long DNA-like chains with $d_p = 0.022b_k$ is 1.23 × 10^7 cm/g$^{1/3}$. This value is in good agreement with the ex-

Table III
Calculated Values of the Coefficient P^{-1}, the Flory–Fox Constant Φ, and the Mandelkern–Flory–Scheraga Constant $\Phi^{1/3}P^{-1}$ for Poly(styrene-*b*-methyl methacrylate) in Cyclohexanol at 81°C[a]

Polymers	N_a	N_b	N_c	P^{-1} from eq 9	Φ, 10^{23} ml/g	$\Phi^{1/3}P^{-1}$, 10^7 cm/g$^{1/3}$
St-MM-St	22	64	22	0.182	2.90	1.21
MM-St-MM	32	44	32	0.191	3.08	1.29
St-MM-MM	44	32	32	0.198	3.10	1.34

[a] Symbols employed are defined in the text. The values of N, ρ/η, b, and $h/N^{1/2}$ are 107, 360 Å, 67 Å, and 0.28, respectively. The values of ρ/ρ_v and b^2/b_v^2 (v = a, b, c) are 1.36 and 2.11 for the poly(methyl methacrylate) block. The values of ρ/ρ_v and b^2/b_v^2 are both unity for the polystyrene block. The value of L_{cv}^*/b_{kv} is 12.6 for both the polystyrene block and the poly(methyl methacryalte) block.

Table IV
Calculated Values of the Coefficient P^{-1}, the Flory–Fox Constant Φ, and the Mandelkern–Flory–Scheraga Constant $\Phi^{1/3}P^{-1}$ for Poly(styrene-*b*-*cis*-1,4-isoprene) in Methyl Isobutyl Ketone at 35°C[a]

Polymers	N_a	N_b	N_c	P^{-1} from eq 9	Φ, 10^{23} ml/g	$\Phi^{1/3}P^{-1}$, 10^7 cm/g$^{1/3}$
St-Ip-St	18	73	17	0.174	3.01	1.16
Ip-St-Ip	36	35	37	0.180	3.25	1.23
St-Ip-Ip	35	36	37	0.196	3.36	1.36
St-Ip-Ip	18	18	19	0.197		
St-Ip-Ip	54	27	27	0.191	3.24	1.31
St-Ip-Ip	22	43	43	0.198	3.33	1.37
St-Ip-Ip	11	48	49	0.196	3.16	1.33

[a] Symbols employed are defined in the text. The values of N, ρ/η, b, and $h/N^{1/2}$ are 107, 410 Å, 75 Å, and 0.28, respectively. The values of ρ/ρ_v and b^2/b_v^2 (v = a, b, c) are 1.97 and 4.22 for the *cis*-1,4-polyisoprene block. The values of ρ/ρ_v and b^2/b_v^2 are both unity for the polystyrene block. The value of $L_{cv}^*/_{kv}$ is 15.9 for the polystyrene block and the *cis*-1,4-polyisoprene block.

perimental value of 1.1 × 10^7 cm/g$^{1/3}$ found by Eigner and Doty[13] for DNA in the limit of high molecular weight.

Table II shows that the calculated value of P^{-1} for flexible polymers is practically constant over a wide range of molecular weight. The average value of 0.187 agrees well with the experimental average of value of 0.200 obtained by Mandelkern et al.[14] for polyisobutylene fractions in cyclohexane. Previously, Zimm[6] has given 0.192 as the value of P^{-1} for the non-free-draining limit of his theory. The calculated value of $\Phi^{1/3}P^{-1}$ is 1.26 × 10^7 cm/g$^{1/3}$, in good agreement with the average experimental value of 1.16 × 10^7 cm/g$^{1/3}$ reported by Flory.[15]

2. Block Copolymer. 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. Tables III and IV give the values of P^{-1}, Φ, and $\Phi^{1/3}P^{-1}$ calculated for poly(styrene-*b*-methyl methacrylate) in cyclohexanol at 81.0°C and for poly(styrene-*b*-*cis*-1,4-isoprene) in methyl isobutyl ketone at 35°C. Cyclohexanol at 81.0°C is nearly a theta solvent for polystyrene and poly(methyl methacrylate),[16] and so is methyl isobutyl ketone at 35°C for polystyrene and *cis*-1,4-polyisoprene.[17] We have therefore used, in the evaluation of the bead-spring model parameters for block copolymers, the homopolymer properties at theta temperatures that are given in Table I of paper I.

The block copolymers of Table III differ from one another only in structure; they have the same composition and the same number of skeletal carbon atoms. A small dependence of P^{-1}, Φ, and $\Phi^{1/3}P^{-1}$ on the structure is evident from Table III. Similarly, the first three block copolymers of Table IV differ from one another only in structure. We see again, for these block copolymers, a small dependence of P^{-1}, Φ, and $\Phi^{1/3}P^{-1}$ on the arrangement of the blocks. The third and the fourth polymers of Table IV are diblock copolymers of the same composition but different molecular weight. Their values of P^{-1} serve to illustrate that the value of P^{-1} for a block copolymer of a given structure and composition is independent of the chain length. The third polymer and the last three polymers of Table IV are diblock copolymers of different composition and different number of skeletal carbon atoms. It is seen that the values of $\Phi^{1/3}P^{-1}$ for these diblock copolymers differ from one another by less than 5%. Thus, the value of $\Phi^{1/3}P^{-1}$ for diblock copolymers is not very sensitive to the composition.

3. Application to Molecular Weight Determination. The Mandelkern–Flory–Scheraga equation, eq 11 above, has often been used to obtain approximate values of molecular weight from measurements of s_0 and $[\eta]$. For example, Gratzer and Doty[18] have used eq 11 with a value of 1.16 × 10^7 cm/g$^{1/3}$ for $\Phi^{1/3}P^{-1}$ to estimate the molecular weight of a block copolymer consisting of a central helical block of poly(L-alanine) and two flanking blocks of poly(D,L-glutamic) acid. Eigner and Doty[13] have also suggested the determination of DNA molecular weight from eq 11 with an empirical value of $\Phi^{1/3}P^{-1}$ close to 1.16× 10^7 cm/g$^{1/3}$ at both high and low molecular weights but somewhat larger at intermediate molecular weights. For diblock copolymers St-Ip-Ip, the calculated values of $\Phi^{1/3}P^{-1}$ have been shown in the last column of Table IV to be rather insensitive to composition. Therefore, we can use the experimental values of $\Phi^{1/3}P^{-1}$ at several compositions to determine by interpolation the value of $\Phi^{1/3}P^{-1}$ for a given composition. The molecular weight of St-Ip-Ip with that composition can then be determined from measurements of s_0 and $[\eta]$, together with the interpolated value of $\Phi^{1/3}P^{-1}$. The molecular weights of symmetric triblock copolymers Ip-St-Ip or St-Ip-St may also be determined in the manner described for diblock copolymers St-Ip-Ip. The procedure described above should also be applicable to other flexible block copolymers.

Alternatively, we can use the Mandelkern–Flory equation, eq 10, to obtain values of molecular weight from measurements of D_t and $[\eta]$. Since the development of techniques for measurement of line widths of scattered light[19] has made translational diffusion a relatively rapid experiment, eq 10 may become preferable to eq 11 for the determination of molecular weight.

V. Concluding Remarks

We have obtained an equation for the translational diffusion coefficient of block copolymers in dilute solution by generalizing the equation obtained by Zimm[6] for homopolymers. For homopolymers, we have shown that the values of P^{-1} and $\Phi^{1/3}P^{-1}$ calculated from the bead-spring model theory of Zimm[6] agree well with the calculations of Yamakawa and Fujii[9] as well as with experiments, if the hydrodynamic interaction parameter h is evaluated in the manner described by Wang and Zimm.[5,11,20] Since, for a given type of block copolymer, say, the block copolymer of styrene and *cis*-1,4-isoprene, the dependence of the predicted Mandelkern–Flory–Scheraga constant $\Phi^{1/3}P^{-1}$ on structure and composition is not very pronounced, we have proposed a procedure to determine the molecular weight of a block copolymer from measurements of its limiting viscosity number and its sedimentation coefficient (or translational diffusion coefficient) together with the interpolated value of $\Phi^{1/3}P^{-1}$.

References and Notes

(1) W. F. Hall and R. E. DeWames, *Macromolecules*, **8**, 349 (1975).
(2) D. R. Hansen and M. Shen, *Macromolecules*, **8**, 343 (1975).
(3) W. H. Stockmayer and J. W. Kennedy, *Macromolecules*, **8**, 351 (1975).
(4) F. W. Wang and E. A. DiMarzio, *Macromolecules*, **8**, 356 (1975)..
(5) F. W. Wang, *Macromolecules*, **8**, 364 (1975).
(6) B. H. Zimm, *J. Chem. Phys.*, **24**, 269 (1956).
(7) L. Mandelkern and P. J. Flory, *J. Chem. Phys.*, **20**, 212 (1952).
(8) H. A. Scheraga and L. Mandelkern, *J. Am. Chem. Soc.*, **75**, 179 (1953).
(9) H. Yamakawa and M. Fujii, *Macromolecules*, **6**, 407 (1973).
(10) "BUMP2: Basic Unified Matrix Package Reference Manual for the 1108", Madison Academic Computer Center, University of Wisconsin, 1969, p 8–3.
(11) F. W. Wang, *J. Polym. Sci., Polym. Phys. Ed.*, **13**, 1215 (1975).
(12) H. Yamakawa and M. Fujii, *Macromolecules*, **7**, 128, (1974).
(13) J. Eigner and P. Doty, *J. Mol. Biol.*, **12**, 549 (1965).
(14) L. Mandelkern, W. R. Krigbaum, H. A. Scheraga, and P. J. Flory, *J. Chem. Phys.*, **20**, 1392 (1952).
(15) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953, p 628.
(16) T. Kotaka, T. Tanaka, H. Ohnuma, Y. Murakami, and H. Inagaki, *Polym. J.*, **1**, 245 (1970).
(17) J. Prud'homme and S. Bywater, *Macromolecules*, **4**, 543 (1971).
(18) W. B. Gratzer and P. Doty, *J. Am. Chem. Soc.*, **85**, 1193 (1963).
(19) B. Chu, *Annu. Rev. Phys. Chem.*, **21**, 145 (1970).
(20) F. W. Wang and B. H. Zimm, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 1619 (1974).

Pressure Dependence of Upper and Lower Critical Solution Temperatures in Polystyrene Solutions

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ABSTRACT: The pressure dependence of the upper critical solution temperature (ucst) and the lower critical solution temperature (lcst) in solutions of polystyrene in *tert*-butyl acetate and diethyl ether has been determined over the pressure range 0 to ~50 atm. The values of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst and lcst over the molecular weight range of $M_w \times 10^{-4} = 67$ to ~345 in the polystyrene–*tert*-butyl acetate system depend on the molecular weight of the polymer and are negative (-0.110 to -0.175 deg atm^{-1}) for the ucst and positive (0.65–0.68 deg atm^{-1}) for the lcst, while the values of $(\mathrm{d}T/\mathrm{d}P)_c$ for the solution of polystyrene of $M_w \times 10^{-4} = 2.04$ in diethyl ether are negative (-0.24 deg atm^{-1}) for the ucst and positive (0.62 deg atm^{-1}) for the lcst. The pressure dependence of the Flory or theta temperatures in the polystyrene–*tert*-butyl acetate system evaluated in the neighborhood of 0 atm are -0.30 deg atm^{-1} for θ_u and 0.70 deg atm^{-1} for θ_l, where the θ_u and θ_l are the θ temperature for the ucst and lcst. The observed behavior of the pressure dependence of the ucst and lcst in polystyrene solutions is qualitatively predicted by the Patterson–Delmas theory of corresponding states and the newer Flory theory of polymer solution thermodynamics through the expression for the χ_1 parameter.

The importance of the phase diagram (P, T, composition) over a wide range of temperature and pressure[1–3] has been recognized for nonpolar polymer solutions[4–11] after the discovery of the lcst in nonpolar polymer solutions.[12] As is well known, the cloud point curves characterized by the ucst and lcst for the (T, composition) phase diagram under the saturated vapor pressure behave like mirror images across the temperature axis of the intermediate region between the ucst and lcst.[13–18] In the (P, composition) phase diagram at constant temperature the cloud point curves in the polymer solution are classified into two types by the shape of the cloud point curve on the pressure–composition plot. One is characterized by the existence of a maximum pressure, the other by a minimum one. For solutions of polymers with a very narrow molecular weight distribution, the maximum pressure corresponds to the upper critical solution pressure (ucsp) and the minimum pressure to a lower critical solution pressure (lcsp), as discussed by Ehrlich and Kurpen[5,8] for solutions of polyethylene in n-alkanes. A critical condition in the (P, T, composition) phase diagram is completely determined by the critical solution temperature and critical solution pressure, i.e., the (P, T) critical line of the polymer solution.[2,3,5–11] The thermodynamic conditions for the ucsp observed in either system with a positive value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the lcst and a negative value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst is a negative excess volume of mixing and corresponds to an increase of the polymer–solvent compatibility with an increase of pressure at constant temperature. The condition for the lcsp observed in either system with a negative value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the lcst or a positive value of $(\mathrm{d}T/\mathrm{d}P)_c$ for the ucst is a positive excess volume of mixing and corresponds to the decrease of the polymer–solvent compatibility with an increase of pressure.[1–3]

Investigation of the excess volume of mixing[19–27] and the pressure effect on the thermodynamic properties of polymer solutions, such as the second virial coefficient[28–30] or the χ_1 parameter, the mean square end-to-end distance of polymer in the dilute solution,[28–30] and the ucst and lcst,[4–11] are of importance in the characterization of polymer solutions. The determination of the (P, T) critical line is also of great importance in connection with the pressure and temperature coefficients of the unperturbed mean-square end-to-end distance of polymer chains in dilute solution.[31]

In this work we supply the (P, T, composition) phase diagram over the middle pressure range of 0 to ~50 atm in the vicinity of the ucst and lcst for solutions of polystyrene in *tert*-butyl acetate and diethyl ether. We also examine the experimental values of $(\mathrm{d}T/\mathrm{d}P)_c$ in the light of the recent theories of polymer solution thermodynamics of Patterson and Flory.

Experimental Section

Polystyrene samples were obtained from the Pressure Chemical Co. Samples designated by 14b-1, 14b-2, and 14b-3 were obtained