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Conformations of Diblock Copolymers in Dilute Solutions

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ABSTRACT: Intrinsic viscosity measurements were carried out by using a series of diblock copolymers of polystyrene (PS) and poly(2-vinylpyridine) (P2-VP) with narrow molecular weight distributions in a common good solvent, pyridine, in a selective solvent, benzene, and in a poor solvent for both PS and P2VP, methyl ethyl ketone (MEK). Intrinsic viscosity–molecular weight relationships ($[\eta]$–M) for the two constituent homopolymers in pyridine are fortunately the same, and also, to our interest, that of the block copolymer is coincident with those of the homopolymers, while the exponents in the $[\eta]$–M relationships as well as the magnitudes of $[\eta]$ of the block copolymer in benzene and MEK are between those of the homopolymers. These facts imply that the block copolymer does not assume a distinct intramolecularly segregated conformation in dilute solutions, regardless of the nature of the solvents used.

Introduction

Considerable efforts have been used to clarify whether or not chemically different blocks of diblock copolymers are segregated from each other in dilute solutions.[2–16] Although recent papers appear to succeed in revealing that an intramolecular segregation does not occur in dilute solutions,[10,11,14] the discussions for reaching the conclusion are not absolutely clear-cut because of large corrections for broad molecular weight distributions of constituting blocks in the block copolymer samples used.[10] It is also somewhat unsatisfactory for us that the molecular weight of the sample used for reaching the conclusion without any correction is very low if the phenomenon is an intramolecular phase separation.[14]

It is well established that the conformation of a homopolymer chain is determined by its unperturbed dimension and the excluded volume effects according to the two-parameter theory. Similar theoretical and Monte Carlo calculations[8,17–20] were applied to diblock copolymers, where the excluded volume effects are determined by the three excluded volume parameters between A–A, between B–B, and between A–B segments, β_{AA}, β_{BB}, and β_{AB}, respectively. The former two parameters β_{AA} and β_{BB}, are the same as those acting in the corresponding homopolymers. If we can use a diblock copolymer molecule consisting of two block chains, having the same unperturbed dimensions and excluded volume parameters, as a sample, the discussion of intramolecular segregation is very much simplified.

The diblock copolymers of polystyrene (PS) and poly(2-vinylpyridine) (P2-VP) were found to be suitable for the present purpose. The intrinsic viscosity–molecular weight relationships ($[\eta]$–M) of PS and P2-VP homopolymers are practically identical in pyridine, which is a common good solvent for both homopolymers, as well as in θ-solvents. It is confirmed in a previous paper that anionically polymerized diblock copolymers of PS and P-2VP have very narrow molecular weight distributions with respect to the molecular weight of each block.[21] Moreover, PS and P2-VP have considerably different solubility parameters,[22] and it was observed in phase separation experiments that they are incompatible even in pyridine, which is a common good solvent, unless the concentration is very low.[23]

Experimental Section

Materials. The diblock copolymers of PS and P2-VP were prepared by an anionic polymerization method with a sequential monomer addition technique described in a previous work.[21] After complete consumption of styrene monomer, a portion of the polymerization solution was sealed off as a precursor for composition check.

Solvents used for measurements were benzene, *p*-dioxane, methyl ethyl ketone (MEK), pyridine, and tetrahydrofuran (THF). Benzene, which was of the spectroscopic grade by Merck, was used without further purification. The other solvents, which were of the special grade by Kishida Chemical Co., were dried according to standard procedures.

Characterization. The number-average molecular weights, M_n, were determined by osmometry in THF at 25 °C by using a Hewlett–Packard Type 502 high-speed membrane osmometer. The weight-average molecular weights, M_w, were determined by a light-scattering method in benzene, *p*-dioxane, and MEK at 25 °C by using a Fica 50 light-scattering photometer. The refractive index increments for PS and P2-VP are 0.109_0 and 0.106_5 in benzene, 0.185_2 and 0.176_0 in *p*-dioxane, and 0.229_0 and 0.214_5 in MEK, respectively. The polydispersity index M_w/M_n was calculated from the GPC chromatograms in THF, assuming that the calibration curve determined with pressure chemical standard polystyrenes is applicable to the block copolymers. Since THF is a common good solvent for both PS and P2-VP, we may safely assume that the values of M_w/M_n thus determined are close to the true values.

Intrinsic Viscosity Measurements. Viscosity measurements were carried out by using dilution viscometers of a modified Ubbelohde type in three solvents, pyridine, benzene, and MEK. Pyridine is a common good solvent for both PS and P2-VP, benzene is a selective solvent (i.e., a good solvent for PS but a poor (θ) solvent for P2-VP), and MEK is a poor solvent for both polymers. The θ-temperature for P2-VP in benzene was previously found to be ca. 11 °C.[24] Measurements were carried out at 25.0 °C in pyridine and MEK and at 10.0 °C in benzene. Intrinsic viscosities of PS and P2-VP homopolymers were also measured

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Table I
Molecular Characteristics of Block Copolymer Samples

sample code	$10^{-5}M^a$	M_w/M_n (GPC)^b	C_s, wt %^{c}
SP-33	0.63 (0.37)	1.03 (1.10)	52
SP-4	2.45 (1.24)	1.11 (1.14)	51
SP-12	4.22* (2.11)	1.03 (1.04)	50
SP-18	15.3* (6.92*)	1.17 (1.07)	49

[a] The value in parentheses is the molecular weight of the polystyrene precursors. The values without an asterisk are the number-average molecular weights, while those with an asterisk are the weight-average molecular weights. [b] The values in parentheses are for polystyrene precursors. [c] Styrene content determined by elemental analysis.

Table II
Apparent Molecular Weights and Correction Terms in Eq 1

sample code	solvent	$10^{-5}M_{app}$	$10^{-3}P^a$	$10^{-3}C_P{}^b$	$10^{-3}Q^a$	$C_Q{}^c$
SP-12	benzene	4.14	−3.07	−0.143	3.07	1.6
	MEK	4.30		−0.402		13.1
SP-18	benzene	16.3	−83.8	−3.89	53.9	29
	dioxane	14.2		−11.0		230

[a] Calculated by eq 5 and 6 with the data in Table I. [b] $C_P = 2P(\nu_A - \nu_B)/\nu$. [c] $C_Q = Q(\nu_A - \nu_B)^2/\nu^2$.

in the three solvents for reference.

Results

Molecular characteristics of block copolymer samples are listed in Table I together with those of precursors. From the values of M_w/M_n in Table I, it is clear that the molecular weight distributions of the whole block copolymers as well as those of their precursors, and, hence, of their blocks, are narrow enough.[21]

The apparent molecular weight M_{app} of a AB two-component copolymer determined by light scattering in a solvent is given by[25]

$$M_{app} = M_w + 2P[(\nu_A - \nu_B)/\nu] + Q[(\nu_A - \nu_B)/\nu]^2 \quad (1)$$

with

$$P = w_A(1 - w_A)[(M_{wA} - M_{nA}) - (M_{wB} - M_{nB})] \quad (2)$$

$$Q = w_A(1 - w_A)[(1 - w_A)(M_{wA} - M_{nA}) + w_A(M_{wB} - M_{nB})] \quad (3)$$

where ν_A and ν_B are the refractive index increments of A and B homopolymers, respectively, and $\nu = \nu_A w_A + \nu_B(1 - w_A)$, w_A being the mass fraction of component A in the copolymer. If we assume that the molecular weight distributions of constituent homopolymer blocks are independent each other,[26] the polydispersity index of a AB block copolymer, M_w/M_n, can be related with those of two components, M_{wA}/M_{nA} and M_{wB}/M_{nB}, by

$$M_w/M_n - 1 = (M_{wA}/M_{nA} - 1)w_A{}^2 + (M_{wB}/M_{nB} - 1)(1 - w_A)^2 \quad (4)$$

From eq 2, 3, and 4 we have

$$P = w_A M_w[M_{wA}/M_w + (1 - w_A)(M_n/M_w) - 1] \quad (5)$$

$$Q = w_A{}^2 M_w[(1/w_A - 2)(M_{wA}/M_w) - 2(1 - w_A)(M_n/M_w) + 1] \quad (6)$$

We insert the values of M_w/M_n, etc., into eq 5 and 6 to estimate the magnitudes of P and Q, which are listed in Table II. The magnitudes of P and Q thus determined and also the difference between ν_A and ν_B are both so small that the second and the third terms in eq 1 can safely be neglected compared with the first term. Thus, the apparent weight-average molecular weights, M_{app}, determined in the two solvents may be close enough to the true weight-average molecular weights M_w. Therefore, we regarded the averaged value of two numbers obtained from the measurements in different solvents as M_w for SP-12 and SP-18 as shown in Table I. We may calculate M_w from two simultaneous equations obtained by introducing the data in benzene and *p*-dioxane into eq 1, deleting the third term, since the third term is particularly small compared with the second one. However, the error in M_w thus determined is too high because the experimental errors in M_{app} exceed the difference in the second terms.

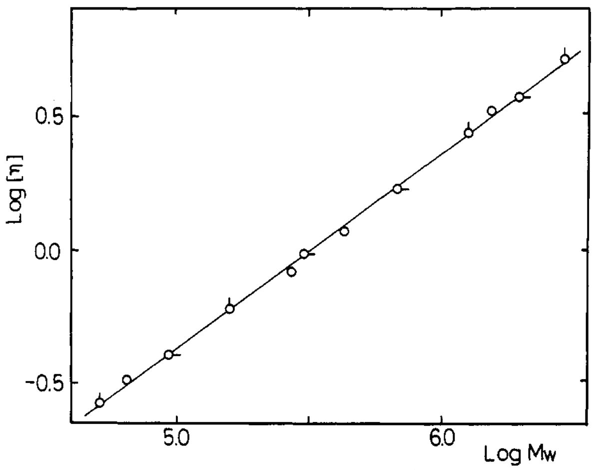

Figure 1. Double-logarithmic plots of intrinsic viscosity against weight-averaged molecular weight for block copolymer (O), polystyrene (ό), and poly(2-vinylpyridine) (o-) in pyridine at 25 °C. The solid lines denote eq 7.

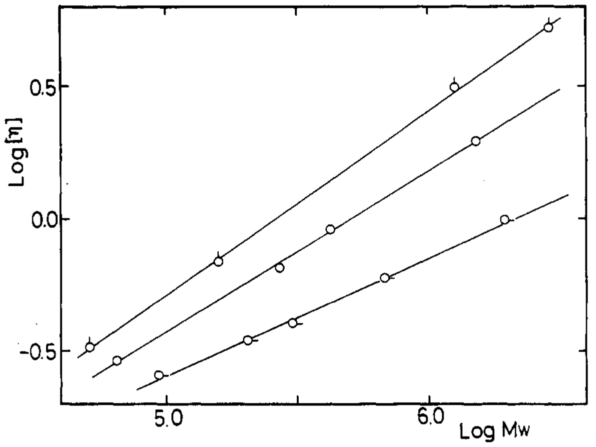

Figure 2. Double-logarithmic plots of intrinsic viscosity against weight-averaged molecular weight for block copolymer (O), polystyrene (ό), and poly(2-vinylpyridine) (o-) in benzene at 10 °C. The solid lines denote eq 8.

The intrinsic viscosities of the diblock copolymers as well as PS and P2-VP homopolymers in a common good solvent (pyridine), in a selective solvent (benzene), and in a poor solvent (MEK) are listed in Table III. Figures 1, 2, and 3 show the double logarithmic plots of intrinsic viscosities against weight-average molecular weights for these samples in the three solvents.

From the data in pyridine at 25.0 °C in Figure 1, we have

$$[\eta] = 9.0_2 \times 10^{-5} M_w{}^{0.73_4} \qquad \text{for diblock copolymer} \quad (7a)$$

$$[\eta] = 9.7_0 \times 10^{-5} M_w{}^{0.72_9} \qquad \text{for PS} \quad (7b)$$

$$[\eta] = 9.8_4 \times 10^{-5} M_w{}^{0.72_7} \qquad \text{for P2-VP} \quad (7c)$$

Figure 1 or eq 7 clearly shows that the $[\eta]$-M relationships of the three samples, i.e., the diblock copolymer and the PS and P2-VP homopolymers, are practically the same

Table III
Intrinsic Viscosities of Samples

sample code	$10^{-4}M_w$	$[\eta]$, dL/g pyridine 25 °C	 benzene 10 °C	 MEK 25 °C
		Block Copolymer		
SP-33	6.5	0.325	0.291	0.225
SP-4	27.2	0.832	0.654	0.464
SP-12	42.2	1.184	0.911	0.613
SP-18	153	3.31	1.96	1.44
		Polystyrenes		
F-5	5.1	0.265	0.326	0.199
TPS-15	11.9			0.328
F-16	16.0	0.603	0.691	
TPS-31	30.9			0.550
F-80	70.6			1.02
F-128	126	2.74	3.10	1.42
F-288	289	5.02	5.15	2.45
		Poly(2-vinylpyridine)		
VPL-1	9.4	0.405	0.256	0.225
VPK-2	20.4		0.347	0.329
VPL-6	30.5	0.970	0.401	0.407
VPL-5	67	1.68	0.595	0.588
VPK-3	196	3.71	0.983	0.967

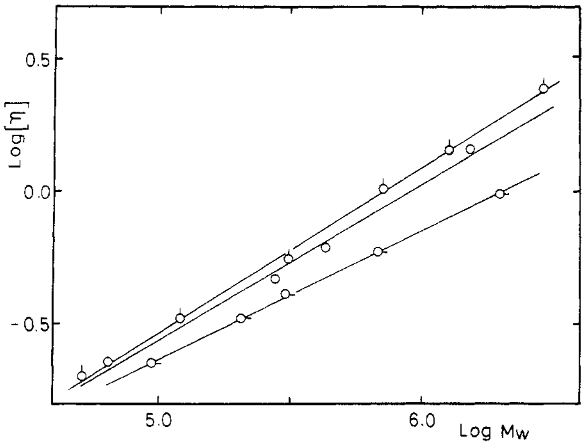

Figure 3. Double-logarithmic plots of intrinsic viscosity against weight-averaged molecular weight for block copolymer (○), polystyrene (o̍), and poly(2-vinylpyridine) (o-) in MEK at 25 °C. The solid lines denote eq 9.

in a common good solvent, pyridine. This fact implies that the conformation of the block copolymer is identical with those of the constituent homopolymers.

From the data in benzene at 10.0 °C in Figure 2, we have

$$[\eta] = 3.5_2 \times 10^{-4}M_w^{0.60_5} \quad \text{for diblock copolymer} \tag{8a}$$

$$[\eta] = 1.7_1 \times 10^{-4}M_w^{0.69_5} \quad \text{for PS} \tag{8b}$$

$$[\eta] = 1.5_1 \times 10^{-3}M_w^{0.44_5} \quad \text{for P2-VP} \tag{8c}$$

It is certain that benzene is a good solvent for PS but a poor solvent for P2-VP at 10 °C. The $[\eta]$–M relationship of diblock copolymers is between those of two homopolymers.

From the data in MEK at 25 °C in Figure 3, we have

$$[\eta] = 3.1_9 \times 10^{-4}M^{0.58_7} \quad \text{for diblock copolymer} \tag{9a}$$

$$[\eta] = 2.2_1 \times 10^{-4}M^{0.62_5} \quad \text{for PS} \tag{9b}$$

$$[\eta] = 9.3_3 \times 10^{-4}M^{0.48_0} \quad \text{for P2-VP} \tag{9c}$$

Apparently, MEK is a poor solvent for both homopolymers, and the $[\eta]$–M relationship of diblock copolymer is also between those of both homopolymers.

The $[\eta]$–M relationships of PS and P2-VP homopolymers in θ-solvents were already reported.[24,27] They are

$$[\eta] = 8.8 \times 10^{-4}M_w^{0.50} \quad \text{for PS (in cyclohexane, 34.5 °C)} \tag{10}$$

$$[\eta] = 8.1 \times 10^{-4}M_w^{0.50} \quad \text{for P2-VP (in benzene, 11.4 °C)} \tag{11}$$

The proportionality constant for PS reported in literature may be in the range (8.5–8.8) × 10^{-4}.[28] The above equations indicate that the unperturbed dimensions of PS and P2-VP are almost the same.

Discussion

The mean-square radius of gyration of A–B diblock copolymer, $\langle s_{AB}^2\rangle$, is given by

$$\langle s_{AB}^2\rangle = Y_A\langle s_A^2\rangle + Y_B\langle s_B^2\rangle + Y_AY_B\langle L^2\rangle \tag{12}$$

where Y_k is the composition of the k-block by number of segment and $\langle s_k^2\rangle$ and $\langle L^2\rangle$ are the mean-square radius of gyration of the k-block and the mean-square distance between the centers of mass of the two blocks, respectively.

For discussion of the conformation of diblock copolymers in comparison with those of the constituent blocks it is useful to define the parameter δ as

$$\delta = \langle L^2\rangle/[2(\langle s_A^2\rangle + \langle s_B^2\rangle)] \tag{13}$$

since $\delta = 1$ for a Gaussian chain. If we apply the variable-contrast method in small-angle neutron scattering to dilute solutions of diblock copolymers,[14] we can evaluate δ by using eq 12 and 13 without serious corrections, but generally it is difficult to measure the radii of gyration of block chains. Since our primary interest is whether or not the conformation of diblock copolymer is different from that of homopolymer, it is reasonable to define another parameter σ in terms of the radius of gyration of homopolymer, $\langle s_{Hk}^2\rangle$, of which the molecular weight is identical with that of the k-block chain in diblock copolymer, according to Tanaka et al.[8]

$$\sigma = \langle L^2\rangle/[2(\langle s_{HA}^2\rangle + \langle s_{HB}^2\rangle)] \tag{14}$$

Combining eq 12 with eq 14 we have

$$\sigma = (\langle s_{AB}^2\rangle - Y_A\langle s_{HA}^2\rangle - Y_B\langle s_{HB}^2\rangle)/[2Y_AY_B(\langle s_{HA}^2\rangle + \langle s_{HB}^2\rangle)] \tag{15}$$

If we assume that the viscosity equation of Flory and Fox is applicable to the diblock copolymer as well as homopolymers, their intrinsic viscosities are

$$[\eta]_k = \Phi_k\langle s_{Hk}^2\rangle^{3/2}/M_k \tag{16}$$

for the k-homopolymer and

$$[\eta]_{AB} = \Phi_{AB}\langle s_{AB}^2\rangle^{3/2}/M_{AB} \tag{17}$$

for the block copolymer, where the subscripts k and AB denote the values for k-homopolymer and diblock copolymer, respectively, and Φ is the Flory viscosity coefficient.

Since the molecular weights of monomers and the unperturbed dimensions of PS and P2-VP are almost the same, M_k is approximately equal to Y_kM_{AB}. Introducing eq 16 and 17 into eq 15 and assuming that $\Phi_{AB} = \Phi_k$, in addition with the above approximation, we have

$$\sigma = ([\eta]_{AB}^{2/3} - Y_A^{5/3}[\eta]_{HA}^{2/3} - Y_B^{5/3}[\eta]_{HB}^{2/3})/[2Y_AY_B[(Y_A[\eta]_{HA})^{2/3} + (Y_B[\eta]_{HB})^{2/3}]] \tag{18}$$

By introducing the viscosity data listed in Table III, or calculated from the $[\eta]$–M relationships (eq 8–10) into eq 18, we evaluated σ values; they are listed in Table IV.

In pyridine or a common good solvent, σ values are constant irrespective of molecular weights, and they are equal to the value 1.26, calculated by assuming that the

Table IV
Calculated σ Values of Block Copolymers

		σ^a		
sample code	$10^{-4}M_w$	pyridine	benzene	MEK
SP-33	6.5	1.26 (1.25)	1.01 (1.03)	1.14 (1.16)
SP-4	27.2	1.26 (1.09)	1.01 (0.96)	1.19 (1.04)
SP-12	42.2	1.26 (1.14)	1.02 (1.04)	1.21 (1.09)
SP-18	153	1.26 (1.24)	1.03 (1.02)	1.28 (1.26)

[a] The σ values were evaluated by using the $[\eta]$–M relationships of eq 7, 8, and 9, while those in parentheses were evaluated from the viscosity data in Table III.

corresponding homopolymer is a hypothetical diblock copolymer consisting of two block chains connected in the middle, since the $[\eta]$–M relationships of block copolymer and homopolymers are the same. If we assume that the block copolymer is uniformly expanded in a common good solvent, on the other hand, we have $\delta = 1$ from eq 13. Therefore, this result suggests that the real value of δ is less than 1.26.

If the lattice model is applied to evaluate the local excess free energy of mixing in diblock copolymer, the excluded volume parameters are written in terms of the thermodynamic interaction parameters χ such as $\beta_A \propto {}^1/_2 - \chi_A$, $\beta_B \propto {}^1/_2 - \chi_B$, and $\beta_{AB} \propto {}^1/_2 - (\chi_A + \chi_B - \chi_{AB})/2$ according to Flory.[29] Since χ_{AB} may be much smaller than χ_A or χ_B,[30] β_{AB} can be well approximated by ${}^1/_2 - (\chi_A + \chi_B)/2$; that is, $(\beta_A + \beta_B)/2$. Since $\beta_A = \beta_B$ in the present case, we have $\beta_{AB} = \beta_A = \beta_B$. Therefore, the present conclusion that the conformation of block copolymer is identical with those of the constituent homopolymers in a common good solvent is understandable in terms of thermodynamic interactions.

In benzene or a selective solvent, σ values are almost equal to unity irrespective of molecular weight. However, this result does not mean that the diblock copolymer is a Gaussian chain. This can be understood if we consider that the dimension of the PS block is much larger than that of the P2-VP block in benzene and the distance between the center of mass of two blocks is predominantly determined by the dimension of the PS block.

In MEK or a poor solvent for both PS and P2-VP, σ values appear to increase slightly with increasing molecular weight, but they level off at a certain high molecular weight, and its value does not become much larger than σ (1.26) in a common good solvent, since the exponent of $[\eta]$–M relationships as well as the magnitude of $[\eta]$ of diblock copolymer is smaller than those of PS, as shown in eq 9. Therefore, the conformation of diblock copolymer in MEK is not much different from those of constituent homopolymers.

In summary we may conclude that the diblock copolymer does not assume a distinct intramolecularly segregated conformation in dilute solutions regardless of the nature of the solvents used, as reported before.[11,14]

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