Chain conformation of block copolymers in dilute solutions measured by small-angle neutron scattering

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Chain dimensions of the polystyrene-d_8 parts of a styrene-d_8-2-vinylpyridine block copolymer (DP-33) and a styrene-d_8-styrene-h_8 block copolymer (DH-44), both with 50:50 compositions, were measured in dilute solutions of pyridine (a common good solvent) benzene (a selective solvent) and methyl ethyl ketone (a poor solvent) by small-angle neutron scattering. The conformation of one block chain within a diblock copolymer is not affected by the existence of another block chain, regardless of the solvent power at least when the composition of the diblock copolymer is 50:50, and the molecular weight is not high.

(Keywords: block copolymer; chain conformation; dilute solution; radius of gyration; small-angle neutron scattering)

INTRODUCTION

It is well known that block copolymers with mutually incompatible block chains have microphase-separated structures in concentrated solutions and in bulk. In this connection, it is interesting to examine whether or not the block copolymer chains segregate intramolecularly in the isolated state. Chain conformations of block copolymers in dilute solutions have been studied by intrinsic viscosity[1–8], light scattering[9–13], small-angle neutron scattering (SANS) measurements[14,15] and Monte Carlo calculations[12,13,16]. By using viscosity, light scattering and Monte Carlo data, Tanaka *et al.* concluded that the conformation of a block copolymer in dilute solution does not differ much from that of a homopolymer[17]. In a previous paper we also drew the same conclusion by using viscosity data of well-defined styrene(S)-2-vinylpyridine (2VP) diblock copolymers[7].

SANS is the most powerful and straightforward method to study the conformation of a block chain in a block copolymer in solution directly. Ionescu *et al.* measured the apparent radii of gyration (R_g values) of S–isoprene diblock copolymers in a common good solvent, toluene, and also in a selective solvent, cyclohexane, and they concluded that the block copolymers do not segregate intramolecularly[15]. They did not study the conformation in a poor solvent for both block polymers, but the thermodynamic interaction between different block polymers might affect the conformations in a poor solvent. In a good solvent the expansion factor of part of a homopolymer chain is smaller than that of the whole chain, but larger than that of a single chain with the same molecular weight as the part of the chain[18]. Since one block chain within a block copolymer is part of the polymer chain, the chain dimension of one block within a block copolymer should be studied in various solvents for comparison with an equivalent part within a homopolymer chain.

A 50:50 S–2VP diblock copolymer can be regarded as a symmetrical block copolymer since the segment lengths of polystyrene (PS) and poly(2-vinylpyridine) (P2VP) are quite similar[19], whereas the two polymers are incompatible[20,21].

EXPERIMENTAL

Materials. Two block copolymers, as shown in *Table 1*, were used. DP-33 is a block copolymer of styrene-d_8 and 2VP, while DH-44 is a block copolymer of styrene-d_8 and styrene-h_8, which is essentially a homopolymer. The former has been used in previous studies[7,20,21] and the latter was synthesized by anionic copolymerization of the two monomers and characterized in the same manner as reported previously[20]. The molecular characteristics of the samples are listed in *Table 1*.

Three solvents were used to study the effects of solvent power*: pyridine, which is a good solvent for both

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* Certain commercial materials and instruments are identified in this paper in order to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology

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polymers, benzene, which is a good solvent for PS and a θ solvent for P2VP at 11.4°C[19], and methyl ethyl ketone (MEK), which is a poor solvent for both components at room temperature[7]. Mixtures of ordinary and deuterated species for all three of the solvents were used to obtain contrast matching with one of the blocks as will be described later. Pyridine-d_5 was 99 atom%D and pyridine-h_5 was spectrophotometric grade (Aldrich Chemical Company). Benzene-d_6 was 99.5 atom%D and benzene-h_6 was spectrophotometric grade. These four solvents were distilled over calcium hydride prior to use. MEK-h_8 was special grade from Fisher Scientific Company, while the partially deuterated MEK was synthesized by employing deuterium–hydrogen exchange[22] as follows. D_2O and MEK were mixed in a ratio of 8 : 1 v/v, followed by the addition of a small amount of K_2CO_3 as catalyst, and the mixture was stirred for 5 days at room temperature. The azeotropic mixture (~90% MEK and 10% water) was then distilled off from the reaction mixture at 70–74°C and dried with calcium chloride. The final product was obtained by distilling the dried product over $CaSO_4$ at 77.5–78.5°C. The chemical composition of the compound was determined by pyrolysis–gas chromatography mass spectrometry as $C_4D_{4.2}H_{3.8}O$.

SANS experiments. The neutron intensity per unit volume scattered from the monodisperse block copolymer composed of species A and B at infinite dilution, $I(q)$, is given by[23]:

$$I(q) \propto MK[Y^2P_A(q) + (1-Y)^2P_B(q) + 2Y(1-Y)P_{AB}(q)] \qquad (1)$$

where $M = M_A + M_B$, M_A and M_B are the molecular weights of the A and B parts, respectively, and $P_A(q)$, $P_B(q)$ and $P_{AB}(q)$ are the scattering functions for the A and B parts and between the A and B parts in terms of the magnitude of the scattering vector q. Moreover, the average scattering factor K and the relative contrast factor Y for species A are defined as

$$K = (K_AM_A + K_BM_B)/M \qquad (2)$$

and

$$Y = K_AM_A/(K_AM_A + K_BM_B) \qquad (3)$$

with

$$K_i = (b_i/m_i) - v_ib_s/v_s \qquad (i = \mathrm{A\ or\ B}) \qquad (4)$$

where b_i and b_s are the coherent scattering lengths for the unit of species i having molecular weight m_i and for the solvent, respectively, v_i is the specific volume of species i and v_s is the molar volume of solvent. Equation (1) indicates that we can observe the R_g of either of these polymer species only when $Y = 1$ or 0. In this work, therefore, SANS experiments in all three solvents were carried out at $Y = 1$ for both samples with the deuterated PS blocks assigned as part A in equation (1). The condition $Y = 1$ is satisfied when the relative contrast factor of part B i.e. K_B, is zero, or from equation (4) we have

$$b'_S \equiv \frac{b_S}{v_S} = \frac{b_B}{m_B\bar{v}_B} \equiv b'_B \qquad (5)$$

where we define the reduced scattering lengths of solvent and part B as b'_S ($\equiv b_S/v_S$) and b'_B ($\equiv b_B/m_B\bar{v}_B$), respectively. Therefore, the mixing ratios of deuterated and ordinary solvents used for measurements (*Table 2*) were determined by equation (5).

The SANS measurements were carried out with the SANS instrument equipped with a 1 mm thick quartz cell at the National Institute of Standards and Technology. The wavelength λ was 6.0 Å with a distribution $\Delta\lambda/\lambda$ of ~0.25. The measuring temperatures were room temperature (~23°C) in pyridine and MEK, but 12°C in benzene because the θ temperature of P2VP in benzene is 11.4°C. The concentrations of sample solutions ranged from 0.5 to 2.5 wt%. The apparent coherent scattering intensity of the labelled parts was obtained by subtracting the scattering intensities of the empty cell and the solvent from that of the sample solution[18].

Table 1 Molecular characteristics of the samples

	M_n ($\times 10^{-3}$)		
Sample code	Labelled part	Total	M_w/M_n
DP-33	34	66	1.04
DH-44	44	84	1.01

RESULTS AND DISCUSSION

A typical angular dependence of the apparent coherent scattering intensity of DP-33 at $Y = 1$ is shown in *Figure 1*. The apparent R_g of the deuterated PS part at a certain

Table 2 Scattering length densities of polymers and solvents

Polymer	b'_P ($\times 10^{-10}$) (cm^{-2})	Solvent		b'_S ($\times 10^{-10}$) (cm^{-2})	ϕ^a
P2VP	1.95	Pyridine	C_5D_5N	5.71	0.041
$-(C_7H_7N)_n-$			C_5H_5N	1.79	0.959
		Benzene	C_6D_6	5.44	0.181
			C_6H_6	1.18	0.819
		MEK	$C_4D_{4.2}H_{3.8}O$	3.10	0.608
			C_4H_8O	0.167	0.392
PS	1.41	Benzene	C_6D_6	5.44	0.057
$-(C_8H_8)_n-$			C_6H_6	1.18	0.943
		MEK	$C_4D_{4.2}H_{3.8}O$	3.10	0.424
			C_4H_8O	0.167	0.576

[a] Volume fraction of solvents to give contrast-matched mixtures for block chains

finite concentration was evaluated by fitting the scattering intensity to the modified Debye function

$$I(q) = A + (B/2)(e^{-X} - 1 + X) \qquad (6)$$

with $X = q^2R_g^2$ and $q = (4\pi/\lambda)\sin\theta$, where λ is the wavelength (6 Å) and 2θ is the scattering angle. A and B are the parameters for the incoherent baseline and an arbitrary intensity scaling factor, respectively. Strictly speaking, the Debye function holds only for the Gaussian chain. However, it was found that the particle scattering factors of a whole chain[24] and also of a partial chain[18] for homopolymers in good solvents can be well expressed by the Debye function if the molecular weight is not high. In this work, therefore, we assume that the particle scattering factors of block chains can be expressed by equation (6) without serious errors since the molecular weights are low. The apparent R_g values thus obtained for DP-33 and DH-44 were plotted against the total polymer concentration c in *Figures 2* and *3*, respectively. The error bars were estimated from the uncertainties in fitting to equation (6). The extrapolation to infinite dilution was made by the weighted least-squares method and the uncertainties are also shown in the figures.

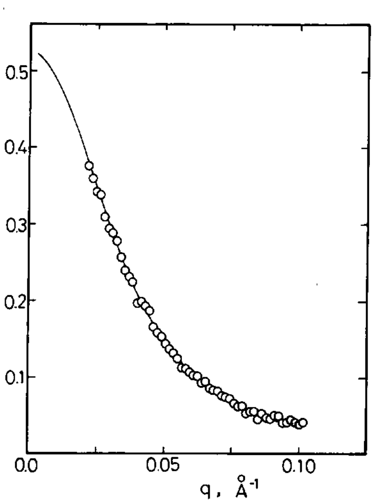

Figure 1 Scattering intensity *versus* q for DP-33 in pyridine at $Y = 1$. The total polymer concentration is 1.92 g dl^{-1}. The solid line denotes the best-fitted Debye function

The R_g of the deuterated PS parts in DP-33 and DH-44 thus obtained, their unperturbed dimensions R_{g0}, and the expansion factors α are listed in *Table 3*. The unperturbed dimensions were calculated from the R_g–molecular weight relationship for PS in cyclohexane at 35°C [equation (7)][18] taking into account the molecular weight ratio of styrene-h$_8$ to styrene-d$_8$, i.e. $m_h/m_d = 104/112 = 0.928$.

$$R_{g0}\,(\text{Å}) = 0.286M^{1/2} \qquad (7)$$

For comparison *Table 3* also lists the radius of gyration $R_{g,h}$ and the expansion factors α_h of PS homopolymer with the same degree of polymerization as the deuterated PS parts in DP-33 and DH-44, and those values of whole PS(DH-44), $R_{g,w}$ and α_w in various solvents. The R_g values in benzene and MEK were calculated from the empirical relationships between R_g and M, equations (8) and (9), respectively, considering that $m_h/m_d = 0.928$

$$R_g\,(\text{Å}) = 0.123M^{0.595} \quad \text{in benzene at 25°C}^{18} \qquad (8)$$

$$R_g\,(\text{Å}) = 0.216M^{0.53} \quad \text{in MEK at 22°C}^{25} \qquad (9)$$

The values of DP-33 in pyridine (in parentheses) in *Table 3* are obtained by assuming that pyridine is a good solvent for both PS and P2VP to the same extent as benzene is for PS.

There are differences in the chain lengths between DP-33 and DH-44 and also between their deuterated PS

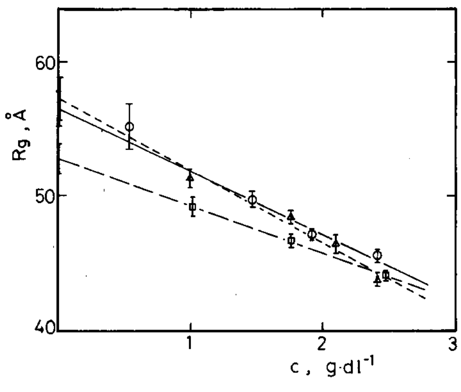

Figure 2 Extrapolation of apparent R_g values to infinite dilution for DP-33 in pyridine (○), benzene (△) and MEK (□)

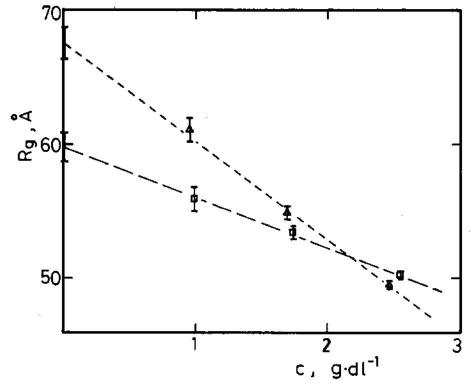

Figure 3 Extrapolation of apparent R_g values to infinite dilution for DH-44 in benzene (△) and MEK (□)

Table 3 Radii of gyration and expansion factors of the deuterated PS part of block copolymers

Sample code	M_d[a] (×10^{-3})	$R_{g,0}$ (Å)	Solvent	R_g (Å)	α_S (≡$R_g/R_{g,0}$)	$R_{g,h}$, α_h (Å)	$R_{g,w}$, α_w (Å)	α_M
DP-33	34	50.7	Pyridine	56.5 ± 1.3	1.11 ± 0.03	(58.5, 1.15)	(88.4, 1.23)	1.19
			Benzene	57.3 ± 1.6	1.13 ± 0.03	58.5, 1.15	–	–
			MEK	52.8 ± 1.1	1.04 ± 0.02	52.4, 1.03	–	–
DH-44	44	57.7	Benzene	67.6 ± 1.2	1.17 ± 0.02	68.1, 1.18	102, 1.25	1.21
			MEK	59.8 ± 1.1	1.04 ± 0.02	60.0, 1.04	–	–

[a] Number-averaged molecular weight of the deuterated PS part

parts, but these differences do not affect the following discussion if the expansion factors are compared. *Table 3* indicates that the R_g values of the deuterated PS part of DP-33 in pyridine and benzene are almost equal irrespective of the difference in solvent power for the P2VP part. They are also in good agreement with the $R_{g,h}$ values for PS with the same molecular weight. Moreover, the α values of the deuterated PS parts of DP-33 and DH-44 in pyridine and benzene, respectively, are almost equal and are in good agreement with the α_h values of PS with the same degree of polymerization as the deuterated parts.

As mentioned in a previous paper[18] the expansion factor of a part of a homopolymer in a good solvent can be evaluated by the empirical equation from a Monte Carlo calculation:

$$\alpha_M^2 = 1.09\left|\frac{i-j}{N}\right|^{1.13+\nu(i,j)} \alpha_W^2 \frac{R_{g0}^2}{R_{g0}^2(i,j)} \qquad (10)$$

with

$$\nu(i,j) = 0.36\left|\frac{i-j}{N}\right|\left|1-\frac{i+j}{N}\right| \qquad (11)$$

where N and $|i-j|$ are the number of segments of the whole polymer and of the part of the chain between the ith and jth segments, respectively, R_{g0}^2 and $R_{g0}^2(i,j)$ are the unperturbed radii of gyration of the whole polymer and of the part of the chain between the ith and jth segments, respectively. Since we can assume that $i = 0$ and $j = N/2$ for the deuterated chain in DH-44, we have

$$\alpha_M = 0.97\alpha_W \qquad (12)$$

From equation (12) we have $\alpha_M = 1.21$ for DH-44 in benzene as listed in *Table 3*. This value agrees with α for DH-44, which is almost equal to α_h within experimental error. This means that the expansion factor of one-half of a polymer chain is mainly determined by the interactions between the segments within that portion. Since the thermodynamic interaction parameter between PS and P2VP, χ_{SP}, is much smaller than the interaction parameter between PS or P2VP and pyridine[26], this is also the case for a 50:50 diblock copolymer in a common good solvent as shown in *Table 3*. Moreover, it is understandable that α of DP-33 is equal to α_h in benzene because the P2VP chain is in the unperturbed state.

In MEK, which is a poor solvent for both PS and P2VP, the α values of the deuterated PS portions in DP-33 and DH-44 are equal and are in good agreement with the α_h values for the homopolymers with the same molecular weights. This implies that the thermodynamic interaction between PS and P2VP hardly affects the conformation of individual block chains, if the molecular weight is small.

In summary, we conclude that the conformation of one block chain within a diblock copolymer is not affected by the existence of another block chain regardless of solvent power at least when the composition of the diblock copolymer is 50:50, and the molecular weight is not high. This produces further evidence to support the conclusion mentioned in the Introduction[7,15,17], though the molecular weights of the samples used here are not high enough to yield a general conclusion.

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