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Chain Conformations of Homopolymers Dissolved in a Microdomain of Diblock Copolymer

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ABSTRACT: Single-chain conformations of styrene homopolymers dissolved in a polystyrene lamellar microdomain of a styrene–2-vinylpyridine diblock copolymer in bulk were measured by small-angle neutron scattering (SANS). The molecular weights of the styrene homopolymers are 13.0K (L), 29.7K (M), and 76.7K (H), and the molecular weight of the diblock copolymer is 63.3K with 34.2K of polystyrene block. The mixing ratios of homopolymer/block copolymer blends are 0.1/0.9 for L, 0.05/0.95 for M, and 0.01/0.99 for H so as not to give rise to macrophase separation. The radii of gyration of homopolymers in the direction parallel to the lamellae are found to be almost equal to the unperturbed dimension irrespective of the molecular weight ratios of homopolymers to the polystyrene block.

Introduction

The microphase-separated structures of block copolymers have been well studied with respect to AB diblock copolymers.[2-12] Among several familiar structures, that is, spherical, cylindrical, and lamellar structures, alternating lamellar structures have been extensively studied,[2,3,5,10-12] so as to be understood at the molecular level; the block chain is elongated in the direction perpendicular to the lamellar interface,[13-15] whereas it shrinks in the parallel direction so as not to change its volume.[14,15] The block chain in the microdomain belongs to the category of "a tethered chain in a confined space", and its conformation is different from the unperturbed chain of the homopolymer in a melt,[16-18] which belongs to the category of "a free chain in a free space". Thus, it is interesting to solve another problem; what is the conformation of "a free chain in a confined space"? This problem can be solved by investigating the chain conformation of an A homopolymer dissolved in a microdomain formed by an A block chain of an AB block copolymer.[19] This study is also useful in clarifying the thermodynamics of block copolymer/homopolymer blend systems.[20-25]

To study the chain conformations of homopolymers dissolved in microdomains of block copolymers by SANS, we should pay particular attention to the contrast-matching procedure. Quan et al. pointed out that two kinds of contrast-matching procedures are necessary to extract a single chain scattering function of homopolymer from the total scattering intensity from the homopolymer/block copolymer blends.[22,26] One is "phase matching", for which they propose to prepare AB diblock copolymers having the A block chain with the same coherent scattering length as the B block chain.[26] Actually the polymer sample called "phase-matched" block copolymer can be prepared by distributing labeled A segments randomly in the A block chain to the right amount. The other is the "composition matching", which can be achieved by mixing labeled and unlabeled A homopolymers in the matching *ratio so that the* mixture has the same scattering length as the phase-matched block copolymer.[27-33]

In this study a phase-matched sample used as a matrix was a diblock copolymer of partially-labeled styrene and 2-vinylpyridine. Chain conformations of styrene homopolymers in a microdomain were determined by measuring SANS intensities for mixtures of styrene homopolymer blends and the phase-matched block copolymer.

Experimental Section

Preparation of the Phase-Matched Polymer and the Homopolymers. The coherent scattering length of poly(2-vinylpyridine) (P) is between those of poly(styrene-d_8) (D) and of poly(styrene-h_8) (S), so that the phase matching can be achieved when D and S are mixed at 0.107/0.893 by volume (0.114/0.886 by weight).[31] Therefore, the styrene-d_8 and styrene-h_8 monomers were purified separately and mixed at D/S = 0.11/0.89 by volume, and the mixture was diluted with pure tetrahydrofuran (THF).[34] The styrene monomer mixture and the 2-vinylpyridine monomer were sequentially polymerized by an anionic polymerization with cumylpotassium as an initiator in THF at −78 °C *in vacuo* and gave the phase-matched block copolymer (PM-1). A part of the polymerization solution was taken out to measure the molecular weight of the polystyrene block. The labeled (L) and unlabeled (U) styrene homopolymers were also prepared in the same manner as the block copolymer.

The number-averaged molecular weights of the homopolymers and the polystyrene precursor of the block copolymer were measured in toluene with a Hewlett Packard membrane osmometer Type 502, while that of the block copolymer was measured in THF. The molecular weight distributions of samples were measured with a Tosoh GPC system Type HLC-802A equipped with two GMH$_{XL}$ columns. The molecular characteristics of the styrene homopolymers and the block copolymer are shown in Table 1.

Preparation of Homopolymer/Block Copolymer Blend Films. The composition-matched polystyrenes were preliminarily prepared by freeze-drying the benzene solution of mixtures of the labeled (L) and unlabeled (U) polymers at the weight ratio of L/U = 0.114/0.886. These homopolymer mixtures and the phase-matched block copolymer, PM-1, were dissolved in THF at the homopolymer/block copolymer weight ratio of 0.1/0.9 for the lowest molecular weight homopolymer to give PMH-L, at the ratio of 0.05/0.95 for the middle one to give PMH-M, and at the ratio of 0.01/0.99 for the highest one to give PMH-H. The dilute THF solutions of blends were cast into thin films with 0.15-mm thickness for 4 days. A pure PM-1 film was also prepared for examining the degree of phase matching and for evaluating

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Table 1. Molecular Characteristics of Homopolymers and a Block Copolymer for Blends

blend code	homopolymer		block copolymer		
		M_n (×10^{-3})	M_n (×10^{-3})	M_w/M_n[d]	ϕ_s[e]
PMH-L	L[a]	16.6 (15.4)[c]	34.2–29.1 (S)–(P)	1.04	0.50
	U[b]	13.0			
PMH-M	L[a]	33.7 (31.3)[c]	34.2–29.1 (S)–(P)	1.04	0.50
	U[b]	29.7			
PMH-H	L[a]	78.1 (72.5)[c]	34.2–29.1 (S)–(P)	1.04	0.50
	U[b]	76.7			

[a] Deuterium-labeled polymer. [b] Unlabeled polymer. [c] Numbers in parentheses are the molecular weights reduced to unlabeled polystyrene. [d] Determined by a GPC chromatogram. [e] Volume fraction of polystyrene.

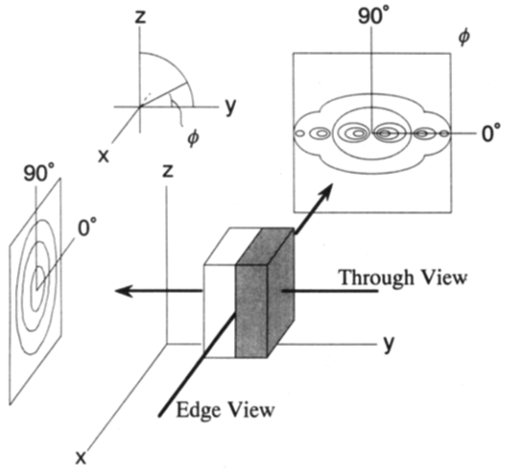

Figure 1. Geometrical relationship between a sample specimen and the two-dimensional position-sensitive detector. The azimuthal angle, ϕ, on the detector is also defined in the figure.

the incoherent scattering intensity in SANS experiments.[31] All the films were dried completely and annealed *in vacuo* at 120 °C for a week.

Morphological Observations. The microphase-separated structures of film specimens stained with OsO_4 were observed with a transmission electron microscope, JEOL 2000FX. Small-angle X-ray scattering (SAXS) was measured in the directions perpendicular (through) and parallel (edge) to the film surface with a Kratky U-slit camera of Anton Parr. (Disclaimer: Certain commercial materials and equipment are identified in this paper in order to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by NIST, nor does it imply necessarily the best available for the purpose.) Details of the experimental conditions for morphological observations were reported previously.[35]

SANS Measurements. SANS measurements were performed with the 8-m SANS spectrometer with a cold-source facility at the National Institute of Standards and Technology.[36] The sample-to-detector distance was 3.6 m, the wavelength λ used was 0.9 nm, and its resolution $\Delta\lambda/\lambda$ was 0.25. Two collimation systems were adopted; one was a regular resolution system for PMH-L and PMH-M and the other was a high resolution one for PMH-H. Details of the collimation systems were reported in previous papers.[31,37] The scattering intensities were measured in both through- and edge-view defined above for all the film specimens. The geometrical relationship among observation views, a sample specimen and the two-dimensional detector, is illustrated schematically in Figure 1. SANS data reduction was carried out in the same manner as reported previously.[15,37]

Results

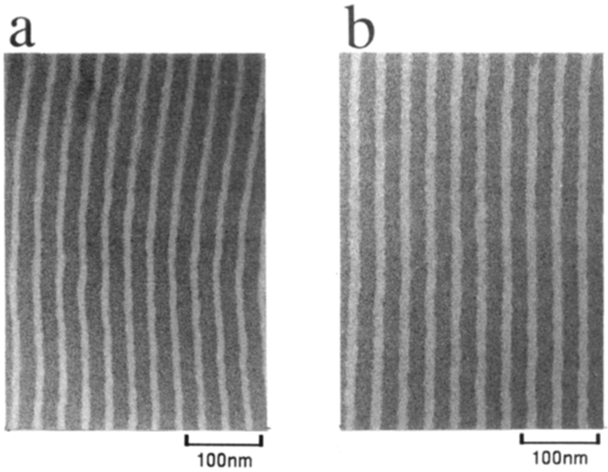

Figure 2. Comparison of transmission electron micrographs. Samples: (a) PM-1; (b) PMH-H.

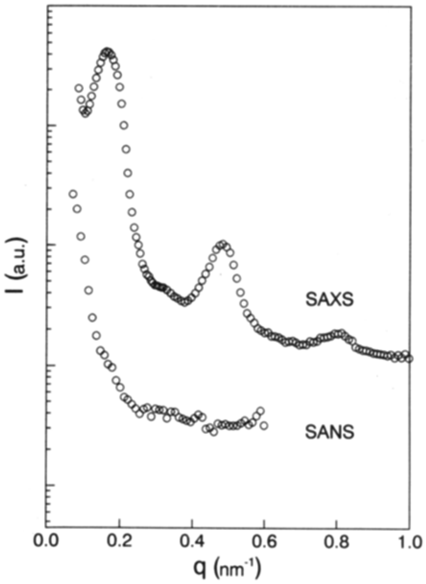

Figure 3. SAXS and SANS intensities in the edge view for PM-1.

Microphase-Separated Structures and Contrast Matching. Electron micrographs of PM-1 and PMH-H are shown in Figure 2. Both show alternating lamellar structures predominantly aligned parallel to the film surfaces, and there is no evidence of the macrophase separation even for PMH-H, whose homopolymer/block copolymer molecular weight ratio is 2.3 though. The other two blend samples, i.e., PMH-L and -M, have also lamellar structures, though they are not shown here. SAXS and SANS diffraction patterns for PM-1 in the edge view are compared in Figure 3. SANS intensities were obtained by averaging the data within the sector of $\phi = 0 \pm 5°$, where ϕ is the azimuthal angle on the detector defined in Figure 1. Distinct peaks of integer order are displayed in the SAXS pattern, reflecting the high degree of orientation of lamellae parallel to the film surface, whereas no distinct peak can be seen in the SANS pattern. Moreover, SANS intensities around $\phi = 0 \pm 5°$ in the edge view for PMH-L and -M are compared with that for PM-1 in Figure 4, where the profiles for PMH-L and -M are shifted every decade along the vertical axis. Apparently the scattering intensities for PMH-L and -M are higher than that for PM-1 especially in the low q range (0.1 nm^{-1} < q < 0.4 nm^{-1}), where $q = (4\pi/\lambda) \sin\theta$, 2θ is the scattering angle, and broad peaks can be recognized at around $q = 0.16$ and 0.32 nm^{-1} for both blends. These q values correspond to the positions of the first- and second-order diffraction peaks for the lamellar structures. These facts mean that the phase matching was achieved reasonably well, but the composition matching was not achieved as expected, which is to be described in the Discussion section.

Radii of Gyration of Homopolymers. Figure 5 shows the contour map of SANS for PMH-H in the through view.

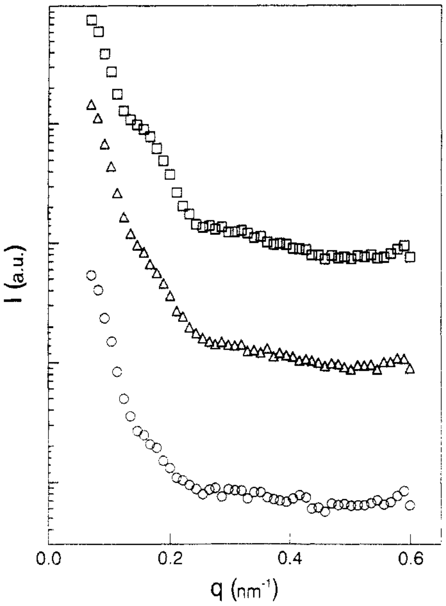

Figure 4. Comparison of SANS diffraction patterns in the edge view. Samples: PM-1 (○), PMH-L (△), PMH-M (□).

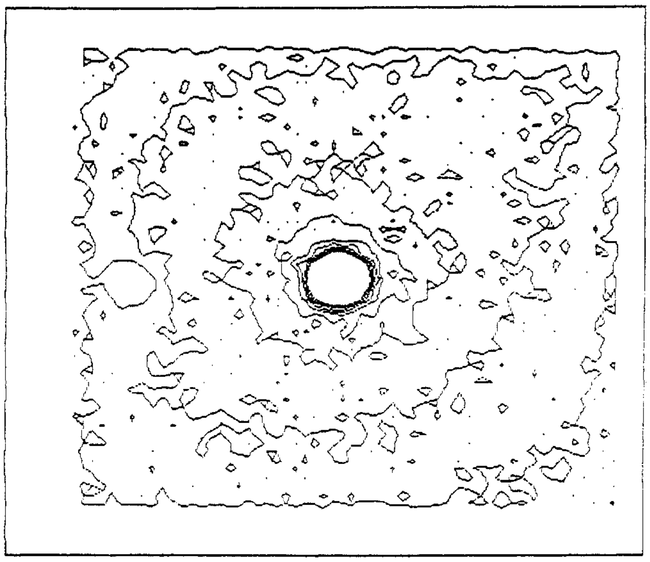

Figure 5. SANS contour map on the two-dimensional detector in the through view for sample PMH-H.

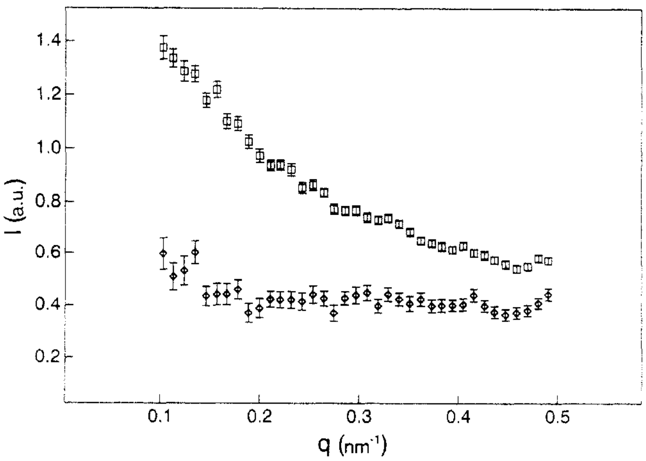

Figure 6. Circular-averaged SANS total scattering intensities in the through view. Samples: PM-1 (◇); PMH-H (□).

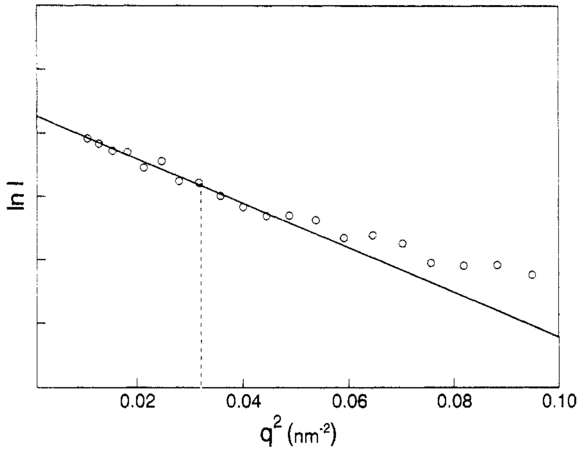

Figure 7. Guinier plots of coherent scattering intensities in the through view for PMH-H.

Table 2. Chain Dimensions of Homopolymers in a Microdomain of a Block Copolymer

blend code	M_n (×10^{-3})	ϕ_h[a]	$R_{g,x}$ (nm)	$R_{g,x0}$[b] (nm)	$R_{g,x}/R_{g,x0}$
PMH-L	13.0	0.10	1.94 ± 0.06	1.88	1.03 ± 0.03
PMH-M	29.7	0.05	2.88 ± 0.10	2.84	1.01 ± 0.04
PMH-H	76.7	0.01	4.23 ± 0.39	4.57	0.93 ± 0.08

[a] Volume fractions of styrene homopolymers in the blends. [b] Unperturbed radii of gyration of homopolymers along the x-axis evaluated by using eq 2 in the text.

Since this map looks isotropic, the intensities are circularly averaged and they are plotted against q in comparison with those of PM-1 in Figure 6. As shown as an example of the PMH series in Figure 5, no distinct peak is observed in the profiles of PMH-H, and the scattering intensity of PM-1 has actually no angular dependence. Therefore, the intensities of the PMH series can be assumed to include only the single chain scattering functions of homopolymers and the incoherent scattering intensity.[15] Figure 7 shows the Guinier plots of the scattering intensity for PMH-H obtained by subtracting the incoherent intensity from the measured total intensity.

The slope of the Guinier plots gives the radius of gyration along the k-axis, $R_{g,k}$ ($k = x$, y, and z), according to eq 1.[13-15]

$$I(q) = I(0)\exp(-q^2 R_{g,k}^{\;2}) \tag{1}$$

Though the x- and z-axes are equivalent, according to the definition in Figure 1, we write, for convenience, $R_{g,x}$ for the component of radii of gyration obtained by circularly-averaged intensities in the through view in Figure 7. The Guinier range adopted was estimated by the relation $q^2R_{g,k}^{\;2} < 1.3^2/3$, and its upper limit is shown by a broken line in Figure 7. Table 2 lists the $R_{g,x}$ values of three homopolymers in lamellar structures in comparison with those for their unperturbed dimensions, $R_{g,x0}$'s. In this table the unperturbed dimensions were evaluated by using the following radius of gyration–molecular weight relationship for polystyrene in bulk along any k-axis.[15]

$$R_{g,k0} = 0.0165M^{1/2}\ \text{(nm)} \tag{2}$$

Here, the number-averaged molecular weights, M_n's, of the unlabeled polymers were adopted instead of the z-average molecular weights, M_z's, which should be used for the R_g–M relationship, because the molecular weight distributions of all homopolymers are quite narrow ($M_w/M_n < 1.05$). Further, we checked that the correction factors on measured radii of gyration resulting from differences in molecular weight between labeled and unlabeled polymers are negligibly small according to the method of Boue et al.[39] It is apparent from this table that $R_{g,x}/R_{g,x0}$ ratios are all close to unity within experimental errors irrespective of homopolymer/block copolymer molecular weight ratios, though the statistical errors are increasing with the increment of the homopolymer molecular weight (M_h) because homopolymer/block copolymer weight ratios are decreasing with the increase of M_h. Thus, we can derive the important result that the homopolymer is unperturbed in the direction parallel to lamellae over the range investigated. The intensity in the edge view in the low q range is much higher than that in the through view, reflecting the effect of mismatching in scattering length between polystyrene lamellae and poly(2-vinylpyridine) lamellae.[15,31] Therefore, it is difficult to extract the single chain scattering function of the homopolymer from these intensity data by using the data of PM-1 because the relative thickness of two adjacent lamellae of PM-1 is different from those of PMH's in addition to the fact that there are no distinct peaks in PM-1 data. Thus, in this study we were not able to evaluate the radii of gyration of homopolymers along the y-axis.

Discussion

Contrary to the reasonably good achievement of phase matching for PM-1, composition matching for the PMH series was not successful. One of the possible reasons for the mismatching is the excess scattering due to the concentration fluctuation of styrene homopolymers in polystyrene microdomains, which should depend on the molecular weight of the homologous polymers, since the interaction parameter between labeled and unlabeled polystyrenes is not equal to zero. As shown in Figure 4, the scattering intensities at the peaks for PMH-M are higher than those of PMH-L; in other words, the degree of mismatching increases with the increase of M_h though the concentration of homopolymers in PMH-M is lower than that in PMH-L.

Another reason for the mismatching may be the chain length differences between labeled and unlabeled homopolymers. If homopolymers could be dissolved into polystyrene microdomains uniformly, the chain length difference would not give rise to the mismatching. However, the homopolymers with the higher molecular weights may be more concentrated in the center of lamellae as reported previously.[32] Thus the chain length difference can cause nonuniform distribution of the scattering length so as to give diffraction.

As described above the homopolymer chains in lamellae are unperturbed at least in the direction parallel to lamellae in contrast to block chains which are contracted in this direction. This result is different from a previous conclusion that a homopolymer chain is extended and contracted in the same manner as block chains in the perpendicular and parallel directions, respectively, so that the homopolymer dissolves uniformly in lamellae.[19] In a previous paper, we reported that deuterated polystyrenes with M_n = 27K are fairly concentrated in the middle of lamellae of the diblock copolymer with M_n = 243K according to SANS and SAXS studies.[32] In the present blend samples homopolymer/block copolymer molecular weight ratios are much higher than that in the previous sample, so that the homopolymers tend to concentrate more easily in the middle of lamellae, even if the homopolymers in the present samples are mixtures of ordinary and deuterated polystyrenes while only a deuterated polystyrene was mixed with a block copolymer in the previous work.[32] Therefore, it is reasonable that the chain is unperturbed in the parallel direction. Although $R_{g,y}$ values were not able to be evaluated as described above, it is natural to speculate that the chain is unperturbed in all directions, because the volume of the polymer coil or the degree of overlapping probably remains unchanged from that in a melt.[15]

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References and Notes

(1) Present address: Idemitsu Petrochemical Co., Ltd., Anegasaki, Chiba, 299-01 Japan.

(2) Meier, D. J. *Block and Graft Copolymers*; Burke, J. J., Weiss, V., Eds.; Syracuse University Press: Syracuse, NY, 1973.

(3) Helfand, E. *Macromolecules* **1975**, *8*, 552.

(4) Leibler, L. *Macromolecules* **1980**, *13*, 1602.

(5) Ohta, T.; Kawasaki, K. *Macromolecules* **1986**, *19*, 2621.

(6) Inoue, T.; Soen, T.; Hashimoto, T.; Kawai, H. *J. Polym. Sci., Polym. Phys. Ed.* **1969**, *7*, 1283.

(7) Gallot, B. R. M. *Adv. Polym. Sci.* **1978**, *29*, 85.

(8) Todo, A.; Hashimoto, T.; Kawai, H. *J. Appl. Crystallogr.* **1978**, *11*, 558.

(9) Richards, R. W.; Thomason, J. L. *Polymer* **1981**, *22*, 581.

(10) Hashimoto, T.; Shibayama, M.; Kawai, H. *Macromolecules* **1980**, *13*, 1237.

(11) Hadziioannou, G.; Skoulios, A. *Macromolecules* **1982**, *15*, 258.

(12) Matsushita, Y.; Mori, K.; Saguchi, R.; Nakao, Y.; Noda, I.; Nagawasa, M. *Macromolecules* **1990**, *23*, 4313.

(13) Hadziioannou, G.; Picot, C.; Skoulios, A.; Ionescu, M.-L.; Mathis, A.; Duplessix, R.; Gallot, Y.; Lingelser, J.-P. *Macromolecules* **1982**, *15*, 263.

(14) Hasegawa, H.; Hashimoto, T.; Kawai, H.; Lodge, T. P.; Amis, E. J.; Glinka, C. J.; Han, C. C. *Macromolecules* **1985**, *18*, 67.

(15) Matsushita, Y.; Mori, K.; Mogi, Y.; Saguchi, R.; Noda, I.; Nagasawa, M.; Chang, T.; Glinka, C. J.; Han, C. C. *Macromolecules* **1990**, *23*, 4317.

(16) Ballard, D. G.; Wingnall, G. D.; Schelton, J. *Eur. Polym. J.* **1973**, *9*, 965.

(17) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974**, *7*, 863.

(18) Higgins, J.; Stein, R. S. *J. Appl. Crystallogr.* **1978**, *11*, 346.

(19) Hasegawa, H.; Tanaka, H.; Hashimoto, T. *J. Appl. Crystallogr.* **1991**, *24*, 672.

(20) Bates, F. S.; Berney, C. V.; Cohen, R. E. *Macromolecules* **1983**, *16*, 1101.

(21) Berney, C. V.; Cheng, P.-L.; Cohen, R. E. *Macromolecules* **1988**, *21*, 2235.

(22) Quan, X.; Gancarz, I.; Koberstein, J. T.; Wignall, G. D. *J. Polym. Sci., Part B: Polym. Phys.* **1987**, *25*, 641.

(23) Tanaka, H.; Hashimoto, T. *Polym. Commun.* **1988**, *29*, 212.

(24) Tanaka, H.; Hasegawa, H.; Hashimoto, T. *Macromolecules* **1991**, *24*, 240.

(25) Hashimoto, T.; Tanaka, H.; Hasegawa, H. *Macromolecules* **1990**, *23*, 4378.

(26) Quan, X.; Koberstein, J. *J. Polym. Sci. Part-B, Polym. Phys.* **1987**, *25*, 1381.

(27) Jahshan, S. N.; Summerfield, G. C. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1859.

(28) Koberstein, J. T. *J. Polym. Sci., Polym. Phys. Ed.* **1980**, *18*, 1859.

(29) Bates, F. S.; Berney, C. V.; Cohen, R. E.; Wignall, G. D. *Polymer* **1983**, *24*, 519.

(30) Hasegawa, H.; Tanaka, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1987**, *20*, 2120.

(31) Matsushita, Y.; Nakao, Y.; Saguchi, R.; Mori, K.; Choshi, H.; Muroga, Y.; Noda, I.; Nagasawa, M.; Chang, T.; Glinka, C. J.; Han, C. C. *Macromolecules* **1988**, *21*, 1802.

(32) Matsushita, Y.; Torikai, N.; Mogi, Y.; Noda, I.; Han, C. C. *Macromolecules* **1993**, *26*, 6346.

(33) Miller, J. A.; McKenna, J. M.; Pruckmayer, G.; Epperson, J. E.; Cooper, S. L. *Macromolecules* **1985**, *18*, 1727.

(34) Matsushita, Y.; Nakao, Y.; Saguchi, R.; Choshi, H.; Nagasawa, M. *Polym. J.* **1986**, *18*, 493.

(35) Mogi, Y.; Kotsuji, H.; Kaneko, Y.; Mori, K.; Matsushita, Y.; Noda, I. *Macromolecules* **1992**, *25*, 5408.

(36) Glinka, C. J.; Rowe, J. M.; LaRock, J. G. *J. Appl. Crystallogr.* **1986**, *19*, 427.

(37) Matsushita, Y.; Noda, I.; Nagasawa, M.; Lodge, T. P.; Amis, E. J.; Han, C. C. *Macromolecules* **1984**, *17*, 1785.

(38) Hasegawa, H.; Tanaka, H.; Hashimoto, T.; Han, C. C. *Macromolecules* **1987**, *20*, 2120.

(39) Boue, F.; Nierlich, M.; Leibler, L. *Polymer* **1982**, *23*, 29.