Macromolecules 1982, *15*, 263–267

Low-Angle Neutron Scattering Study of the Lateral Extension of Chains in Lamellar Styrene/Isoprene Block Copolymers

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Received December 19, 1980

ABSTRACT: The chain conformation of lamellar styrene/isoprene block copolymers oriented in large single crystals has been studied by low-angle neutron scattering. The mean size of the labeled polystyrene blocks has been measured about the normal to the interfaces. It has thus been shown that the lateral interpenetration of the sequences is smaller than expected.

Introduction

The technique of low-angle X-ray diffraction has been widely used in structural studies of block copolymers in the solid state.[1-5] It provides useful information concerning the morphology of the segregated microdomains (lamellae, cylinders, and spheres) and their spatial relationships. It also provides a means of calculating the dimensions of the structural elements: the thickness of lamellae, the diameter of the cylinders or spheres, and the molecular area. In order to better specify the structure, it is necessary to describe in greater detail the conformation of the macromolecular chains within the segregated microdomains. Recent spectroscopic and optical experiments, in particular infrared dichroism,[6-7] nuclear magnetic resonance,[8] and optical birefringence,[9] demonstrated that the angular distribution of the chain segments is very nearly isotropic. Nevertheless, these techniques give no information concerning the long-distance conformation of the chains and the symmetry of the density distribution of the segments.

One can indeed imagine a variety of different conformational situations intermediate to the extremes depicted schematically in Figure 1. For the sake of simplicity, we confine the discussion to the case of the lamellar structure and focus our attention on one of the two sublayers that comprise the elementary lamellae. Starting from the interface and maintaining a random conformation, the blocks can place themselves in either single or double layers. In the first case, their extension perpendicular to the interface is limited to half of the sublayer thickness (Figure 1b), whereas in the second case the extension traverses the entire distance (Figure 1a). Similarly, blocks can spread laterally, far from their anchoring points, and display a pronounced degree of interpenetration and entanglement with neighboring chains (Figure 1c). However, they can also, while conserving disordered statistics on a local scale, juxtapose without interpenetrating to any appreciable extent (Figure 1d).

The extension of sequences in a direction normal to the interfaces is discussed elsewhere.[10] A systematic experimental study by X-ray diffraction of the thickness of the lamellar layers as a function of the molecular weight and a comparison of two- and three-block copolymers suggest that the sequences do not interpenetrate significantly. Terminal sequences of two-block copolymers tend to form double layers.

In order to obtain information concerning the extension of sequences in transverse directions, we decided to employ the technique of coherent elastic low-angle neutron scattering. By measuring the radius of gyration of the sequences around the normal to the interface, it appeared possible to evaluate directly the lateral dimension of the chains and to characterize the degree of transverse interpenetration by comparing this lateral dimension with the average chain separation (which is given by the molecular area, i.e., the surface available at the interface for each covalent bond linking the blocks together).

Principle of the Method

The capabilities of small-angle coherent neutron scattering have been demonstrated in the study of molecular conformation in polymers in the solid state.[11] The advantage of this technique over traditional techniques such as X-ray scattering or light scattering is twofold. The wavelengths available to cold neutrons fall in the range 4–16 Å. They permit the attainment of a very wide range of scattering vector (10^{-1} Å^{-1} > $|\vec{q}|$ ($=2\pi|\vec{s}| = 4\pi(\sin\theta)/\lambda > 2 \times 10^{-3}$ Å^{-1}) and in particular over a range that enables one to characterize macromolecular chains from a scale of several statistical segments to the overall size of the macromolecule. The second advantage is a consequence of the large difference in the amplitude of coherent scattering for hydrogen ($b_H = -0.374 \times 10^{-12}$ cm) and for deuterium ($b_D = +0.667 \times 10^{-12}$ cm).[12] This difference allows the selective labeling of chains and the study of their conformation in a solid-state sample.

Analogously to X-ray experiments, coherent neutron scattering can be used to study the crystalline structure of the material as well as the spatial correlations, allowing the characterization of the conformation of isolated chains.

In the present work, we have chosen to use neutrons to evaluate the conformation of sequences "trapped" in a well-organized lamellar structure. The labeling by deuteration of a number of these sequences allowed us to study their conformation. In addition, by orienting the samples into large "single-crystalline" domains[13] it was possible to study the conformation of the chains in specific directions, notably about the interface normal. It is obvious that one must therefore have available samples not only exhibiting excellent "single-crystalline" orientation but also exhibiting the lamellar structure, for which the interfaces are planar.

We chose to utilize the neutron scattering technique in two different, but complementary, ways. First, when the lamellae of the "single-crystalline" lamellar copolymer are oriented parallel to the neutron beam, one obtains equatorial diffraction spots. The angular position of these spots in reciprocal space allows the calculation of the Bragg spacing, that is, the stacking period of the lamellae. Their azimuthal spread about the beam allows the evaluation of the quality of the "single crystal", that is, the angular

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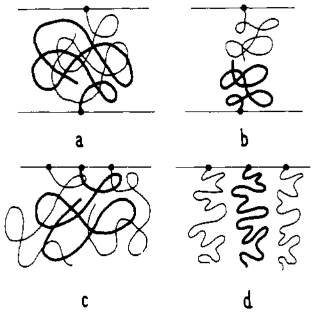

Figure 1. Extreme conformational models for polystyrene blocks.

Table I
Molecular and Structural Characteristics of Polymers

	M_n[a]	M_w/M_n	x_{PS}[b]	d,[c] Å	d_{PS},[d] Å	S,[e] Å^2
S_DI-7	114 800	1.20	0.60	650	359	570
S_DI-12	205 000	1.30	0.54	988	496	705
SI-6	98 000	1.30	0.52	595	288	561
SI-11	185 000	1.35	0.49	943	422	672

[a] ±8%. [b] ±0.01. [c] ±1%. [d] ±2%. [e] ±10%.

distribution of the lamellae in space.

Second, when the lamellae of the "single crystal" are oriented perpendicular to the beam and when samples containing chains labeled with deuterium are used, one obtains a low-angle diffuse scattering pattern. The analysis of the radial distribution of the intensity then allows the calculation of the radius of gyration of the marked chains about the direction defined by the beam. In this type of experiment, the center part of the reciprocal space in principle contains only scattered signals, but taking into consideration the inevitable imperfection of the "single crystals", it may also contain a contribution due to diffraction from the lamellar structure.

Experimental Section

Samples. The samples we chose to study were two-block copolymers of polystyrene/1,4-*cis*-polyisoprene, which have been utilized extensively in this laboratory.[10] Synthesis was effected anionically under vacuum in benzene solution, with *sec*-butyllithium as initiator. Physicochemical and crystallographic characteristics are listed in Table I. The chemical composition of the products, that is, their weight fraction in polystyrene, x_{PS}, is approximately 0.50 by weight, so that a lamellar structure is obtained.[1,2]

Copolymers S_DI-7 and S_DI-12, in which the polystyrene sequences are completely deuterated, were combined with hydrogenated copolymers SI-6 and SI-11 of about the same molecular weights to form solid solutions. Concentrations chosen were c = 1, 4, and 8% by weight of labeled polymer. The mixtures were prepared by dissolving in benzene at low concentration (<2%) and freeze-drying.

Orientation of the samples to "single-crystalline" domains was obtained by the shearing technique described earlier.[13] The processing of the material consists of molding under vacuum and shearing above the glass transition temperature. This leads to compact, homogeneous, and well-degassed test samples.

The two-block copolymers we examined exhibit a lamellar structure whose characteristics (Table I) were determined by low-angle X-ray diffraction.[10] The parameter d corresponds to the overall thickness of the elementary lamellae, whereas the parameters d_{PS} (and $d_{PI} = d - d_{PS}$) characterize the thickness of the sublayers of polystyrene (and polyisoprene). The average surface area at the interface occupied by a junction point between sequences is represented by S. The parameters were calculated by using the values of partial specific volume of polystyrene ($\bar{v}_{PSH}$ = 0.953 cm^3 g^{-1}), deuterated polystyrene ($\bar{v}_{PSD}$ = 0.885 cm^3 g^{-1}), and polyisoprene ($\bar{v}_{PI}$ = 1.106 cm^3 g^{-1}).

Neutron Diffraction Experiments. These were carried out at the Insitut von Laue-Langevin in Grenoble (France) with the D17 spectrometer using pinhole collimation, a wavelength of 15.5 ± 0.5 Å, and a two-dimensional multicounter (64 × 64 cells) placed 2.82 m from the sample.

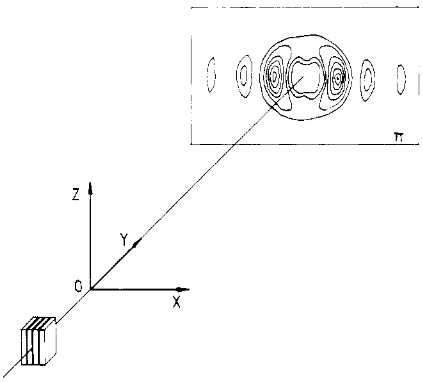

Figure 2. Diffraction geometry.

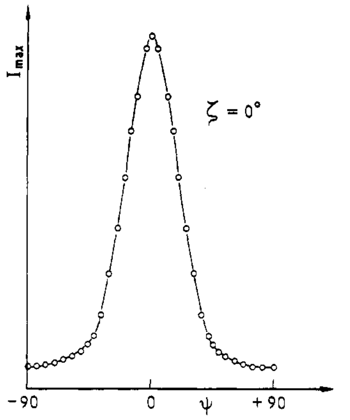

Figure 3. Azimuthal dependence of maximum intensity diffracted (see Figure 2).

Two geometries of experiment were used. The first is depicted in Figure 2. The lamellae within the sample are parallel to the YOZ plane referred to laboratory coordinates. The neutron beam is directed along the OY axis, perpendicular to the plane of the detector, Π.

The diffraction patterns recorded (see Figure 2) consist of a series of equidistant equatorial spots characteristic of a lamellar structure. Their angular position corresponds perfectly to that obtained from the parallel X-ray diffraction experiments. Their shape and intensity require two comments. First of all, the spots are not pointlike, revealing imperfect orientation of the lamellae relative to the YOZ plane. As they appear as arcs, the azimuthal variation of intensity (Figure 3) allows the characterization of the degree of orientation. The diffraction intensity for a given angle ψ is proportional to the number (more precisely, to the orientation probability) of lamellae that diffract in this direction. The distribution $I(\psi)$ thus allows the deduction of the angular distribution of lamellae within the sample. The degree of orientation is characterized by

$$\langle \cos^2 \psi \rangle = \int_0^{\pi/2} (\cos^2 \psi) I(\psi) \sin \psi \, d\psi \Big/ \int_0^{\pi/2} I(\psi) \sin \psi \, d\psi$$

For our samples, the calculated values of $\langle \cos^2 \psi \rangle$ fall in the range 0.85 ± 0.05. Figure 4 illustrates an electron micrograph of sample SI-6 where one can easily see the defects and dislocations that are responsible for the slight disorientation observed.

Second, examination of the intensity of the neutron diffraction spots reveals a difference relative to the X-ray patterns. We note the presence of second-order reflections. Considering the relative thicknesses of polystyrene and polyisoprene layers, these should in fact have zero intensity.[3] As has been shown by neutron diffraction experiments performed on samples of various thicknesses, this anomaly is a result of multiple scattering, related to the very large difference in diffusion length of the two types of sublayers.

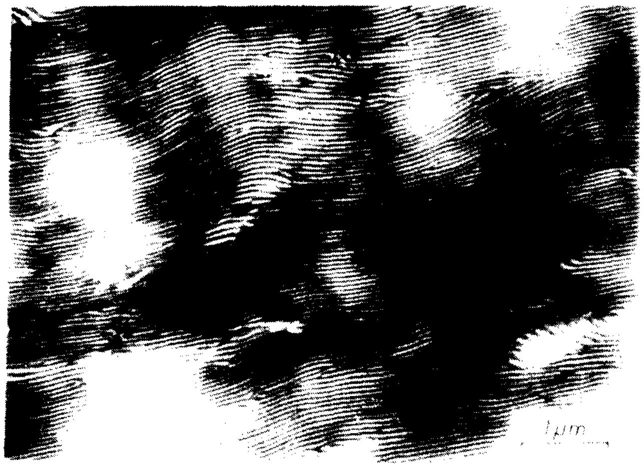

Figure 4. Electron micrograph of lamellar SI-6.

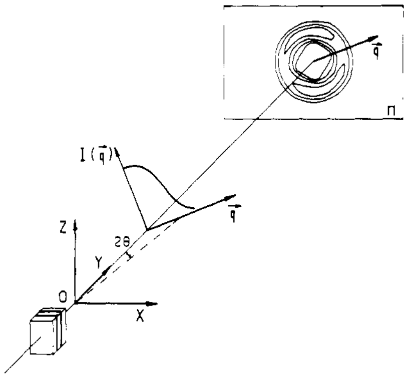

Figure 5. Low-angle scattering geometry.

The second geometry used in our neutron scattering experiments is depicted in Figure 5. The lamellae within the sample are now parallel to the XOZ plane referred to laboratory coordinates. The neutron beam is directed normal both to the interface and to the plane of the detector, Π. The scattered intensity is measured along the direction $\vec{q}$ and gives information about the spatial correlations of scattering elements projected onto the XOZ plane.

In order to carry out the experiments under the best possible conditions, we took care first, to use a direct neutron beam presenting the lowest possible divergence, second, to choose samples thin enough to avoid undue multiple scattering, and third, to measure the scattered intensity in the appropriate $\vec{q}$ Guinier range ($qR < 1$).[14] A further precaution was taken to avoid the diffraction-contaminating effects due to the internal lamellar structure of the specimen. Indeed, in spite of all the efforts to utilize well-oriented "single-crystalline" samples and to align them carefully with respect to the incident neutron beam, it was impossible to avoid contamination completely. Fortunately, contamination was not symmetric around the direct beam. It thus was possible to measure the scattered intensity $I(\vec{q})$ along those privileged $\vec{q}$ directions for which the contamination effect could be neglected.

Every scattering experiment was carried out by making three successive scattering measurements: first, the background, with the fully hydrogenated copolymer used as solvent; second, the solid solution itself; and last, pure water (whose scattering is totally incoherent), to calibrate the detector efficiency. The coherent signal of interest in this work was obtained by subtracting the signals of the two copolymer samples, normalized with reference to the water signal. Transmission coefficients were also taken into account. Figure 6 illustrates an example of a scattering curve resulting from such a treatment.

Interpretation and Discussion of Results

Before proceeding to the interpretation of the experimental results, it may be helpful to recall a few fundamentals of X-ray or neutron scattering at small angles.[14]

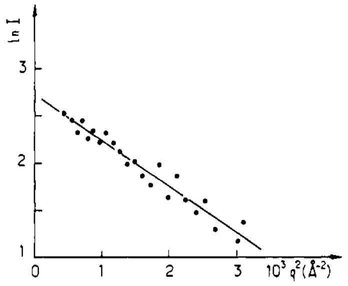

Figure 6. Guinier plot of scattered intensity as a function of scattering vector.

Table II
Mean-Square Distance $\langle R_D^2 \rangle$ (Å^2) of Deuterated Styrene Blocks

sample	c, wt %	obsd	Gaussian model	compact, cylindrical model
S_DI-7	1 4 8	936 936 } 950 972	1875	250
S_DI-12	1 4	1141 1121 } 1130	2945	450

Let us consider the case of an isolated particle centered at O (Figure 5) in an incident beam following OY. The intensity of scattered radiation at the point defined by the vector $\vec{q}$ (supposed for simplicity to lie along axis OX) can be expressed in the form

$$I(\vec{q}) = I_0 \exp(-|\vec{q}|^2 R_D^2)$$

In this expression, $\vec{q}$ is the scattering vector ($|\vec{q}| = 2\pi|\vec{s}| = 4\pi(\sin\theta)/\lambda$) and R_D^2 is the mean-square distance of scattering elements within the particle relative to the plane YOZ. If $\rho(X,Y,Z)$ is the density distribution of these elements, R_D^2 is given by the relation

$$R_D^2 = \int\int\int X^2 \rho(X,Y,Z)\, dX\, dY\, dZ \Big/ \int\int\int \rho(X,Y,Z)\, dX\, dY\, dZ$$

In the case of a system formed of several independent particles, the scattered intensity depends on the average value of R_D^2, $\langle R_D^2 \rangle$.

In this theoretical framework, one generally interprets the experimental observations using the Guinier representation, which consists of plotting ln I as a function of q^2 (Figure 6). The slope of the resulting line gives $\langle R_D^2 \rangle$ directly. This was the procedure utilized in our work. The values of $\langle R_D^2 \rangle$ measured are shown in Table II. Each polymer is characterized by a well-defined average value $\langle R_D^2 \rangle$ that within the experimental precision is independent, as it should be, of the concentration: $\langle R_D^2 \rangle$ = 950 Å^2 for copolymer S_DI-7 and $\langle R_D^2 \rangle$ = 1130 Å^2 for copolymer S_DI-12.

Let us try now to analyze these values in terms of the conformation of the chains, starting with the first extreme model which we mentioned in the Introduction, that is, the Gaussian model in which the chains are completely free to interpenetrate (Figure 1c). In this case, the radius of gyration of the polystyrene sequences measured about the interface normal should be equal to that exhibited by ideal chains of the same chemical nature and molecular weight. From a conformational standpoint, the segregation of the blocks, that is, the presence of interfaces acting as "absorbing walls", involves an elongation of the coils

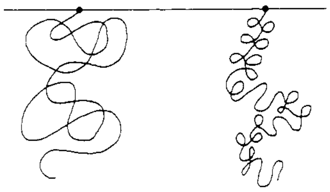

Figure 7. Models for lateral spreading of blocks.

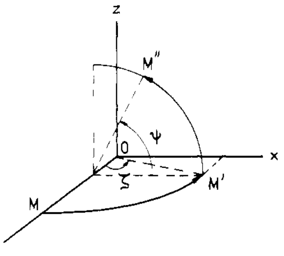

Figure 8. Orientation of scattering object.

perpendicular to the layers. On the other hand, it leaves their lateral dimension unaffected. A simple calculation of moment of inertia shows that $\langle R_D^2 \rangle$ equals $R_0^2/3$, where R_0 is the radius of gyration of an isotropic particle relative to its center of gravity. Recent experiments using low-angle scattering of neutrons[11] have shown that chains of polystyrene homopolymer in the melt have the conformation of the ideal chain, the law relating the radius of gyration to the molecular weight being

$$R_0 = 0.283 M_n^{1/2}$$

Starting from this expression, one calculates for homopolystyrenes having the same molecular weight as the corresponding sequences in copolymers S_DI-7 and S_DI-12 values of R_0 = 75 and 94 Å, respectively, that is, values of $\langle R_D^2 \rangle$ = 1875 and 2945 Å^2 (Table II). These are much higher than the observed values.

Let us consider now the second extreme model envisaged (Figure 1d), that is, the model in which lateral interpenetration is forbidden. In this hypothesis, the chains adopt a compact conformation and an elongated form, assumed to be cyclindrical for simplicity. Knowing that the chains, anchored at the interfaces, are juxtaposed in the lamellae, we further assume that the cross section of the cylinders is equal to the molecular area S and that the length L is equal to half[10] the thickness d_{PS} of the corresponding (deuterated) polystyrene sublayer. From the known values of S and L (Table I), we thus calculate (see Appendix) that $\langle R_D^2 \rangle$ for copolymers S_DI-7 and S_DI-12 should be 45 and 56 Å^2, respectively. In fact, these values, which are much too low, are purely fictitious since they correspond to perfectly oriented lamellar systems. If one takes into account the slight angular dispersion of the "single-crystalline" samples used, characterized by $\langle \cos^2 \zeta \rangle = 0.85 \pm 0.05$ (see above), one finds (see Appendix) for $\langle R_D^2 \rangle$ of copolymers S_DI-7 and S_DI-12 corrected values of 250 and 450 Å^2, respectively (Table II).

Comparing the values of $\langle R_D^2 \rangle$ found experimentally for S_DI-7 and S_DI-12 (950 and 1130 Å^2; see Table II) with those calculated assuming ideal chains (1875 and 2945 Å^2) or assuming chains confined to straight, compact, juxtaposed cylinders (250 and 450 Å^2), we observe that the real situation must fall between these two extreme models. Whatever the actual conformation, it is perfectly clear that the lateral extension of the chains about the normal to the interfaces is smaller than that predicted by Gaussian statistics. This is all the more significant since we know[15] that the presence of the interfaces cannot produce perturbations which would modify the lateral segment density distribution in any way. The smaller lateral extension observed might correspond either to random coils stretched along the normal to the interfaces or to sequences confined to thin, compact, wormlike tubes (Figure 7). Needless to say, at this stage of the work it is not possible to decide which of the two models better fits the data.

Acknowledgment. We thank Dr. B. Lotz for help with the electron microscopy observations and Dr. G. Kiss for help with the translation to English. G.H. is grateful to the French Government for financial support with a foreign postgraduate student fellowship.

Appendix

We know that the radius of gyration $R_\parallel$ of cylindrical homogeneous objects of radius R, cross section S, and length L about their axis of revolution is given by

$$R_\parallel^2 = R^2/2 = S/2\pi$$

that the radius of gyration $R_\perp$ about a perpendicular axis passing through the center of gravity is given by

$$R_\perp^2 = (3R^2 + L^2)/12 = (3S + \pi L^2)/12\pi$$

and that the mean quadratic distance R_D^2 relation to a plane passing through the axis of revolution is given by

$$R_D^2 = R_\parallel^2/2$$

Let us consider now the case where the axis of the object is oriented along a direction OM″ (Figure 8) which is defined by a rotation ζ about the axis OZ, followed by a rotation ψ about the axis OY. A simple change of coordinates leads to the value

$$\begin{aligned} 2R_D^2(\zeta,\psi) = {} & \\ & R_\parallel^2(\cos^2\zeta + \sin^2\zeta \sin^2\psi - \sin^2\zeta \cos^2\psi) + R_\perp^2(\sin^2\zeta \\ & + \cos^2\zeta \sin^2\psi + \cos^2\psi - \cos^2\zeta \cos^2\psi - \sin^2\psi) \end{aligned}$$

In the hypothesis of a set of objects whose axes are distributed with cylindrical symmetry about the axis OY and with a probability $I(\zeta)$ of finding the axis of the object rotated through an angle ζ around OZ, the average value of R_D^2 takes the form

$$\langle R_D^2 \rangle = \frac{R_\parallel^2}{2} + \frac{R_\parallel^2 - R_\perp^2}{2} \langle \cos^2 \zeta \rangle$$

where

$$\langle \cos^2 \zeta \rangle = \int_{-\pi/2}^{+\pi/2} I(\zeta) \cos^2\zeta \sin\zeta \, d\zeta \Big/ \int_{-\pi/2}^{+\pi/2} I(\zeta) \sin\zeta \, d\zeta$$

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Structural Study of Mixtures of Styrene/Isoprene Two- and Three-Block Copolymers

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Received December 19, 1980

ABSTRACT: This is a study of the influence of the chemical architecture and polydispersity on the mesomorphic structure and on the structural parameters of styrene/isoprene block copolymers. A set of binary mixtures of two- and three-block copolymers with cylindrical, lamellar, and disordered structures has been examined with low-angle X-ray and neutron scattering. It was shown that the mixture proceeds on a molecular scale, that the quality of the organization and the sharpness of the interfaces are not affected by the mixing, that the transition between the lamellar and the cylindrical structure depends primarily on chemical composition, and, finally, that the transition between the lamellar and the disordered structure at 25 °C depends primarily on molecular weight.

Introduction

All studies to date of the mesomorphic structure and morphology of block copolymers[1] have used copolymers synthesized by anionic polymerization,[2] that is, very high quality polymers characterized by a sharp distribution in both molecular weight and composition. Consequently, one could ask the question whether the mesomorphic organization and the crystal "lattices" observed require such homogeneity. Certain studies[3] on the solubilization of homopolymers in mesomorphic block copolymers have led us to believe that heterogeneities, on the contrary, are quite well tolerated, at least up to a certain limit.

In order to provide answers to this question we have used Bragg low-angle scattering of X-rays and neutrons to study binary mixtures of block copolymers having different molecular weights, chemical compositions, and architectures.

The molecular and structural characteristics of the copolymers we have used are shown in Table I. The samples were obtained by direct mixing of the required proportions of the two copolymers in dilute benzene solution (concentration <2%). After vigorous stirring, the solutions were freeze-dried until the solvent had been removed completely. The solid residue, which corresponded to an intimate mixture of the two copolymers, was then molded under vacuum and oriented according to the technique described previously.[5]

Throughout this paper the molar fraction of the components and the average molecular weights of the mixtures are quantities which have been calculated from the number-average molecular weight for the two-block or half the M_n for the three-block copolymers.[4]

Transition from the Lamellar to the Cylindrical Structure

As an attempt to study the phase transition from the lamellar to the cylindrical structure with demixing on a macroscopic scale, we have considered binary mixtures of two copolymers having different structures. More precisely, we have considered the binary mixture of the copolymer SIS-2C with the copolymers SI-5, SIS-2, ISI-2, and SI-3 (see Table I). The copolymer SIS-2C has a cylindrical structure; it is a three-block copolymer containing a central polyisoprene block. The other four copolymers all exhibit lamellar structure; SI-5 and SI-3 are two-block copolymers, while SIS-2 and ISI-2 are three-block copolymers having central sequences of polyisoprene and polystyrene, respectively.

Table I
Molecular and Structural Characteristics of Polymers[a]

sample	M_n ± 8%	M_w/M_n	x_{PS}	d ± 1%, Å
SI-2	17 000	1.15	0.495	138
SI-3	27 000	1.25	0.503	203
SI-4	51 000	1.20	0.504	321
SI-5	72 000	1.15	0.494	414
S_DI-7[b]	114 800	1.20	0.606	650
SIS-2	63 000	1.30	0.504	247
SIS-3	96 000	1.20	0.532	320
ISI-1	48 500	1.20	0.474	278
ISI-2	59 900	1.25	0.496	268
SIS-2C	105 000	1.18	0.257	263

[a] M_n = number-average molecular weight; M_w/M_n = polydispersity; x_{PS} = weight fraction of polystyrene; d = Bragg spacing of the fundamental reflection. [b] Perdeuterated styrene blocks.

Low-angle X-ray diffraction has led to a number of conclusions. First, the diffraction patterns of the mixtures remain as detailed as those of the two components taken separately and contain equally sharp Bragg reflections. We will return to this point in more detail later in this work when we consider the case of mixtures keeping the same structure as a function of composition.

The second observation is that each copolymer can incorporate appreciable quantities of a copolymer of different structure, without changing its structure. Only the geometrical parameters that characterize the lattice change with the molar concentration. This compatibility is, however, limited. Above a certain concentration, the mixtures occur in the form of two coexisting macroscopic

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