Macromolecules **1982**, *15*, 267-271

(11) Cotton, J. P.; Decker, D.; Benoit, H.; Farnoux, B.; Higgins, J.; Jannink, G.; Ober, R.; Picot, C.; des Cloizeaux, J. *Macromolecules* **1974**, *7*, 863. Daoud, M.; Cotton, J. P.; Farnoux, B.; Jannink, G.; Sarma, G.; Benoit, H.; Duplessix, R.; Picot, C.; de Gennes, P.-G. *Ibid.* **1975**, *8*, 804.
(12) Bacon, G. E. "Neutron Diffraction"; Oxford University Press: London, 1962.
(13) Hadziioannou, G.; Mathis, A.; Skoulios, A. *Colloid Polym. Sci.* **1979**, *257*, 136.
(14) Guinier, A. "Thêorie et Technique de la Radiocristallographie"; Dunod: Paris, 1953. Guinier, A.; Fournet, G. "Small-Angle Scattering of X-Rays"; Wiley: New York, 1955.
(15) Chandrasekhar, S. *Rev. Mod. Phys.* **1943**, *15*, 1.

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

George Hadziioannou[†] **and Antoine Skoulios***

CNRS, Centre de Recherches sur les Macromolécules, 67083 Strasbourg-Cedex, France.
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

---

[†] Present address: Polymer Research Institute, University of Massachusetts, Amherst, Mass. 01003.

0024-9297/82/2215-0267$01.25/0

Table II
Molecular and Structural Parameters of Binary Mixtures[a]

sample	structure	c	$[c]$	d, Å	x_{PS}	M
SI-5	L	0.000	0.000	414	0.494	72 000
	L	0.140	0.182	402	0.461	68 500
	L	0.267	0.333	389	0.431	65 500
	L + C	0.384	0.461	381 + 362	0.403	63 000
	L + C	0.453	0.531	381 + 362	0.387	61 600
	C	0.593	0.667	333	0.353	59 000
	C	0.697	0.759	321	0.328	57 200
	C	0.773	0.824	301	0.311	55 900
	C	0.854	0.889	287	0.292	54 700
	C	0.929	0.947	271	0.274	53 500
SIS-2C	C	1.000	1.000	263	0.257	52 500
SI-3	L	0.000	0.000	203	0.502	27 000
	L	0.359	0.223	233	0.414	32 700
	L	0.564	0.400	267	0.364	37 200
	C	0.700	0.546	254	0.331	40 900
	C	0.796	0.668	250	0.307	44 000
	C	0.861	0.761	255	0.291	46 400
	C	0.921	0.858	255	0.276	48 900
	C	0.963	0.931	255	0.266	50 700
SIS-2C	C	1.000	1.000	263	0.257	52 500
SIS-2	L	0.000	0.000	244	0.504	31 500
	L	0.300	0.205	267	0.430	35 800
	L	0.416	0.299	292	0.401	37 800
	L	0.526	0.400	284	0.374	39 000
	L	0.625	0.500	297	0.350	42 000
	L + C	0.714	0.600	279 + 265	0.328	44 100
	C	0.794	0.699	267	0.308	46 200
	C	0.859	0.786	262	0.292	48 000
	C	0.938	0.901	261	0.272	50 400
SIS-2C	C	1.000	1.000	263	0.257	52 500
ISI-2	L	0.000	0.000	268	0.496	30 000
	L	0.163	0.100	281	0.457	32 300
	L	0.304	0.199	293	0.423	34 500
	L	0.428	0.299	295	0.394	36 700
	L	0.539	0.400	275	0.367	39 000
	C	0.636	0.500	276	0.344	41 200
	C	0.721	0.596	271	0.324	43 400
	C	0.802	0.698	267	0.304	45 700
	C	0.872	0.796	262	0.287	47 900
	C	0.940	0.900	265	0.271	50 300
SIS-2C	C	1.000	1.000	263	0.257	52 500

[a] c and $[c]$ = weight and molar fraction of SIS-2C; L and C = lamellar or cylindrical structure; L + C = coexisting lamellar and cylindrical structures; d = Bragg spacing; x_{PS} = weight fraction of polystyrene; M = average molecular weight (M_n is taken for two-block and $M_n/2$ for three-block copolymers[4]).

phases, each one being a "saturated solution" of one copolymer in the other. Figure 1, which illustrates this behavior, concerns the binary mixture of lamellar copolymer SI-5 with cylindrical copolymer SIS-2C.

Figure 1 represents the variation of the reciprocal spacing of the low-angle Bragg reflections with the molar concentration. For the lamellar phase rich in SI-5, we have considered the Bragg reflections of order 2, 3, 4, 5, and 6; for the cylindrical phase, we have considered the eight reflections for which the reciprocal spacings are in the ratio $\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}:\sqrt{12}:\sqrt{13}:\sqrt{16}:\sqrt{19}$. In all cases, we have neglected the first order of diffraction which corresponds to a very intense reflection, situated immediately on the edge of the direct X-ray beam and therefore very difficult to measure accurately. One observes for molar concentrations of SIS-2C less than 0.4 that the structure is lamellar, while for a molar concentration greater than 0.6 the structure is cylindrical. For concentrations between 0.4 and 0.6 the system is a two-phase mixture, the diffraction patterns containing both lamellar and cylindrical reflections. To complete these results we have presented the structural parameters of the mixture SI-5/SIS-2C in Figure 2 and those for the other three systems considered in Table II.

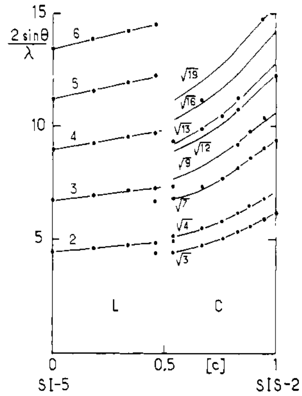

Figure 1. Variation of the reciprocal spacing of the low-angle Bragg reflections observed as a function of concentration in the binary mixture SI-5/SIS-2C; each reflection is indicated by its Miller index h for the lamellar structure and by $(h^2 + k^2 + hk)^{1/2}$ for the cylindrical structure.

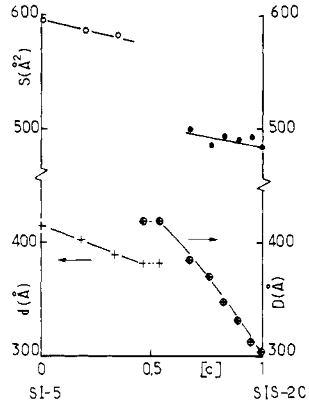

Figure 2. Variation with concentration of the molecular area S, the lamellar spacing d, and the distance D between the axes of neighboring cylinders in the binary mixture SI-5/SIS-2C.

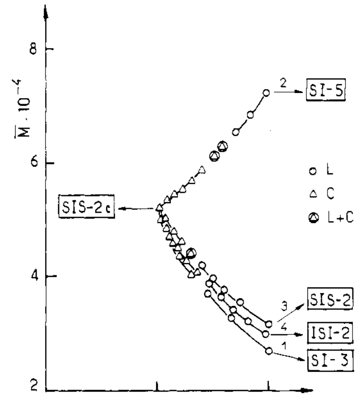

Figure 3. Phase diagram for binary mixtures of SIS-2C with, respectively, SI-5, SIS-2, ISI-2, and SI-3; L = lamellar phase, C = cylindrical phase, L + C = coexisting lamellar and cylindrical phases. The average molecular weight of the mixtures is plotted as a function of concentration. As described previously,[5] the molecular weight for three-block copolymers is half the real one measured experimentally.

The third and last observation concerns the proportion of polystyrene, x_{PS}, at which the structural transition occurs. This corresponds to an overall proportion of polystyrene in the binary mixture between 0.32 and 0.40 (Figure 3). This result is in perfect agreement with the

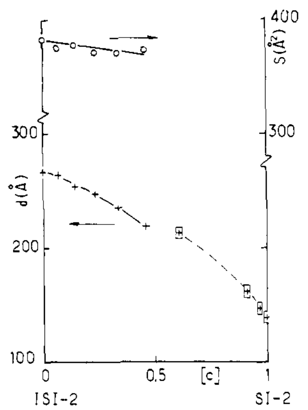

Figure 4. Variation of the lamellar spacing d and the molecular area S as a function of the molar concentration of SI-2 in the binary mixture with ISI-2. The boxed points represent the Bragg spacing measured at the maximum of the diffuse scattering band for the "molten" mixtures.

previous observations of Molau.[6] It is interesting to note that this transformation occurs in a relatively broad concentration range which is, however, the same for all mixtures regardless of whether these contain two- or three-block copolymers or whether they contain copolymers with low or high molecular weight.

Transition from the Lamellar to the Disordered Phase

As an attempt to study the phase transition from the lamellar to the disordered phase with demixing on a macroscopic scale, we have considered the possibility of the melting process being a function of molar concentration of the binary mixture. More precisely, we have considered a mixture of the copolymer ISI-2, for which the structure is lamellar, with the copolymer SI-2, which is disordered. These two copolymers have the same proportion of polystyrene (Table I).

Low-angle X-ray diffraction as a function of molar concentration is very simple. The copolymer ISI-2 is capable of incorporating appreciable quantities of SI-2 without destruction of the lamellar structure as shown in Figure 4. Only the geometric parameters which characterize the organization, the Bragg spacing d and the molecular area S, change with molar concentration. Judging by the sharpness of the diffraction peaks, the quality of the lamellar ordering remains unchanged. In the same way, judging by the number of reflections[4] (which exceeds six for the pure copolymer ISI-2 and which does not decrease with increasing molar concentration of SI-2), the thickness of the interface between layers of polystyrene and polyisoprene also remains unchanged.

Nevertheless, above a molar concentration of SI-2 of 0.5, the diffraction patterns show only one relatively broad band. The system becomes disorganized abruptly. It is interesting to note that this transition occurs in a relatively narrow molar concentration range, corresponding to an average molecular weight for the mixture between 22 200 and 24 000. This is in perfect agreement with what we reported previously[4] regarding the occurrence of the lamellar structure as a function of molecular weight. It is also interesting to note that, within the accuracy of our measurements, the transition would be first order since the number of sharp Bragg reflections remains equal to six up to the "melting" point.

Macroscopically Homogeneous Mixtures

In the preceding paragraphs we have considered the case where the structure of the mixture changes as a function of the molar concentration. We will now consider the opposite case where the structure does not change, that is to say the case where the two copolymers to be mixed have identical structures. The question to be answered now is whether the mixing occurs at the molecular level or at the level of the structural elements (here, the lamellae).

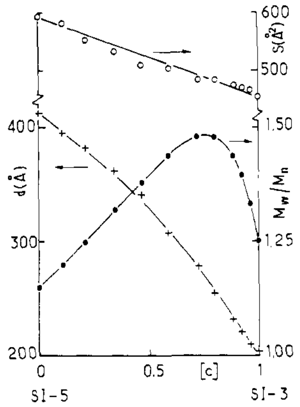

Figure 5. Variation of the lamellar spacing d, the molecular area S, and the polydispersity M_w/M_n of binary mixture SI-5/SI-3 as a function of molar concentration c.

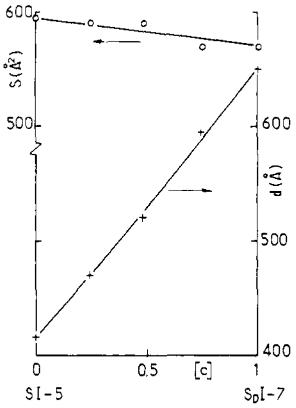

Figure 6. Variation of the lamellar spacing d and the molecular area S as a function of molar concentration in the binary system SI-5/S_DI-7.

If one refers to the electron micrographs of styrene/isoprene or styrene/butadiene block copolymers[1,4] showing the cylindrical or the lamellar structure, one sees that the dimensions of the structural elements (cylinders or lamellae) do not seem to vary from place to place within the samples. This indicates the absence of segregation of the polymer chains according to their molecular weight. Yet, from the value of the polydispersity of the sample examined, such an effect should be easily observable. Apparently, the mixture of the copolymer is occurring on a molecular scale.

To verify this interpretation, we have undertaken a systematic low-angle X-ray scattering study of several binary mixtures of lamellar copolymers of different chemical architectures (two- and three-block copolymers: SI, SIS, and ISI) and of different molecular weights (Figures 5-12).

The diffraction patterns that we were able to record for these mixtures were extremely detailed and rich. They contained a series of equidistant peaks (indicating the lamellar structure), the sharpness of which always remained very pronounced. This observation alone is sufficient to convince us that the lamellar system does not result from the piling up of lamellae with different thicknesses. Such an organization would result either in the

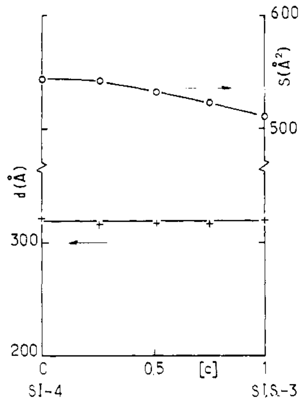

Figure 7. Variation of the lamellar spacing *d* and the molecular area *S* as a function of molar concentration in the binary system SI-4/SIS-3.

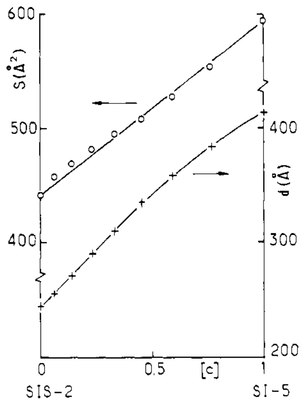

Figure 8. Variation of the lamellar spacing *d* and the molecular area *S* as a function of molar concentration in the binary system SIS-2/SI-5.

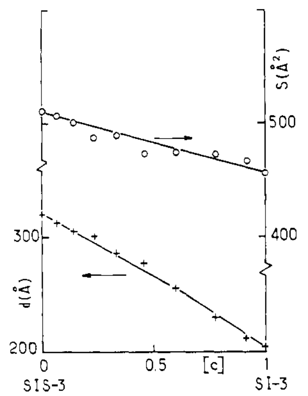

Figure 9. Variation of the lamellar spacing *d* and the molecular area *S* as a function of molar concentration in the binary system SIS-3/SI-3.

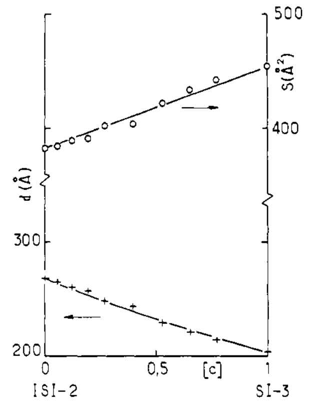

Figure 10. Variation of the lamellar spacing *d* and the molecular area *S* as a function of molar concentration in the binary system ISI-2/SI-3.

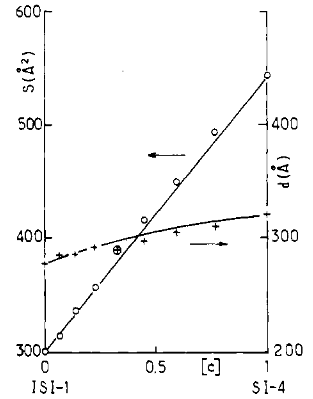

Figure 11. Variation of the lamellar spacing *d* and the molecular area *S* as a function of molar concentration in the binary system ISI-1/SI-4.

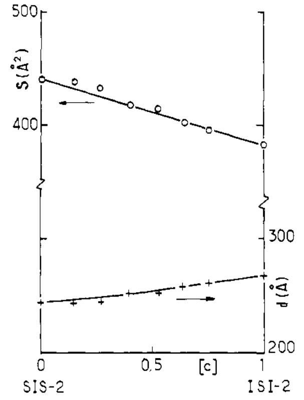

Figure 12. Variation of the lamellar spacing *d* and the molecular area *S* as a function of molar concentration in the binary system SIS-2/ISI-2.

appearance of extra reflections characteristic of a superstructure brought about by the piling up of the lamellae in a sequential way or in the broadening of certain reflections and the disappearance of others due to the stacking of the lamellae in a random fashion.[7]

Other crystallographic arguments also reinforce this belief. The number of Bragg reflections observed does not depend much on concentration; the thickness of the interfaces between the polystyrene and polyisoprene sublayers thus remains constant.[4,8] This invariance is not consistent with a random piling up. In fact, with such an assumption the intensity of the diffracted beams would correspond to the average electron density distribution of all the lamellae present in the system, that is, to an electron density distribution with a more spread out profile.

In addition, the relative intensities of the successive Bragg reflections taken two by two show that the relative thickness[8,9] of the polystyrene and polyisoprene sublayers is exactly that which can be calculated[1] from the specific volumes of the constituents and the chemical composition of the mixture.

Finally, the low-angle neutron diffraction patterns that we recorded for the mixture of copolymer S_DI-7 with copolymer SI-5 are identical with those recorded by X-ray diffraction. Now, the copolymer S_DI-7 contains polystyrene blocks that are entirely deuterated, while the copolymer SI-5 is entirely protonated. If then the molecules of the deuterated copolymer were to be localized in distinct lamellae stacked at random with the lamellae from the

Macromolecules **1982,** *15,* 271-273

protonated copolymer, the neutron diffraction patterns would certainly be affected because of the privileged interferences among the deuterated layers.

All these observations suggest that the mixing of the molecules, at least in the binary systems that we have considered in this work, occurs at a molecular level, independently of the molecular weight of the species present or of their chemical architecture (two or three blocks). It is worthwhile to note, however, that the mixtures examined are not, strictly speaking, binary mixtures, since their constituents taken separately are polydisperse. Actually, mixtures have a binodal distribution of molecular weights and a polydispersity that may be quite important[10] (Figure 5).

To complete this work, we have calculated the molecular area S from the Bragg spacing d measured as a function of the molar concentration (Figures 5-12) using the well-known formula[1]

$$S = 2\bar{v}M_n/Nd$$

where N is Avogadro's number ($N = 6.02 \times 10^{23}$), $\bar{v}$ the specific volume, and M_n the number-average molecular weight of the mixture (calculated by taking for the three-block copolymers half the real molecular weight[4]). We have thus verified that as a function of molar concentration the molecular area varies continuously.

Acknowledgment. We thank Dr. A. Hodge for help with the translation to English. G.H. is grateful to the French Government for financial support with a foreign postgraduate student fellowship.

References and Notes

(1) Skoulios, A. *Adv. Liq. Cryst.* **1975,** *1,* 169. Gallot, B. "Liquid Crystalline Order in Polymers"; Blumstein, A., Ed.; Academic Press: New York, 1978; p 191. Folkes, M. J.; Keller, A. "Physics of Glassy Polymers"; Haward, R. N., Ed.; Applied Science Publishers: London, 1973; p 548.
(2) Szwarc, M. "Carbanions, Living Polymers and Electron Transfer Process"; Interscience: New York, 1968.
(3) Skoulios, A.; Helffer, P.; Gallot, Y.; Selb, J. *Makromol. Chem.* **1971,** *148,* 305. Ptaszynski, B.; Terrisse, J.; Skoulios, A. *Ibid.* **1975,** *176,* 3483.
(4) Hadziioannou, G.; Skoulios, A. *Macromolecules,* accompanying paper in this issue.
(5) Hadziioannou, G.; Mathis, A.; Skoulios, A. *Colloid Polym. Sci.* **1979,** *257,* 136.
(6) Molau, G. E. "Block Polymers"; Aggarwal, S. L., Ed.; Plenum Press: New York, 1970; p 79.
(7) Guinier, A. "Théorie et Technique de la Radiocristallographie"; Dunod: Paris, 1953.
(8) Skoulios, A. "Block and Graft Copolymers"; Burke, J. J., Weiss, V., Eds.; Syracuse University Press: Syracuse, N.Y., 1973; p 121.
(9) Ionescu, M. L.; Skoulios, A. *Makromol. Chem.* **1976,** *177,* 257.
(10) The polydispersity of the mixture is $M_w/M_n = [M_{w_1}c + M_{w_2}(1 - c)][c/M_{n_1} + (1 - c)/M_{n_2}]$, where M_{n_1}, M_{n_2}, M_{w_1}, and M_{w_2} are, respectively, the number- and weight-average molecular weights of copolymers 1 and 2 and where c is the weight fraction of polymer 2 in the mixture.

Melting of Styrene/Isoprene Block Copolymers as a Function of Temperature and Time

George Hadziioannou[†] **and Antoine Skoulios***

CNRS, Centre de Recherches sur les Macromolécules, 67083 Strasbourg-Cedex, France.
Received December 19, 1980

ABSTRACT: The melting of a series of styrene/isoprene block copolymers was studied as a function of temperature with low-angle X-ray diffraction. It was found that the disappearance of the lamellar structure on heating proceeds through an irreversible stage where the lamellae thicken considerably. The kinetics of the thickening effect was found to be faster the higher the temperature and the lower the molecular weight. Quite surprisingly, and contrary to any classical thermodynamic expectation, it appeared that the melting temperature (~180 °C) does not depend in a decisive way on molecular weight or on structure.

Introduction

The liquid-crystalline state of block copolymers has been studied rather extensively in recent years.[1-3] Quite surprisingly, however, their structural behavior with temperature, notably above the glass transition temperature of the blocks, has rarely been analyzed. The few experimental investigations[1,4-6] which have approached this question show that the structural parameters change very little with temperature and, in the case of styrene/vinylpyridine block copolymers swollen with a solvent, that the mesomorphic phases disappear beyond a certain temperature, leaving a disordered micellar solution.[4] The stability of the ordered phases depends also on molecular weight. It is generally agreed that below a certain molecular weight block copolymers would not organize into well-developed periodic structures, but a direct experimental proof was given only very recently in a systematic X-ray study of the lamellar structure of styrene/isoprene block copolymers,[7] where it was demonstrated in particular that the occurrence of the ordered state as a function of molecular weight resembles in many respects a true phase transition. In the meantime, from a theoretical point of view, a microscopic statistical study[8] examining how the mesomorphic order is brought about as a function of the degree of polymerization and of the repulsive interactions between the two kinds of blocks has been elaborated.

We thought that it might be of interest to analyze the role of temperature in more detail, especially its influence on the fusion process. The question to be answered is indeed how the melting occurs with systems which are made up of periodically superposed microdomains of large dimensions, the size of which is in the range from 100 to 1000 Å. In other words, the point is to know if the fusion proceeds, as with ordinary crystals, by a rapid breakup of the crystalline network in a very narrow temperature range or if it is achieved progressively by a gradual disorganization of the medium. The difference in scale between the crystal lattice of block copolymers (~500 Å) and that of

---

[†] Present address: Polymer Research Institute, University of Massachusetts, Amherst, Mass. 01003.

0024-9297/82/2215-0271$01.25/0