starting line as a somewhat dispersed shape. All polymer IV molecules have, therefore, a negative charge, whereas the polymer (A) molecules are macrozwitterions. These results lead to the conclusion that transfer or termination reactions did not occur during the polymerization.

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Molecular Weight Dependence of Lamellar Structure in Styrene/Isoprene Two- and Three-Block Copolymers

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ABSTRACT: The lamellar structure of three homologous series of SI, SIS, and ISI block copolymers, 50% by weight polystyrene, was studied as a function of molecular weight with low-angle X-ray diffraction. From the structural standpoint, the three-block copolymers behave identically with the corresponding two-block copolymers of half the molecular weight. Helfand's thermodynamic predictions for the value of the lamellar thickness are in fair numerical agreement with the experimental facts; however, the observed lamellar spacing increases with molecular weight a little more steeply than predicted. Finally, the molecular area, calculated from Helfand's theory as a function of chemical composition at constant lamellar thickness, is independent of the exact position of the interface within the lamella. The general impression is that for two-block copolymers the arrangement of the sequences in the lamellae would be close to a double-layer arrangement. This would imply little interpenetration of the molecules in a direction normal to the interfaces.

Introduction

Since their discovery, the mesomorphic phases of block copolymers have been the subject of many studies. Some of these aimed to establish the generality of the spontaneous liquid-crystalline organization observed and to describe the main structures involved. Others analyzed the dependence of the structure on various factors such as temperature, solvent concentration, composition of the copolymer, and molecular weight.[1-5]

Most of the studies that considered the role of molecular weight were carried out with binary mixtures of copolymer and solvent. They showed that the dimensions of the segregated microdomains were comparable to those of the macromolecules themselves and that they increased monotonically with the length of the blocks.[1,2] Their quantitative analysis is, however, complicated because it is necessary to take into account the particular role of each solvent used. Whether good or bad, the solvents can in fact be preferential to some extent for each type of block.

Several studies have nevertheless been performed in the absence of solvent. Based on scattered results obtained from an incomplete and truncated series of styrene/isoprene or styrene/butadiene block copolymers, the conclusions are still neither very coherent nor convincing. For instance, Vanzo[6] and Kawai[7] pointed out for the case of the lamellar structure that the thickness of the layers is proportional to the square root of the molecular weight. Later, Krömer[8] stated that the dimensions of the segregated microdomains are proportional to the molecular weight raised to the 0.55–0.60 power. Later still, Gallot[9] simply announced that the structural parameters increase with the length of the blocks in a monotonic fashion. Concerning the role of the molecular structure, he added that on going from a given two-block to the related three-block copolymer (obtained from the former by the addition of a new block), the thickness of the lamellae decreases markedly.

Regarding the role of the molecular weight on the occurrence and the stability of the mesomorphic phases, it has not been possible to tackle the problem experimentally. As far as we are aware, only one study has touched on this question. This study[10] concerns the change in the mechanical behavior of styrene/butadiene block copolymers which was observed above a threshold of molecular weight of about 10000 and which was interpreted as being related to microphase separation.

All previous studies, the earliest of which were made 15 years ago, have been accompanied by theoretical explanations based on thermodynamics.[7,8,11-22] We will return to this later.

In order to try to clarify the situation, we decided to repeat the earlier work and study further styrene/isoprene

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Table I
Molecular Characteristics of Polymers

sample	$M_n \pm 8\%$	$M_w + 5\%$	M_w/M_n	$_{UV}x_{PS} \pm 0.005$
SI-1	8500	10200	1.27	0.550
SI-2[a]	17000	18800	1.15	0.495
SI-3[a]	27000	31000	1.25	0.500
Si-4[a]	51000	56300	1.20	0.505
SI-5[a]	72000	81000	1.15	0.490
SI-6	98000	118300	1.30	0.525
SI-7[b]	114800	130000	1.20	0.597
SI-8[b]	130300	172000	1.32	0.525
SI-9[b]	155000	190000	1.30	0.495
SI-10	181000	210000	1.16	0.490
SI-11	185000	240000	1.35	0.472
SI-12[b]	205000	245000	1.30	0.535
SIS-1[a]	32500	41200	1.27	0.494
SIS-2[a]	63000	81000	1.30	0.504
SIS-3[a]	96000	113500	1.20	0.542
ISI-1[a]	48500	57000	1.20	0.476
ISI-2[a]	59900	73800	1.25	0.494
ISI-3[a]	77000	97000	1.30	0.502
ISI-4[a]	134000	175000	1.35	0.545

[a] Obtained from Ecole d'Application des Hauts Polymères, Strasbourg, France. [b] Perdeuterated styrene blocks.

block copolymers in the dry state. We chose to consider only polymers of the highest possible homogeneity with regard to molecular weight distribution and chemical composition. In addition, we were careful to select samples that consisted of a homologous series of two- and three-block copolymers. However, we limited our investigation to copolymers containing equivalent volumes of styrene and isoprene and showing therefore only lamellar structure, which is easier to analyze.

Experimental Section

The polymers used were synthesized anionically in benzene at 25 °C with *sec*-butyllithium as the initiator.[23] Their molecular characteristics (Table I) were carefully determined following the usual physicochemical methods. Number-average molecular weights, M_n, were measured with a 502 Mechrolab osmometer at 30 °C, using toluene as solvent. Weight-average molecular weights, M_w, were determined at 25 °C with a Sofica light scattering apparatus provided with a He–Ne laser source (632 nm), using tetrahydrofuran as solvent. Due to the homogeneity of the samples with regard to molecular weight distribution and chemical composition, the apparent molecular weights measured[24] could be safely assumed to be very close to the real weight-average molecular weights that were sought. Polydispersities were calculated from the experimental M_w and M_n values and corroborated by gel permeation chromatography. The GPC measurements were performed at 25 °C with a Waters instrument with Styragel columns and tetrahydrofuran as the solvent. The weight fraction of styrene in the copolymers, $_{UV}x_{PS}$, was determined from the UV absorption at 262 nm in tetrahydrofuran solutions.

The X-ray diffraction experiments were carried out with a Baro-Luzzati small-angle camera.[25] This was equipped with a bent quartz monochromator and was operated under vacuum using Cu $K\alpha_1$ radiation. The diffraction patterns were recorded at room temperature on a photographic film placed 400 mm from the specimen. Samples were molded under vacuum and oriented into large single-crystalline domains using a shearing technique described elsewhere.[26] They were finally annealed for a long time above the glass transition temperature of polystyrene. To be precise, it should be noted that at the ambient temperature at which they were examined, the copolymers were, of course, not in equilibrium since the polystyrene blocks were in the glassy state. However, the measured spacings remained valid since they do not differ significantly from those measured at 130 °C. From the relative intensity of the successive diffraction lines taken two by two, it was possible to measure the relative thicknesses of the polystyrene and polyisoprene sublayers and to determine

Table II
Structural Characteristics of Polymers

sample	$d \pm 1\%$, Å	$_{XR}x_{PS} \pm 0.005$	x_{PS}[a]	$d_{PS} \pm 2\%$, Å	d',[b] Å	$S \pm 10\%$, Å^2
SI-1	(111)					
SI-2	(138)					
SI-3	203	0.505	0.503	94	223	454
SI-4	321	0.502	0.504	150	347	543
SI-5	414	0.497	0.494	189	439	595
SI-6	595	0.520	0.522	288	540	561
SI-7	650	0.614	0.606	359	592	570
SI-8	715	0.529	0.527	337	653	599
SI-9	760	0.511	0.503	340	737	673
SI-10	860		(0.490)	390	819	720
SI-11	943	0.497	0.485	422	832	672
SI-12	988	0.542	0.539	496	884	705
SIS-1	(147)					
SIS-2	244	0.505	0.504	114	251	441
SIS-3	320	0.522	0.532	158	335	510
ISI-1	278	0.472	0.474	111	280	300
ISI-2	268	0.497	0.496	123	248	382
ISI-3	340	0.507	0.505	159	292	387
ISI-4	439		0.545	239	403	518

[a] $x_{PS} = (_{UV}x_{PS} + _{XR}x_{PS})/2$; see $_{UV}x_{PS}$ in Table I. [b] d' = lamellar thickness calculated with Helfand's theory and numerical values of thermodynamic parameters.[19-22]

therefrom the volume fraction and also the weight fraction, $_{XR}x_{PS}$ (Table II), of polystyrene in each copolymer.[27-29]

Determination of the Structural Parameters

The X-ray patterns that we registered generally showed many, sometimes up to 15, sharp and equidistant diffraction lines indicative of a well-developed lamellar structure. The thickness, d, of the lamellae, that is, the thickness of one polystyrene and one polyisoprene sublayer superposed, was measured from the weighted average of the reciprocal spacings ($d^{-1} = \sum i d_i^{-1}/\sum i$; i is the order of diffraction) of all observed reflections (Table II). However, the patterns of copolymers SI-1, SI-2, and SIS-1 contained only one diffraction band. This will be discussed later in the section devoted to the melting of the mesophases. Let us say at the moment that we also characterized these bands (probably in an improper sense) by their "Bragg spacing" calculated from the position of the maximum in the intensity distribution.

From these data and all the molecular characteristics (Table I) that we have been able to gather for the copolymers considered in this work, we have derived several extra structural parameters that are of interest in the discussion of the conformational behavior of the blocks. In particular, we have calculated[1] the thickness of the polystyrene sublayers

$$d_{PS} = d/[1 + \bar{v}_{PI}(1 - x_{PS})/\bar{v}_{PS}x_{PS}]$$

and the molecular area

$$S = 2M_{PS}\bar{v}_{PS}/\nu N d_{PS}$$

which is the average surface occupied at the interfaces by each covalent junction point between styrene and isoprene blocks (Table II). In these formulas, $\bar{v}_{PI}$ and $\bar{v}_{PS}$ are the specific volumes of polyisoprene (1.106 cm^3 g^{-1}) and polystyrene blocks (0.953 or 0.885 cm^3 g^{-1}, depending upon whether polystyrene is hydrogenated or deuterated). M_{PS} is the number-average molecular weight of polystyrene blocks, N is Avogadro's number (6.02×10^{23}), and ν is the number of polyisoprene blocks linked to each polystyrene block.

Finally, on close inspection of the intensity of the diffraction lines and more specifically from its overall decay

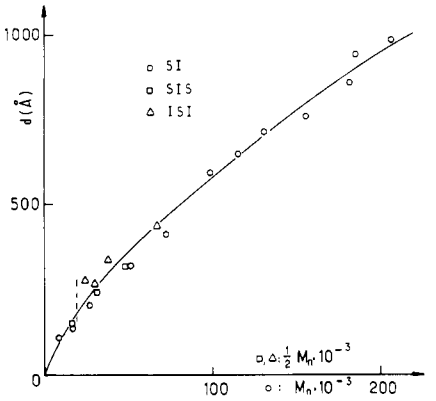

Figure 1. Variation of lamellar spacing d as a function of molecular weight (M_n) for the two-block copolymers and as a function of half of it ($M_n/2$) for the three-block copolymers.

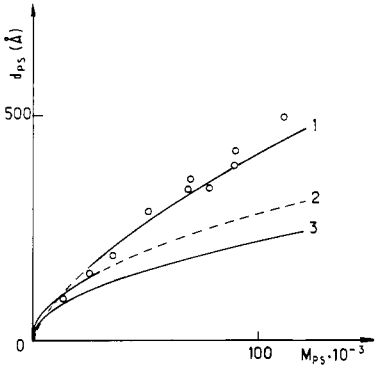

Figure 2. Variation of the thickness of the polystyrene sublayers as a function of the molecular weight of the corresponding blocks: curve 1 is calculated from the theory of Helfand;[19-22] curve 2 is calculated from the theory of Leibler;[32] curve 3 shows the variation of the root-mean-square end-to-end distance of ideal polystyrene homopolymers in the bulk.

in reciprocal space, it was possible to appraise the width of the interfacial region.[27] We noted that this remained well below 50 Å, whatever the molecular weight of the sample. This was in good agreement with the value (~30 Å) observed experimentally by Kawai[30] or calculated theoretically by Helfand.[19,20]

Variation of the Structural Parameters

Figure 1 represents the lamellar spacing d plotted as a function of the total molecular weight (M_n) for the two-block copolymers or as a function of half of it ($M_n/2$) for the three-block copolymers. Quite remarkably, all the data fall, within the accuracy of the measurements, on a single curve passing through the origin and increasing monotonically with molecular weight. Clearly, the joining of two two-block copolymer molecules by the ends of their polystyrene or polyisoprene blocks, transforming them into three-block copolymer molecules with the same chemical composition but with double the molecular weight, involved no detectable change in the thickness of the layers.[33] Since the chain conformation seems to be unaffected, the corresponding entropic contribution of the coils presumably does not play a specific role in the overall stability of the system and in the fixing the structural parameters.

Figure 2 shows how the thickness d_{PS} (Table II) depends upon the molecular weight of the polystyrene blocks. By way of comparison, we plotted in the same figure the variation of the root-mean-square end-to-end distance $\langle h^2 \rangle^{1/2}$ of ideal polystyrene chains as a function of molecular weight (curve 3). The data used were obtained from a low-angle neutron scattering study of the radius of gyration of polystyrene in the bulk.[31] It is worth noting that d_{PS} definitely increases with molecular weight much more quickly than predicted by Gaussian statistics of ideal coils. This is clear in Figure 3, where log d is plotted as a function of log M. Practically, d seems proportional to M^{α}, and the power calculated from the slope of the straight line, $\alpha = 0.79 \pm 0.02$, is significantly larger than that ($\alpha = {}^1/_2$) predicted for ideal coils. It also is more than the values predicted by all the phenomenological thermodynamic theories,[7-8,14,17] which consider explicitly the entropy of the polymer chains.

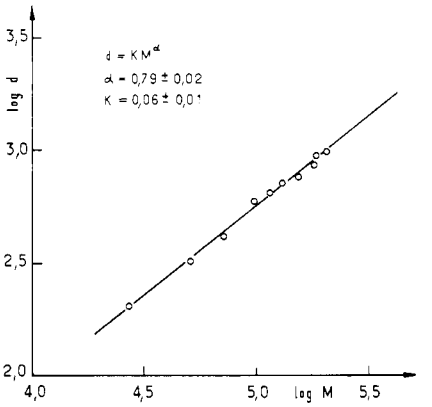

Figure 3. Double-logarithmic plot of the variation of the spacing d as a function of M_n.

Correspondingly, the molecular area S (Table II) increases weakly with molecular weight ($S \sim M^{0.21}$), particularly when the latter is important. The nonideal behavior of the blocks is, of course, not surprising since the blocks are incompatible with one another (the interfaces are sharp) and are therefore subjected to interactions that are rather strong.

Curve 2 of Figure 2 corresponds to the predictions of Leibler's theory.[32] This is a microscopic statistical theory of phase equilibria in noncrystalline block copolymers. We will return to this later when we discuss the melting of the mesophases. Without going into detail regarding the method used for the calculations, let us say simply that for a lamellar two-block copolymer containing equal amounts of polystyrene and polyisoprene, the theory predicts that near the phase transition leading from the disordered to the lamellar state, the thickness of the lamellae will be $d = \pi R$, where R is the radius of gyration of the copolymer chains, assumed to be ideal. As is proper, theory is found to agree with experiment (Figure 2) only in the region of low molecular weights, where, as we will see later, the ordering transition of the system occurs.

Curve 1 of Figure 2 represents the thickness d_{PS} as calculated with Helfand's theory.[19-22] Assuming that the interface between segregated microdomains is thin compared to the total thickness of the layers, in accordance with the experimental facts, this statistical mechanical theory solves the problem of the uniform density distribution of the segments by applying a self-consistent-field method. The only parameters needed are taken from experimental data in the literature such as the interaction parameter χ of the styrene and isoprene units, the length of Kuhn's statistical elements, etc. As has already been observed by Helfand on grounds of scattered experimental data, the agreement of theory with experiment is good. The discrepancy between calculated and measured thicknesses hardly exceeds 10%. This is all the more significant because the theoretical calculations do not contain any adjustable parameters, as is generally the case for all the other phenomenological thermodynamic theories presented

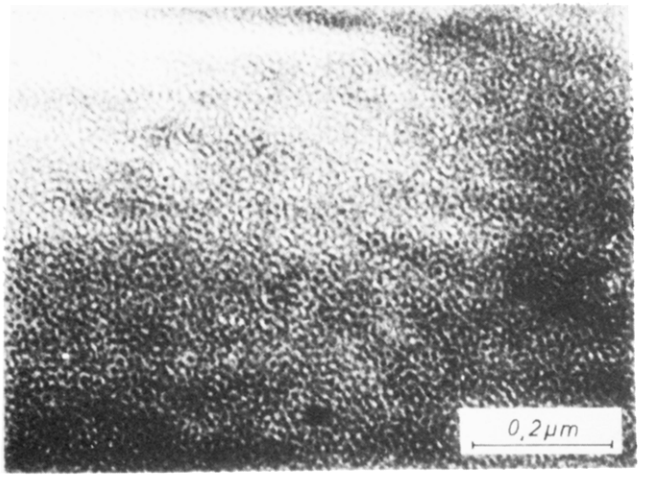

Figure 4. Electron micrograph of the disordered phase of copolymer SIS-1.

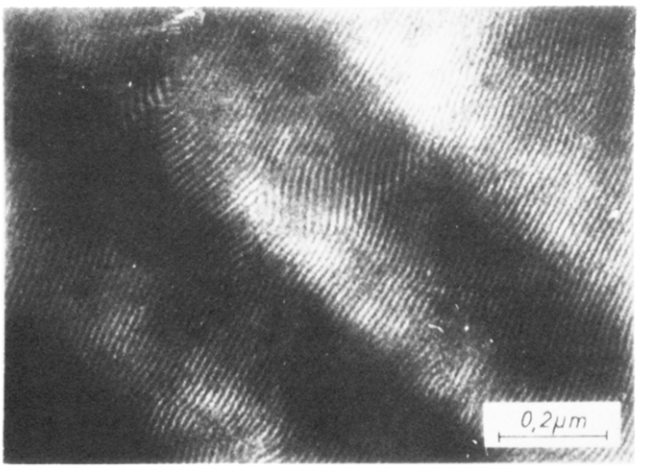

Figure 5. Electron micrograph of the lamellar phase of copolymer SIS-2.

in the literature. It should be noted, however, that, expressed as a power law, Helfand's numerical results (see Table II) lead to an exponent ($\alpha \approx 0.64$) that is much lower than that obtained experimentally by us ($\alpha \simeq 0.79$).

Melting of the Mesophase

All of the X-ray diffraction patterns that we recorded showed from 3 to 15 sharp Bragg reflections, indicating a well-developed lamellar organization. As we have said in the section devoted to the determination of the structural parameters, the patterns of copolymers SI-1, SI-2, and SIS-1 contain only one diffraction band which, in addition, is relatively large. The difference between the two types of patterns is striking. Taking into consideration the fact that this abrupt change occurs as a function of molecular weight at about 20 000 for two-block and 40 000 for three-block copolymers (see Figure 1), one is tempted to speak of a phase transition between the well-organized lamellar phase and a disordered phase. Electron microscopy of copolymers SIS-1 and SIS-2, whose molecular weights are similar (Table I) but lie on both sides of the molecular weight threshold mentioned above, fully corroborates this interpretation (Figures 4 and 5). It clearly shows that SIS-2, whose X-ray diffraction pattern is formed of three very sharp Bragg reflections, is lamellar in structure. Furthermore, SIS-1, whose X-ray pattern contains only one broad diffraction band, is actually in the disordered state. Its structure corresponds to a simple interdispersion of nodular polystyrene and polyisoprene microdomains. Based on this observation, the change in mechanical behavior reported by Bishop[10] for styrene/butadiene block copolymers is no doubt due to the ordering and to the establishment of a true periodic arrangement and not only (as claimed) to the segregation of the blocks into distinct microphases.

As far as the microphase separation is concerned, it is easy to understand the role of molecular weight. Segregation in a binary polymer mixture is merely due to the decrease of entropy of mixing with increasing degree of polymerization. Assuming that the segregation of the blocks in a copolymer is not very different from the segregation of the corresponding homopolymers in a binary mixture, Fedors[16] has shown by simple thermodynamic calculations based on the Flory–Huggins theory that the segregation in styrene/isoprene block copolymers, and the ordering itself, should occur for molecular weights lying in the range from 10 000 to 20 000. Quite surprisingly, the result is nicely in agreement with the facts, in spite of the unrealistic assumptions made. Other thermodynamic theories have tried to treat the observed mesomorphic phases by considering the presence of the covalent bonds linking the blocks at the interfaces[14,15] but they have led to similar conclusions.

In a recent microscopic statistical theory of phase equilibria in amorphous two-block copolymers,[32] the onset of ordering was interpreted in terms of only two relevant parameters: first, the product χN of the Flory χ parameter characterizing the repulsive interaction of the two types of monomer and the degree of polymerization N and second, the chemical composition of the system. It was shown that ordering occurs when χN exceeds a threshold value that depends only on the chemical composition of the copolymer. Thus, for a copolymer with a given chemical composition at a fixed temperature (χ is constant), organization should occur for N lying above a well-defined value.

Discussion

It is interesting to note that, within their respective ranges of applicability, the two theories mentioned above account quantitatively for the structural parameters observed. Helfand's theory applies over the whole range of molecular weights considered because the interfaces have indeed negligible thickness almost all the way down to the melting threshold and Leibler's theory is valid in the low molecular weight range, where, as we have seen, the ordering process begins to occur. Furthermore, it should be stated that both theories admit implicitly that the conformation of the chains differs from the ideal. However, they do not, at least for the time being, expand on this deviation, which nevertheless seems very large.

In order to obtain information on this point, we have proceeded in the following indirect way. From the theory of Helfand[19–22] we have calculated for a styrene/isoprene copolymer having an overall molecular weight of about 100 000 the molecular area S as a function of the weight fraction x_{PS} of polystyrene. For each composition we have simply corrected the molecular weight in such a way that the overall thickness of the lamellae remains equal to 600 Å. The result suggests (Table III) that the molecular area S remains independent of the composition. It seems that the lateral space occupied by the junction points between blocks does not depend on the ratio d_{PS}/d, which is the exact position of the interface within the lamellae. The polymer chains seem to keep the same lateral bulkiness at any distance from the interface. This bulkiness is presumably determined almost entirely by small-scale interactions located in the interfacial region.

Table III
Variation of the Molecular Area as a Function of the Composition for a Lamellar System of Thickness 600 Å Calculated by Helfand's Theory[19-22]

x_{PS}	M_n	d_{PS}/d	S, Å^2
0.2	96000	0.177	569
0.3	97000	0.269	567
0.4	98000	0.364	566
0.5	100000	0.462	568
0.6	103000	0.563	576
0.7	106000	0.667	585
0.8	110000	0.775	598

In summary, we have first shown that from a structural standpoint three-block copolymers behave identically with the corresponding two-block copolymers of the same chemical composition but of half the molecular weight. It seems therefore that the detailed conformation of the chains on a macromolecular scale and as a consequence the entropy of the blocks does not play a decisive role in the stability of the system and in the determination of the values of the geometrical parameters characterizing the mesophase. It was then shown that as a first approximation the lamellar spacing is proportional to the molecular weight raised to the 0.79 power. This exponent is much higher than that ($^1/_2$) predicted for ideal random coils and still higher than the exponent (0.64) that would numerically fit Helfand's theory. Its value is not excessively far from unity, which means that the structural parameters are not far from being fully determined, on the one hand, by the molecular area of the molecules at the interfaces, and on the other (in a trivial way), by their molar volume. It was finally shown that, for a given total lamellar thickness, the molecular area is consistently independent of the exact position of the interface in the layers. As a whole, this information suggests that everything behaves like sequences in two-block copolymers, hardly interpenetrating one another in a direction normal to the interfaces and adopting within each sublamella a type of double-layer configuration.

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(33) This property has already been used in the form of an assumption by Uchida and then by Helfand (see: Uchida, T.; Soen, T.; Inoue, T.; Kawai, H. *J. Polym. Sci., Part A-2* **1972**, *10*, 101; see also ref 21) for the purpose of simplifying the theoretical thermodynamic discussion of block copolymers. However, this assumption was considered (see Uchida et al. on p 109) only as "a crude but simple expedient..., so that micelles of two- and three-block copolymers could...be discussed to the same order of approximation by a relatively simple thermodynamic approach." It is of interest to note that, in fact, this assumption turns out to be conspicuously realistic.