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.

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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

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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

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common crystals (~10 Å) raises the question of the exact nature and spatial range of the interactions which are responsible for the liquid-crystalline order observed.

To answer this question we began a low-angle X-ray diffraction study of the melting process of styrene/isoprene block copolymers. We first observed the thermal behavior[9] of the lamellar two-block copolymer SI-6 (M_n = 98 000, M_w/M_n = 1.30; 52.2 wt % of styrene[7]). We noticed that, on heating the specimen (~20 °C/day) stepwise, the thickness of the lamellae stayed almost constant (~600 Å) in the range from 20 to 180 °C and that it then started to increase steeply with temperature so as to attain at 250 °C values as high as 1200 Å. During the thickening process, the diffraction lines remained sharp and numerous, indicating that the lamellar order was well developed all the way to 250 °C. We also investigated the temperature dependence[10] of a three-block copolymer (SIS-1C; M_n = 50 900, M_w/M_n = 1.25; 32.4 wt % of styrene) presenting the cylindrical structure. But here we noted quite a different behavior: the position and shape of the sharp Bragg reflections characteristic of the hexagonal lattice of the system remained unchanged with temperature and then disappeared suddenly at 153 °C, leaving a broad diffraction ring indicative of a disordered structure. In order to clarify these results, we carried out some further experiments, which we report here. Our intention was to see how much the thickness of the lamellae can increase with temperature for a series of homologous lamellar styrene/isoprene block copolymers of various molecular weights and to study at the same time the kinetics of the thickening phenomenon itself.

Experimental Section

The polymers that we used are all lamellar in structure. They are part of those studied previously in a work devoted to determining the effect of molecular weight on the structural parameters.[7] For the sake of clarity, let us emphasize that four of them are made up of two blocks [SI-3 (M_n = 27 000, M_w/M_n = 1.25; 50.2 wt % of styrene), SI-4 (M_n = 51 000, M_w/M_n = 1.20; 50.3 wt % of styrene), SI-5 (M_n = 72 000, M_w/M_n = 1.15; 49.4 wt % of styrene), SI-6 (M_n = 98 000; M_w/M_n = 1.30; 52.2 wt % of styrene)] and that the other two are formed of three blocks [SIS-2 (M_n = 63 000, M_w/M_n = 1.30; 50.4 wt % of styrene), ISI-1 (M_n = 48 500, M_w/M_n = 1.20; 47.4 wt % of styrene)].

Results and Discussion

In a first set of experiments, we tried to generalize the preliminary results that we had obtained with copolymer SI-6[9] and to extend them to as many copolymers as possible. To this end, we repeated the study of SI-6 with five other lamellar styrene/isoprene block copolymers of different molecular weights and chemical architectures. The molecular characteristics of these polymers are specified in the preceding section. The working procedure applied was the same. The temperature was raised stepwise from 20 to about 250 °C. At each step, the sample was allowed to reach thermal equilibrium (~18 h) and then examined with X-rays (~6 h). The temperature dependence of the structural parameters observed is plotted in Figures 1 and 2.

The outcome of this work is very clear. Up to 180–200 °C, the lamellar spacing hardly changes with temperature, at least to a first gross approximation (see ref 3, 6, and 9). The sharpness and the number of diffraction lines also remain unchanged, indicating that on the whole the quality of the lamellar order and the fineness of the interfaces between the styrene and isoprene layers are not affected in a very significant way. However, above 200 °C the lamellar thickness begins to increase appreciably, attaining, and even exceeding values as high as 1000 Å. To be precise, we should emphasize that copolymer SI-3, whose molecular weight is just sufficiently[7] high so that the polymer is able to exhibit the lamellar structure, behaves differently; like copolymer SIS-1C,[10] it melts suddenly without any preliminary change of the spacing in the ordered state. We should also add that the thickening effect observed is irreversible. On cooling, the spacing does not return to its original value, at least within a reasonable time, i.e., a lapse of several days.

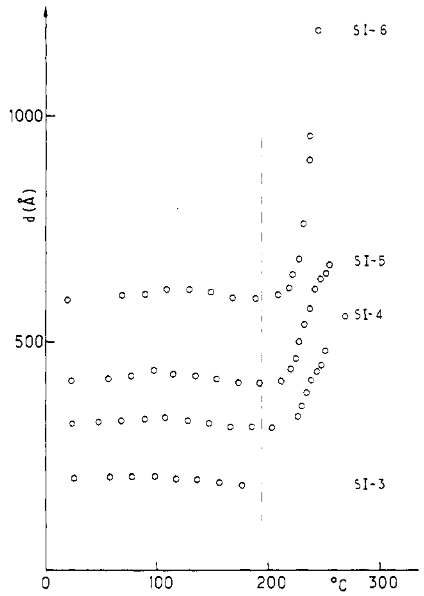

Figure 1. Variation of the lamellar spacing as a function of temperature (heating rate of about 20 °C/day) for the copolymers SI-3, SI-4, SI-5, and SI-6.

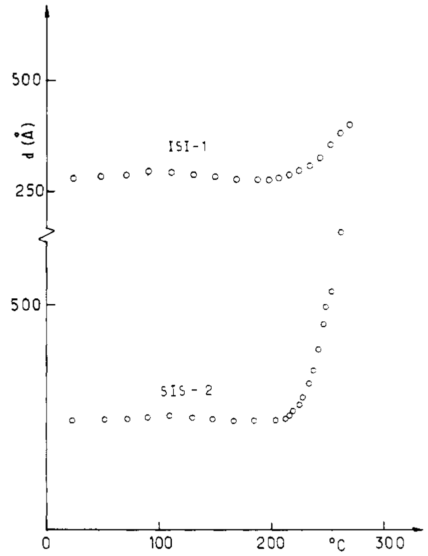

Figure 2. Variation of the lamellar spacing as a function of temperature (heating rate of about 20 °C/day) for the copolymers SIS-2 and ISI-1.

In a second set of experiments, we tried to study the kinetics of the spacing increase observed at high temperature. For this purpose, we observed the variation with time of the lamellar thickness for samples taken directly from room temperature to a given constant temperature above 180 °C. We thus noted that, far from being invariable, the spacing measured actually increased continuously with time to a considerable extent. In this evolutionary process, the Bragg reflections drew nearer to the direct beam and finally were systematically buried in the very low-angle region behind the beam stop where they could not be detected. To determine whether the spacing really diverges with time above 180 °C, whether it levels off at a certain value corresponding to a new "thick" lamellar structure, or whether the lamellar structure ends by simply disappearing, we employed electron microscopy. Quite easily we were thus able to see that, above 180 °C and after a long time, it is the last possibility that occurs. The electron micrographs taken at room temperature after the samples were allowed to cool showed no lamellar organization; they showed instead, as for the styrene/isoprene block copolymers of low molecular weight,[7] a random interspersion of small styrene and isoprene segregated microdomains.

Despite all our efforts, we could not evaluate quantitatively the kinetics of the thickening effect over a sufficiently large time/temperature range. The reason for this is that the exposure times necessary for us to register the X-ray patterns under good operating conditions were rather long ($\sim$6 h). We were satisfied, therefore, with observing the kinetics only qualitatively. We, nevertheless, came to the conclusion that the thickening process of the lamellae starts above a certain temperature, which could be situated at approximately 180 °C, and that it is more rapid at higher temperature. Thus the lamellar spacing of copolymer SI-6, which is 592 Å at room temperature, reaches only 710 Å after 1000 h at 182 °C, while it already exceeds 1000 Å after 10 h at 255 °C. To be complete, we should add that the kinetics are also more rapid the lower the molecular weight. This is why copolymer SI-3, whose very low molecular weight is just above the threshold of ordering, melts rapidly by going directly from the ordered lamellar structure to the disordered state.

The increase in lamellar thickness—which, let us repeat, is not reversible—seems consequently not to correspond to thermodynamic equilibrium. Rather it takes place during the process of fusion itself. Contrary to what happens with common crystals, which maintain constant their intensive thermodynamic properties during fusion, block copolymers seem to melt through a stage wherein their intensive properties change progressively with time.

To conclude, we can say the following. In two very recent papers,[9,10] we described the melting process of two styrene/isoprene block copolymers, one having a lamellar structure, the other a cylindrical structure. In the former case, we noted that melting proceeds through a stage where the dimensions of the segregated microdomains increase considerably with temperature; in the latter, the melting occurs suddenly, at a well-defined temperature, in exactly the same way as for common crystals. From the present study it emerges, however, that both systems behave identically, but with different kinetics of thickening of the structural elements; although slow enough so as to be easily detected in the one case, the kinetics would be extremely rapid in the other and, for that very reason, difficult to observe.

Whatever the kinetics, the interesting phenomenon is the fusion process itself. It is quite uncommon, indeed, at least for first-order phase transitions, that the system undergoes at constant temperature and pressure a quantitative change of its inherent (intensive) properties. Undoubtedly, this must be related not only to the uncommonly high viscosity of the medium but also to the very nature of the block copolymers.

The melting point of the mesophases does not appear to depend on either the molecular weight or the structure: copolymer SIS-1C, the structure of which is cylindrical, melts at about 153 °C, while the lamellar copolymers SI-3, SI-4, SI-5, SI-6, ISI-1, and SIS-2, the molecular weights of which are in the range 25 000–100 000, melt at about 180–200 °C. We should emphasize that, while the copolymers with molecular weights less than 23 000 are disordered at room temperature, all the others remain stable up to at least 150–180 °C. This is quite unexpected from a thermodynamic point of view, as the entropy (and therefore the melting point) should be a smooth function of molecular weight.

References and Notes

(1) Folkes, M. J.; Keller, A. "Physics of Glassy Polymers"; Haward, R. N., Ed.; Applied Science Publishers: London, 1973; p 548.
(2) Gallot, B. "Liquid Crystalline Order in Polymers"; Blumstein, A., Ed.; Academic Press: New York, 1978; p 191 *Adv. Polym. Sci.* **1979**, *29*, 85.
(3) Skoulios, A. "Block and Graft Copolymers"; Burke, J. J., Weiss, V., Eds.; Syracuse University Press: Syracuse, N.Y., 1973; p 121. *Adv. Liq. Cryst.* **1975**, *1*, 169.
(4) Grosius, P.; Gallot, Y.; Skoulios, A. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *270*, 1381.
(5) Douy, A.; Gervais, M.; Gallot, B. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1970**, *270*, 1646.
(6) Terrisse, J. Ph.D. Thesis, University of Strasbourg, 1973.
(7) Hadziioannou, G.; Skoulios, A. *Macromolecules*, accompanying paper in this issue.
(8) Leibler, L. *Macromolecules* **1980**, *13*, 1602.
(9) Hadziioannou, G.; Skoulios, A. *Polymer* **1980**, *21*, 845.
(10) Hadziioannou, G.; Skoulios, A. *Makromol. Chem., Rapid Commun.* **1980**, *1*, 693.