Temperature dependence of the lamellar structure of a styrene–isoprene two-block copolymer

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The lamellar structure of a styrene–isoprene two-block copolymer has been studied by low-angle X-ray diffraction as a function of temperature. It has been shown that the diffraction lines remain sharp up to ~250°C. The thickness of the lamellae, of the order of 600 Å in the range from 20°–180°C, suddenly starts increasing drastically to attain values as high as ~1200 Å. This thickening effect has been discussed briefly in terms of chain conformation, and a tentative model of local 'organization' has been suggested.

INTRODUCTION

Block copolymers are known to give well organized mesomorphic phases, characterized by a number of sharp low-angle X-ray diffraction lines. Insoluble in one another, the blocks segregate and settle down in distinct microdomains, periodically arranged in space. The size of the microdomains is typically of the order of the dimensions of the polymer chains (~500 Å), and the thickness of the interfaces is usually rather very small (~30 Å)[1–4].

The question arises as to how this type of system behaves as a function of temperature, and, more specifically, how it melts when both blocks are in the amorphous state. A systematic study of the melting phenomenon itself is now in progress and we hope to publish it soon. Our intension in this paper is to present a few preliminary observations regarding the temperature dependence of the lamellar structure of a given copolymer, and of proposing a tentative molecular interpretation of the experimental results.

The thermal behaviour of block copolymers has been much considered during the past decade. The general opinion is that the structural parameters are little affected by a change of temperature; only a slight decrease in spacing has been detected in the presence of a solvent[5,6], or in the dry state above the glass transition temperatures of the blocks[2,7]. The data we are going to describe in this work complement those previously quoted in a rather unexpected way.

EXPERIMENTAL

Materials

The polymer we have studied is a styrene–isoprene two-block copolymer synthesized *in vacuo* by anionic polymerization in benzene, using secondary butyllithium as an initiator. Its number-average molecular weight, $\bar{M}_n$, = 98 000, and its styrene content is 54% by wt. Its lamellar structure corresponds to the periodic and alternate pile-up of polystyrene and polyisoprene layers of approximately the same thickness (~300 Å at 25°C). The samples were all oriented to form large single crystals[8], and the low-angle X-ray patterns were recorded using a gold-plated glass mirror: the exposure times were thus rather short (a few hours). However, some of the diffraction patterns were obtained using a bent-quartz monochromator, in order to show that the Bragg reflections are very sharp and that the lamellar structure developed perfectly throughout the whole temperature range explored.

Experiments

These were carried out as follows. The temperature was increased stepwise from 20° to approximately 250°C. At each step, the sample was allowed to reach thermal equilibrium (~18 h)*. The diffraction pattern was then registered, and the corresponding Bragg spacing was deduced (*Figure 1*). In order to avoid any major irreversible chemical change of the polymer, we worked *in vacuo*. We checked for crosslinking and degradation using a variety of physicochemical tests (e.g. solubility, g.p.c.) we found that no crosslinking and little chain scission had occurred (the number average molecular weight reduction was less than 5%).

RESULTS AND DISCUSSION

Close inspection of *Figure 1* permits two observations. Firstly, we consider the thermal behaviour of the system at temperatures lower than 180°C. In agreement with the experimental data first reported by Terrisse[7,9], the spacing seems to increase slightly with temperature in the range from 20° up to 110°C, then to decrease to reach, and even to go below, the initial value of 592 Å. In all probability, this is due to the difference in thermal expansion of polyisoprene and polystyrene, especially around the glass transition of polystyrene. Secondly, our discussion on the thermal behaviour of the system above 180°C constitutes the

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* The kinetics of the change in spacing, especially at high temperatures, is now under study

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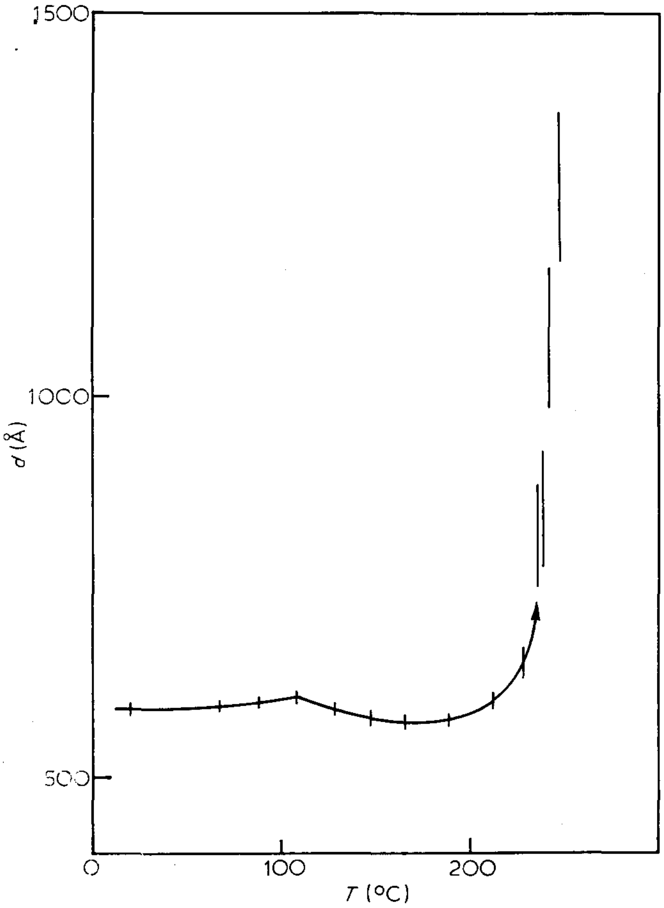

Figure 1 Bragg-spacing of the lamellar structure as a function of temperature

main point of our paper. At about 180°C, the spacing begins to increase again with temperature, and it attains large values very rapidly (~1200 Å), twice as large as those quoted at room temperature.

Before analysing this dramatic thickening of the lamellae, it is worth considering some complementary experimental observations. The number of the diffraction lines in the X-ray patterns is ~10 for the whole temperature range from 20°–200°C; the interfaces between the polystyrene and polyisoprene layers therefore seem to remain fairly sharp[7,9] up to rather high temperatures. Beyond this limit, the number of diffraction lines decreases very rapidly down to only 3 at 248°C. Apparently, the interfaces then become diffuse, in agreement with what one would predict from elementary thermodynamic considerations on miscibility. However, the progressive extinction of the diffraction lines might also be related to the loss of orientation of the single-crystalline specimen which is kept in a rigid sample-holder and which is therefore submitted to strong internal flow due to the thickening of the lamellae. On further heating above 250°C, the X-ray patterns become devoid of any diffraction signal; without ruling out the possibility of a gathering of the diffraction lines in the very low Bragg-angle region, just behind the beam stop where they can hardly be detected, one is tempted to conclude that the mesomorphic phase has become molten. On subsequent lowering of the temperature, the X-ray patterns remain blank; this might be due to the loss of the single-crystalline orientation of the sample, or else to the high viscosity of the medium which holds up the change of structure, and, in case the system had become molten, to the usual hysteresis which goes with first-order transitions.

The rapid and large increase of the Bragg spacing on approaching 250°C is so distinct that we feel justified in trying to give it physical meaning. According to the prevailing ideas on bulk polymers, the polystyrene and the polyisoprene blocks should each have in its own layer the conformation of a random coil[10], and should therefore be deeply interpenetrated and jumbled together in great disorder. With this picture in mind, however, it is difficult trying to imagine how the thickness of the lamellae could increase so readily with temperature: either the polymer coils elongate a great deal parallel to the normal to the interfaces, or they partially disentangle so as to pass from a 'monolayer' to a 'bilayer' disposition*. Entropically unfavourable, both changes could presumably happen only if the mixing of the incompatible blocks at the interfaces modified sufficiently the local energetics so as to bring about the reduction of the extension of the interfaces.

Recent neutron-scattering measurements of the radius of gyration of the polystyrene blocks around the normal to the interfaces[11], and also X-ray studies of the dependence of the lamellar thickness on molecular weight[12], do not really favour such a perfect random-coil conformation for the blocks. Instead, they seem to better support a model of elongated, little interpenetrated and rather compact polystyrene chains, the lateral extension of which would be small compared with that of a random coil. From this point of view, the important increase of the Bragg spacing as a function of temperature (*Figure 1*) would indicate a change in the conformation of the coils, which would strongly expand above a certain temperature and deeply interpenetrate one another. This change would be altogether similar to what is currently observed in the presence of solvents when the temperature is raised above its θ-value.

Further neutron scattering and X-ray diffraction studies are necessary for this point of view to be better supported and definitely accepted. We feel it is of interest to analyse it here without waiting longer for some of its aspects, and to present some tentative implications for understanding bulk polymers in the amorphous state. What this interpretation amounts to is that, at low temperature, the chains in the bulk should have a locally collapsed conformation, corresponding to a succession of collapsed Kuhn subchains linked together. The polymer molecules should interpenetrate one another little on a local scale and should be considered as hardly miscible. At high temperature, the chains would adopt the usual expanded conformation of what is agreed upon as a Gaussian coil; they would then mix up intimately, deeply interpenetrate one another and get strongly entangled. Thus, the mutual solubility of polymer chains, even if they were of the same chemical nature, appears to proceed on a scale which is a function of temperature. This effect must not be confused, of course, with the usual phase transition; it merely corresponds to a subtle evolution of the short range distribution of monomer units. Although it is progressive, it is, however, detected at a temperature which is easy to define accurately.

The conformational change reported in this paper has been observed for the polystyrene blocks of a styrene–isoprene two-block copolymer presenting a lamellar structure. Yet, it corresponds remarkably well to what has been claimed to be a liquid–liquid transition for high molecular weight

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* Further X-ray diffraction experiments will hopefully help us determine whether the spacing really diverges in the vicinity of the 'melting point', or if it levels off beyond a certain temperature at a value corresponding to double the coil dimensions

polystyrenes ($T_{ll} \sim 180°C$)[13]. At this transition, the activation energy of the viscous flow increases significantly with temperature. According to our model, this could be due to the onset of entanglements among the expanding coils. If the locally collapsed conformation that we have suggested previously is correct, then it will become necessary to use it in order to interpret the properties of amorphous polymers in the bulk: plasticity, glassy state and plastification, mechanical properties, . . .

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11 The radius of gyration of the polystyrene blocks around the normal to the interfaces was found to be abnormally small compared to the radius of gyration which might be expected for a Gaussian chain attached to an interface (G. Hadziioannou *et al.*, to be published)

12 The variation of the lamellar thickness as a function of molecular weight for two-block styrene–isoprene copolymers and as a function of molecular weight *divided by two* for three-block copolymers was found to be identical. This indicates that the free ends of the polystyrene blocks are not distributed uniformly throughout the whole polystyrene sublayer, but rather located near the centre of it, giving rise to a 'bilayer' organization (G. Hadzilioannou *et al.*, to be published)

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