Eutectic solidification and oriented growth in mixtures of polyethylene and 1,3,5-tribromobenzene

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(*Received* 16 *September* 1981)

The melting and crystallization behaviour of mixtures of linear polyethylene and 1,3,5-tribromobenzene has been investigated by differential scanning calorimetry, optical and electron microscopy. The phase diagram reveals the existence of a pseudo-binary eutectic (polymer volume fraction of about 58%; T_m=116°C). The experimental observations are compared with the predictions of the Flory–Huggins theory of melting point depression. The polyethylene component of the eutectic assumes a habit in which lamellae are highly oriented with the chains in the [110] contact plane parallel to the tribromobenzene needle axes. This well defined orientation is most probably based on an epitaxial relation between polymer and substrate.

Keywords Polymers; eutectic solidification; morphology; oriented growth; polyethylene; binary mixtures

INTRODUCTION

The preparation and properties of binary eutectic systems in which at least one of the components is a polymer have recently received some interest. In one of the first detailed studies of such systems, Smith and Pennings[1] have shown that mixtures of polyethylene and 1,2,4,5-tetrachlorobenzene form a pseudo-eutectic solid with a melting point depressed by about 15°C compared with that of the pure polymer.

Similar results were obtained by Wittmann and St John Manley for other polymer–non-polymer eutectic systems, namely poly(ε-caprolactone)–trioxane[2] and poly(ethylene oxide)–trioxane[3]. In the first of these systems, it was also observed that in the hypoeutectic mixtures, the polyester crystals deposit epitaxially on the freshly grown trioxane substrate crystals, thus providing one of the first examples of polymer epitaxy on an organic substrate. In addition, the *in situ* solid-state polymerization of trioxane into polyoxymethylene in such highly oriented systems offers an interesting means to create a novel type of polymer–polymer composite[4]. Further investigations of the epitaxial growth of polyethylene and linear polyesters were conducted using both condensed aromatic hydrocarbons and linear polyphenyls as crystallizable solvents and substrates[5,6].

In this paper, we report the crystallization and the crystalline morphology of the binary system polyethylene–1,3,5-tribromobenzene which again displays both eutectic solidification and oriented growth of the polymer crystals.

EXPERIMENTAL

The high density polyethylene used was Marlex 50 but similar behaviour was observed with other whole polymers and also narrow fractions. The polymer was used in powder form if necessary after freeze-drying of the manufacturer's pellets. The 1,3,5-tribromobenzene (Fluka high purity grade) was used as supplied.

The phase diagrams were determined by differential scanning calorimetry (Perkin Elmer DSC 1B) on 4 mg samples of the weighed mixtures having various compositions sealed in d.s.c. sample pans. The thermal treatment was initial melting at 160°C for 15 min (to homogenize the mixtures) followed by cooling at 64°C min^{-1} to 85°C; melting endotherms were subsequently recorded at heating rates of 2, 4, 8 and 16°C min^{-1}.

The morphology of the recrystallized mixtures was investigated using a variety of optical and electron microscopic techniques. In all cases, the samples were crystallized under known conditions from prehomogenized mixtures (160°C, 1 h) in the form of films between microscope slide and cover slip. After selective dissolution of the tribromobenzene crystals in acetone, the residual polymer structures were examined in the electron microscope either as such or after gold enhancement. Thicker polymer films were etched with a permanganic reagent (5 min at 20°C) followed by detachment replication[7] (5 min at 99°C in xylene). Finally, the particular sample examined by scanning electron microscopy was crystallized by passing (at a speed of 3 mm min^{-1}) in a temperature gradient (10°C mm^{-1}) while kept in a sealed tube to avoid evaporation of the solvent.

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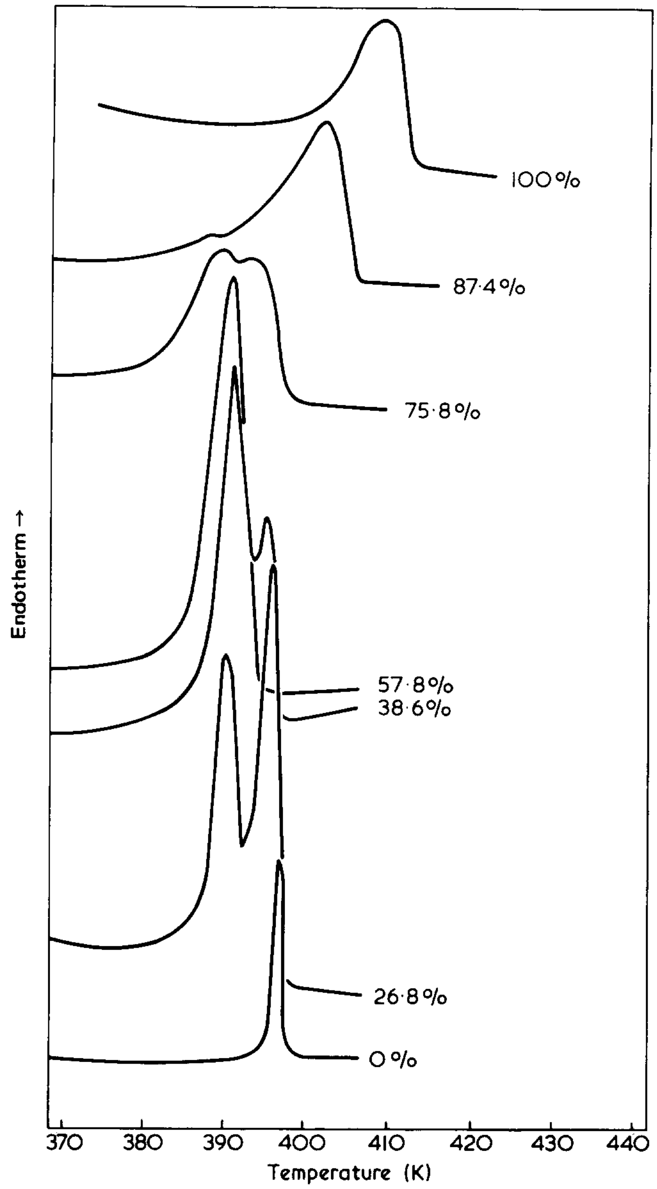

Figure 1 Representative melting endotherms (at 8°C min^{-1} scan speed) for polyethylene—1,3,5-tribromobenzene mixtures with volume percentage of PE as indicated

RESULTS

Calorimetry

Examples of the d.s.c. melting endotherms obtained for various polyethylene-tribromobenzene mixtures are shown in *Figure 1.* Apart from the pure components, only a mixture with ~30% by weight of polymer corresponding to the eutectic composition displays a single peak. The phase diagram shown in *Figure 2* has been drawn up by plotting against the polymer volume fraction the peak melting temperatures of the eutectic (open circles) and the end melting temperature for the higher peaks (triangles), both after extrapolation to zero scan speed[1]. In converting from weight to volume fractions, the density of molten polyethylene was taken as 0.80 and that of tribromobenzene as 2.5 g cm^{-3}. In the absence of literature values, the latter one was obtained by extrapolating from densities of mono- and 1,3-dibromobenzene, a procedure which gives good results for the corresponding series of chlorobenzenes[8,9].

The eutectic composition derived from *Figure 2* is approximately 58% polyethylene by volume and the eutectic solid has a melting temperature of 116°C, compared with 122.5°C and 134.5°C for pure tribromobenzene and polyethylene respectively when measured under the same conditions.

The curves presented in *Figure 2* can be compared with those predicted by the following simplified equations[1]:

$$\frac{1}{T_{m,1}}-\frac{1}{T^{\circ}_{m,1}}=-\frac{R}{\Delta H_1}[\ln\varphi_1-\varphi_1+1+\chi(1-\varphi_1)^2] \qquad (1)$$

for the diluent liquidus curve, and

$$\frac{1}{T_{m,2}}-\frac{1}{T^{\circ}_{m,2}}=\frac{R}{\Delta H_u}\frac{V_u}{V_1}(\varphi_1-\chi\varphi_1^2) \qquad (2)$$

for the polymer liquidus curve.

ΔH_1 is the molar heat of fusion of the solvent at the thermodynamic equilibrium melting point $T^{\circ}_{m,1}$, φ_1 and φ_2 the volume fractions of the diluent and the polymer respectively, χ the Flory–Huggins interaction parameter, R the gas constant, ΔH_u the heat of fusion per mole structural unit of the polymer at the thermodynamic equilibrium melting temperature $T^{\circ}_{m,2}$; V_u is the molar volume of the polymer structural unit and V_1 the molar volume of the diluent.

By substituting values of $R=1.98$ cal deg^{-1} $mole^{-1}$ and $\Delta H_1=5000\pm300$ cal $mole^{-1}$ in equation (1), the best fit to the diluent liquidus (solid line on the left hand side of *Figure 2*) is found for $\chi=0.55$, neglecting its concentration and temperature dependence. Taking this value for χ and values for $\Delta H_u=980$ cal $mole^{-1}$, $V_u=14.6$ cm^3 $mole^{-1}$, $V_1=125.9$ cm^3 $mole^{-1}$, $T^{\circ}_{m,2}=146.5$°C[10], and substituting in equation (2) gives the dot–dash line in *Figure 2*, which, as already noticed in previous studies[1,2], is far from the experimental values. This discrepancy appears to be due to the fact that the melting point depression theory applies to the equilibrium state which is hardly ever reached with

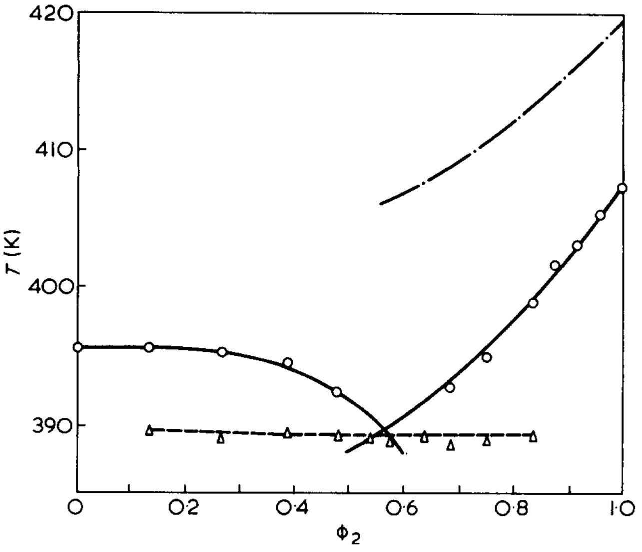

Figure 2 Phase diagram of the binary system polyethylene—1,3,5-tribromobenzene. Peak melting temperatures of eutectic (△) and end melting temperatures of pure component in excess (○) (extrapolated to zero scan speed), as a function of polymer volume fraction ϕ_2. Solid and dot-dashed lines have been derived from the Flory—Huggins theory of melting point depression (see text)

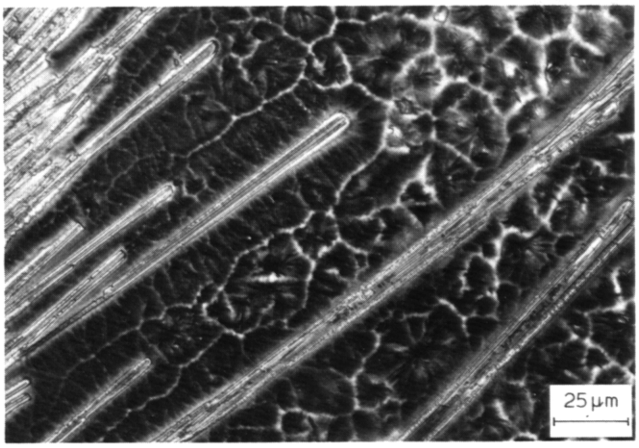

Figure 3 Detail of the edge of a spherulite showing first formed tribromobenzene needles surrounded by the eutectic phase crystallized later. Sample initially containing 41% by volume of PE, photographed in phase contrast after dissolution of the tribromobenzene

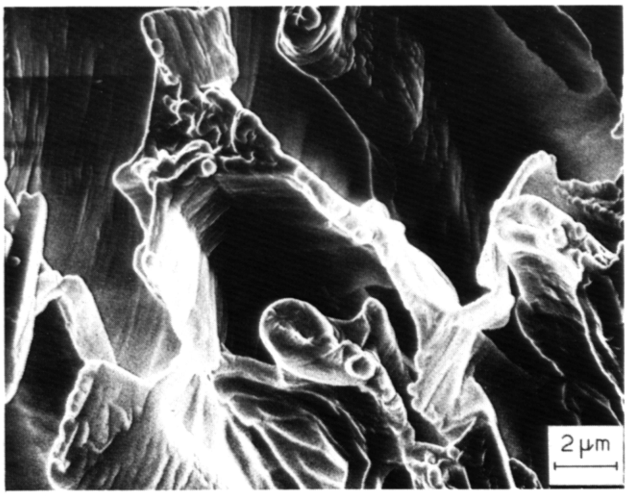

Figure 4 Scanning electron micrograph of a sample with 14% by volume of PE crystallized in a temperature gradient viewed at an angle to the channels remaining after dissolution of the tribromobenzene needles

polymer crystals[11]. Taking however the experimental value for ΔH_u (i.e. 690 cal mole^{-1}) and the measured melting temperature of the pure polymer, the agreement with the experimental curve becomes remarkable (solid line on the right hand side of *Figure 2*).

Morphology

Overall morphology. As already described for similar systems, crystallization of hypereutectic mixtures (i.e. PE rich mixtures) yields common morphologies. The initial crystallization of excess pure polymer results in a somewhat open spherulitic structure within which the eutectic mixture subsequently crystallizes.

Crystallization of the hypoeutectic mixtures (i.e. tribromobenzene rich) was investigated more intensely since it gives rise to unusual morphologies and yields more information on the polymer–solvent interactions. When quenched from the melt, the two step crystallization of such mixtures results in very large spherulites (often more than 1 cm in diameter) composed of long radiating needles of tribromobenzene surrounded by the solid eutectic fraction.

After selective dissolution of the tribromobenzene, the polymer spherulites remaining are found to be optically positive, implying that the PE chain axis is radial, in sharp contrast with its usual tangential orientation in bulk crystallized samples. This conclusion is further supported by several optical and electron microscopic observations of molecular orientation in the polyethylene.

Figure 3 shows a phase contrast micrograph of a thin region at the edge of a spherulite after selective dissolution of the tribromobenzene. The eutectic mixture is, in most cases, nucleated as a distinct transcrystalline layer around the radiating needles. In fact, as seen in scanning electron micrographs of a hypoeutectic sample crystallized in a temperature gradient (*Figure 4*), these tribromobenzene needles have a polygonal cross section. Furthermore, all the facets of these needles are covered with a transcrystalline layer of PE which forms the walls of the polygonal holes left after dissolution of the solvent.

The orientation of the constituent polymer stacks of lamellae is most clearly seen in *Figure 5* which shows a photomicrograph of a thin film of PE deposited in a highly ordered fashion on both sides of fairly large tribromobenzene crystals. It is interesting to note that in one rectangular zone, this polyethylene film has been broken during sample preparation. Deformation has occurred, resulting in fibres being pulled across the gap. The sites from which these fibres emanate are clearly defined and, in one case, a 'twisted loop' fibre still attached at both ends suggests the unravelling of polymer chains which occurred during deformation.

Fine structure: oriented growth. Still smaller scale detail in the polyethylene layers was exposed by transmission electron microscopy.

Figure 6 shows lamellae lying edge-on to the surface of a gold enhanced polymer film and approximately perpendicular to the direction of the spherulite radius (located by inspection of larger areas) i.e. again the exact opposite from that of pure bulk-crystallized polyethylene.

In these thin films, the lamellae are generally grouped into small stacks separated by more or less distinct spaces which are possibly the sites of tribromobenzene in the eutectic prior to dissolution. In many cases, lamellae are pleated at an angle, sometimes repeatedly. In *Figure 7* which is a micrograph obtained from an extremely thin film, the field of view is virtually covered with a network of such angled polymer lamellae.

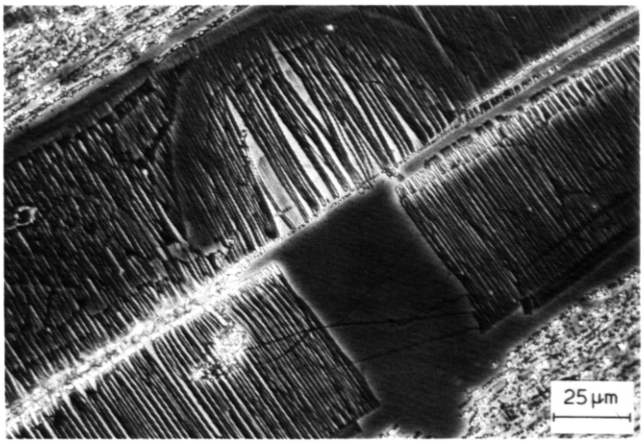

Figure 5 Highly oriented thin film of PE deposited on top of large tribromobenzene needles. Phase contrast photomicrograph

Figure 6 Lamellar structure revealed by gold decoration on the surface of a thin film prepared from a 14% by volume PE mixture

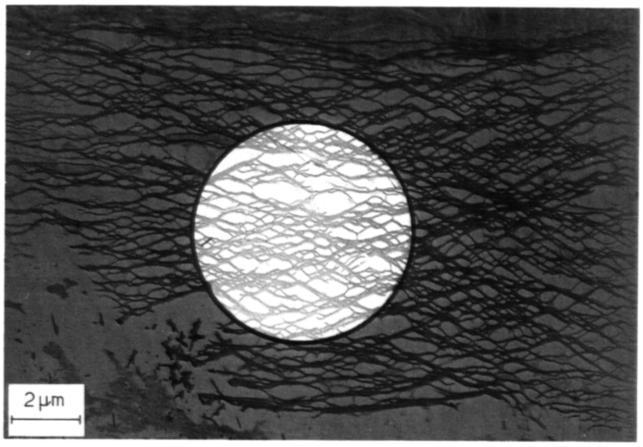

Figure 7 Bright field electron micrograph of a network of angled lamellae in a very thin oriented PE film (the bright circled area was selected for electron diffraction)

From the electron diffraction patterns obtained from these highly oriented thin films (*Figure 8*), it is obvious that epitaxial growth resulting in a unique polymer chain orientation is at play. As deduced from the positions of the 002 reflections, the chain axis of the polymer, *c*, is parallel to the spherulite radius, i.e. parallel to the tribromobenzene needle axis.* The diffraction pattern shows this single *c* axis orientation even when the lamellae are angled, which means that the chain axis is perpendicular to the planar lamellae but must be inclined at an angle to the basal surfaces of the angled lamellae. The presence on the equator of intense 310 and 210 reflections further indicates that the polymer planes in contact with this organic substrate are the crystallographically dense [110] planes (a [110] plane is indeed nearly perpendicular to the [$\bar{3}$10] plane which is therefore in diffracting position).

The observations made so far for thin films are also valid for thicker ones, which are more representative of bulk crystallized samples. *Figure 9* is a bright field electron micrograph of an etched thicker film. The black bands are probably the residual polyethylene walls of the cells initially containing the pure tribromobenzene. Again, around the tribromobenzene needles transcrystalline layers of approximately planar lamellae can be identified together with a considerable proportion of angled lamellae. These are reminiscent of the ridged crystals (as viewed down their length parallel to *b*) formed during the slow crystallization of certain polyethylene fractions at low supercooling from the melt[13]. The angle between adjacent facets is larger here than the average value of 104° reported in that case.

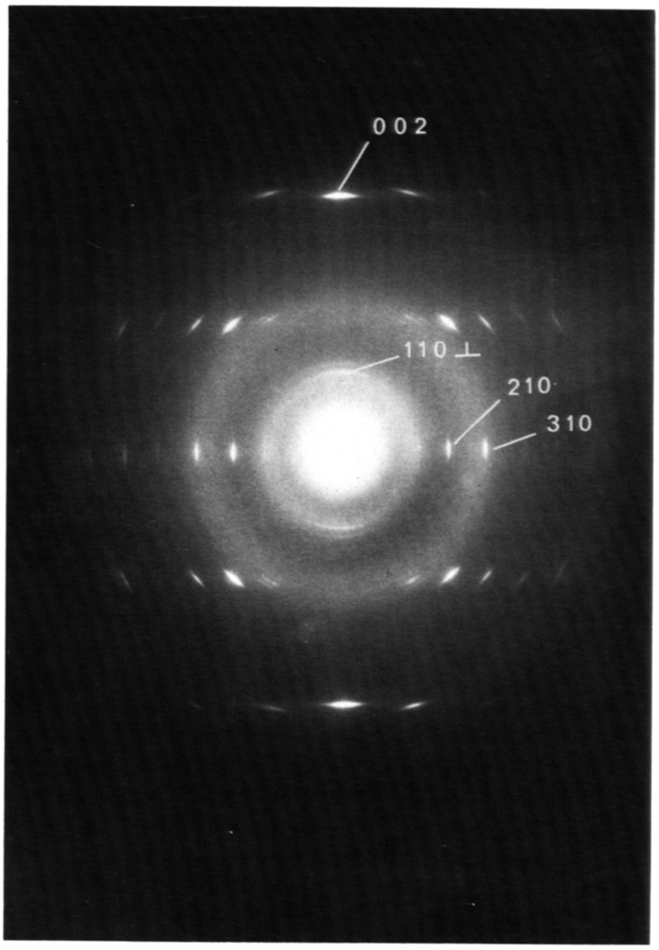

Figure 8 Electron diffraction pattern from thin oriented layer of PE as in *Figure 7*

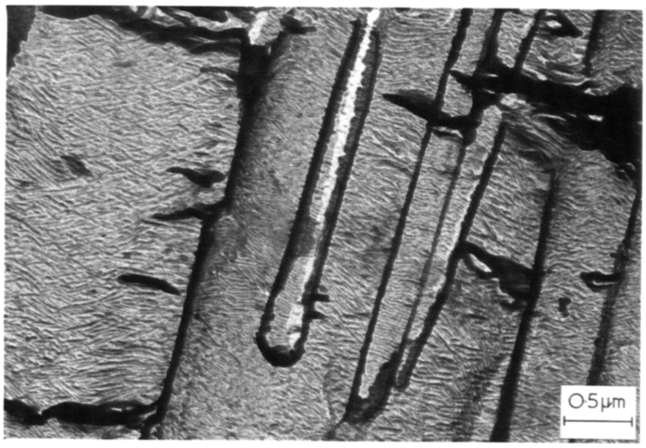

Figure 9 Lamellar structure exposed by etching and detachment replication of a fairly thick film sample initially having 41% by volume of PE

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* Electron diffraction patterns of pure tribromobenzene needles grown from the melt show that the needle axis is parallel to the *c* axis of the orthorhombic unit cell (with $a = 14.23$ Å, $b = 13.55$ Å and $c = 4.08$ Å[12])

The electron diffraction patterns from etched films are characterized by the presence of additional strong 110 reflections on the equator, which are not normally observed for oriented thin films. The presence of these reflections, which suggests the existence of two sets of [110] PE planes almost at right angles to each other but with a common chain axis orientation is linked to the growth of polymer crystals on the side faces of the tribromobenzene needles. Indeed, if not only the top and bottom but also the side faces of these needles belong to a same set of say [*hk*0] planes, epitaxial growth with [110] contact planes of PE on these side faces would bring the [110] polymer planes into reflecting position.

Additional features of the polyethylene crystallization in the presence of tribromobenzene are more readily apparent in thin films than in thicker ones. As is best visualized in the gold enhanced thin films (cf. *Figure 6*) a number of fibres lying parallel to the spherulite radius link adjacent lamellae across the gaps already noted. Furthermore, small subsidiary fibres in turn bridge these interlamellar links and thus lie approximately perpendicular to them. The presence of the first type of links (with an assumed fibre symmetry) offers an alternative explanation for the presence of 110 (and 200) reflections observed on the equator of the diffraction patterns recorded for thick films and sometimes also for fairly thin ones. The subsidiary links would in turn give rise to the faint and broad 110 reflections on the meridian (cf. *Figure 8*) which implies the presence of chains oriented with their *c* axes perpendicular to the general chain direction.

DISCUSSION AND CONCLUSION

The system PE–tribromobenzene under investigation belongs to the class of pseudo-binary polymeric mixtures containing a crystallizing solvent. Such binary systems, may, as recently discussed by S. P. Papkov[14], lead to various types of phase diagrams according to whether the low molecular weight material is well above or below its melting temperature or whether the polymeric component remains in the liquid or glassy state or becomes crystalline upon cooling. Among the systems considered by Papkov, the more relevant ones are:

(i) binary mixtures involving the precipitation or crystallization of the organic compound out of a polymeric glassy solution. The properties and morphology of two phase systems with amorphous polymer matrices and *in situ* crystallized organic components have been studied by Kardos *et al.*[15] and more recently by Narkis *et al.*[16,17]. As suggested by these authors, such systems may after precipitation or oriented crystallization of the low molecular weight component, give rise to polymer composites or materials with highly anisotropic properties.

(ii) a second class of polymeric binary systems display eutectic type phase diagrams due to the simultaneous crystallization of the polymer and the low molecular weight species. If the organic solvent forms with the polymer a congruently melting molecular complex or crystallosolvate, the phase diagram exhibits two eutectic points separating the molecular complex from the pure components (as for example with PE–perhydrotriphenylene[18] or poly(ethylene oxide)–resorcinol mixtures[19]). More often however, as shown in a number of previous studies and in the present for PE–tribromobenzene mixtures, the phase diagrams of systems containing a semi-crystalline polymer and a crystallizable solvent exhibit a single eutectic point.

The general conditions required for the formation of a polymeric eutectic solid are miscibility of the components in all proportions in the liquid state (one phase system) and total immiscibility in the solid state (two phase system). An additional condition is that the melting temperatures of the pure components do not differ appreciably[1], a condition satisfied by the binary system under investigation here.

The eutectic point being defined as that point at which a solution is in equilibrium with two different solid phases, the composition and temperature at which it occurs can be estimated theoretically by calculating the solvent and polymer liquidus with help of the Flory–Huggins equilibrium melting point depression theory. In order to plot the theoretical polymer liquidus, one must estimate the Flory–Huggins interaction parameter χ. This is done by first fitting the experimental solvent liquidus which is relatively constant, rather than the polymer liquidus which is known to vary considerably with the crystallization conditions[1,2]. Doing so, the calculated polymer liquidus is found to be markedly different from the experimental one. The use of experimentally determined polymer melting temperature and heat of fusion to fit the calculated and experimental polymer liquidus is not rigorous since the Flory–Huggins theory applies, in a strict sense, to equilibrium conditions. This procedure results in a correct description of the system's behaviour. In this respect, we may note that the eutectic composition is slightly shifted to lower polymer concentrations and that the parameter χ has a rather high value. The phase diagram shown in *Figure 2* is characteristic of systems with relatively unfavourable polymer–solvent interactions, as reflected for example by the flatness of the solvent liquidus curve.

Although the polymer–solvent interactions in the liquid state are rather weak, the crystalline morphology displayed by solidified hypoeutectic mixtures of PE–tribromobenzene reveal specific interactions between the crystallizing polymer chains and the crystalline solvent substrate. The resulting polymer structure is characterized by the fact that in the layer nearest the substrate surface, the chain axes are oriented in a single direction, parallel to solvent needle axes, and that the [110] closest-packed plane is in contact with that substrate surface. Our attempts to determine the exact nature of the latter surface have failed, since it has not been possible to obtain diffraction patterns from polymer and substrate together. Electron diffraction could be performed on thin tribromobenzene crystals grown from the melt, which showed that in this case, the most extended growth faces are [110]. Assuming that these growth faces are also present in the PE–tribromobenzene mixtures, the structural relationship between polymer and substrate contact faces is not readily apparent: indeed, while the specific mutual orientation of polymer and substrate suggests a definite epitaxial relationship, lattice matching can only be found when considering periodicities corresponding to multiples of the fundamental unit cell dimensions. Although such large periodicities have already been considered in the past, they do not lend strong support to an epitaxial deposition mechanism. Alternatively, other growth faces of tribromobenzene may well be present in the polymer–solvent mixtures, as suggested for example by the polygonal, rather than square, cross-section of the tribromobenzene needles evident in *Figure 4*. If these growth faces were [100] or [010], matching of substrate and lateral packing of polymer chains would be more readily apparent (for example 13.55 Å compares favourably with 3 times the 4.45 Å interchain distance in the PE [110] contact plane). A detailed discussion of the nature of the substrate interactions therefore remains speculative at this stage and further, more conclusive evidence is needed before it can be settled.

In spite of this uncertainty, it remains that the present system provides a further example of polymer/low molecular weight, crystallizable solvent mixture in which a combination of eutectic solidification and oriented growth of the polymer on the freshly formed solvent crystals results in highly anisotropic films. Such films, made of stacks of lamellae standing edge-on and tied by interlamellar links are a rather faithful model of the lamellar organization in melt crystallized polymers, and may therefore be used for investigations of, for example, deformation processes[20], in addition to their increasing use in crystal structure determinations[21–24].

ACKNOWLEDGEMENTS

The authors wish to thank K. Kiss for helpful assistance in scanning electron microscopy and A. Schierer for the photographic work. Financial support for this work was provided by the Délégation Générale à la Recherche Scientifique et Technique (DGRST no. de décision 78 7 1030).

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