Compound formation in binary mixtures of polyethylene with fused-ring aromatic molecules

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The phase diagrams of the systems low-density polyethylene–acridine and high-density polyethylene–phenazine have been determined using differential scanning calorimetry. Three eutectics and two compound crystals were observed in the LDPE–acridine system whereas two eutectics and one compound crystal were detected in the HDPE–phenazine system. The LDPE–acridine system shows additional changes in the solid state due to the crystal–crystal transformation of acridine from orthorhombic to monoclinic. High-temperature X-ray diffraction studies have confirmed the accuracy of the phase diagram. The X-ray diffraction patterns of the individual compound crystals have been determined but the unit cells have not yet been elucidated.

(Keywords: binary mixtures; polyethylene; aromatic molecules)

INTRODUCTION

Many of the successes of modern physical metallurgy in controlling physical properties through alloying depend on the existence of compound crystals. In polymeric binaries, compound crystals are virtually unknown, as is the partial solubility of one component in the crystals of the other, common to most metallic binaries. Binary systems constituting one polymer with an organic molecule have received little attention. The first study involving polyethylene was that of Smith and Pennings[1,2] in which the high-melting diluents 1,2,4,5-tetrachlorobenzene and hexamethylbenzene were used, leading to eutectic mixtures. Recently the system polyethylene–1,3,5-tribromobenzene was investigated by Hodge *et al.*[3]. It proved to be a simple eutectic, also having interesting oriented growth mechanisms.

Attention has also been paid to binaries involving a polar polymer. The systems poly(ethylene oxide)–trioxane[4] and poly(ε-caprolactone)–trioxane[5] have been investigated extensively, but again only single eutectics were observed. A compound has been reported in the system poly(ethylene oxide)–resorcinol[6]. In the system polyurethane–urea[7], a compound was claimed on the basis of spectroscopic evidence. Molecular complexes are known in cellulose–dye systems[8] and polycarbonate–dye systems[9] which are also believed to be crystalline in nature. In the latter case special photoconducting properties resulted. One report of non-polar compound formation is to be found in the literature[10] and involves polyethylene with perhydrotriphenylene.

Our interest in this subject arose from long-term research on the ability of stretched polyethylene to orient fused-ring aromatic molecules[11–13]. It was recently demonstrated that the orientation mechanism is epitaxial crystallization of the solute molecules on the (1 1 0) and (1 0 0) faces of polyethylene crystals exposed during drawing to the microfibrillar state[14,15]. It was decided to determine the phase diagrams in order to ascertain whether the epitaxial crystallization was simply adventitious or whether the aromatic molecules were trying to enter the polyethylene crystal for thermodynamic reasons. The result was the discovery of complex phase diagrams containing compound formation.

EXPERIMENTAL

The polymers used were a low-density polyethylene (Dow 530) having a weight-average molecular weight of 73 342 and M_w/M_n of 9.48 and a high-density polyethylene (DuPont of Canada; Sclair 2907) having a weight-average molecular weight of 61 000 and a polydispersity of 3.5. The aromatic molecules were obtained from Aldrich Chemicals (Gold Label; >99.5% pure) and were not further purified. They were acridine (three linear fused rings with a nitrogen atom replacing the 9-CH of the central ring of anthracene) and phenazine (three linear fused rings with nitrogen atoms replacing both the CH groups of the central ring). The melting points of acridine and phenazine are 110 and 177°C respectively.

Samples were prepared using either of the polyethylenes in powder form. Powder was made by dissolution of pellets in *p*-xylene at 130°C followed by dropwise addition to methanol cooled by dry ice. The polyethylene powder was collected by filtration followed by two washings with methanol and drying in a vacuum oven at 50°C for 48 h. Absence of xylene and methanol was confirmed by infra-red spectroscopy.

The polyethylene used was chosen so that the melting-point difference between the polymer and the aromatic molecule was minimized. Samples for differential scanning calorimetry were prepared by weighing 2–3 mg

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of a chosen composition and sealing in aluminium volatile-sample pans. The samples were weighed before and after each run to ensure an absence of sample loss. The samples were melted in a Perkin–Elmer DSC7 differential scanning calorimeter to at least 10°C above the melting point of the highest-melting component and the temperature held for 15 min. Cooling to ambient temperature was then achieved at a rate of from 2.5 to 80°C min^{-1}. Melting endotherms were then obtained at a heating rate of 10°C min^{-1}. Specimens were cycled to ensure reproducibility of data acquisition.

Specimens for X-ray diffractometry were prepared as thin films between coverslips in a Mettler hot stage mounted on a Reichert microscope using the same heat treatments as were used in the preparation of d.s.c. specimens. X-ray diffractometry was carried out on a Rigaku-Denki X-ray diffractometer in a high-temperature cell having beryllium windows. A copper–constantan thermocouple was touching the sample as close to the beam spot as possible. The cell was made from an aluminium block having built-in heat exchangers. Temperature was controlled through a combination of cartridge heaters and heated silicone oil circulating through grooves.

RESULTS

Low-density polyethylene–acridine

The polyethylene had a melting point of 109.0°C whereas acridine shows both a melting point (110°C) and a crystal transformation from monoclinic to orthorhombic at 104°C. A typical melting curve of a polyethylene–acridine mixture is shown in *Figure 1*, the two peaks corresponding to a eutectic and the melting of a compound. When the specimens were cooled from the melt at 80°C min^{-1}, time–temperature–transformation effects occurred, as occur in metallic systems, resulting in non-equilibrium diagrams. Cooling at a rate of 10°C min^{-1} was slow enough to produce ‘equilibrium’ phase diagrams. The phase diagram of polyethylene–acridine is shown in *Figure 2*. Three eutectic points can be seen at 28.5, 78 and 96 % (by weight) acridine and located at 104, 104.9 and 108.85°C respectively. Two compounds can be observed at 50 and 84 % acridine. The phase transformation from orthorhombic to monoclinic acridine can also be seen when acridine crystals are present, but no similar transformations occurred for the compound crystals.

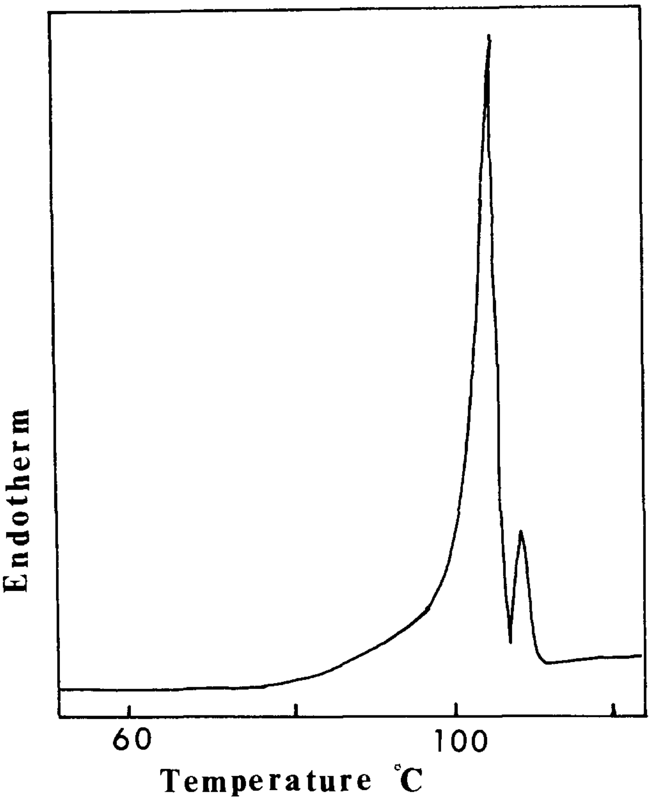

Figure 1 Melting curve of a mixture of 54.8 % acridine and 45.2 % low-density polyethylene

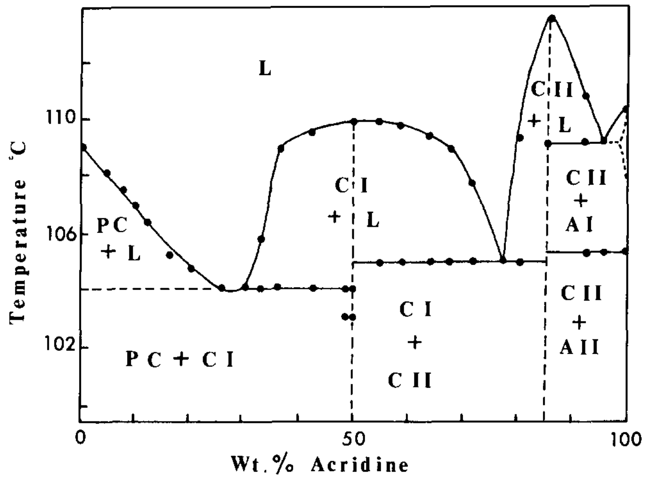

Figure 2 Phase diagram of acridine and low-density polyethylene: PC, polymer crystals; L, liquid; CI, compound I; CII, compound II; AI, orthorhombic acridine; AII, monoclinic acridine

X-ray diffraction patterns taken at ambient temperature confirm the presence of new phases. Patterns for pure acridine, pure LDPE and a 66/34 LDPE–acridine mixture are shown in *Figure 3*. This specimen should contain both LDPE and compound I. The polyethylene (2 0 0) peak can be resolved but it is of lower intensity than normal, as expected. The (1 1 0) peak is now combined with a new intense peak occurring ~ 1° higher. Additional new broad peaks can be seen and none of the major acridine peaks can be detected. A pattern for 53/47 LDPE–acridine is also shown in *Figure 3* and should be composed of mainly compound I diffraction peaks. This situation clearly exists.

Two mixtures have been studied as a function of temperature in order to observe changes occurring between 25°C and the single-phase compound regions. First a specimen of composition 37.8/62.8 LDPE–acridine will be considered (*Figure 4*). Several changes do occur, some of which are major. The phase diagram indicates the presence of both compounds I and II, with compound I predominating at temperatures below 104.9°C but compound I alone above that temperature. No other transitions were detected by differential scanning calorimetry. Major changes occur between 83 and 96.6°C when the major peak at 26.5° virtually disappears. The other major peaks at 7 and 15.5° decrease in intensity as the temperature is raised. An additional sharp peak occurred in the vicinity of 7.5° at temperatures of 69.2 and 83°C. The diffraction pattern obtained at 106°C and characteristic of compound I alone is presented in *Figure 5*.

A specimen of composition 19.9/82.1 LDPE–acridine

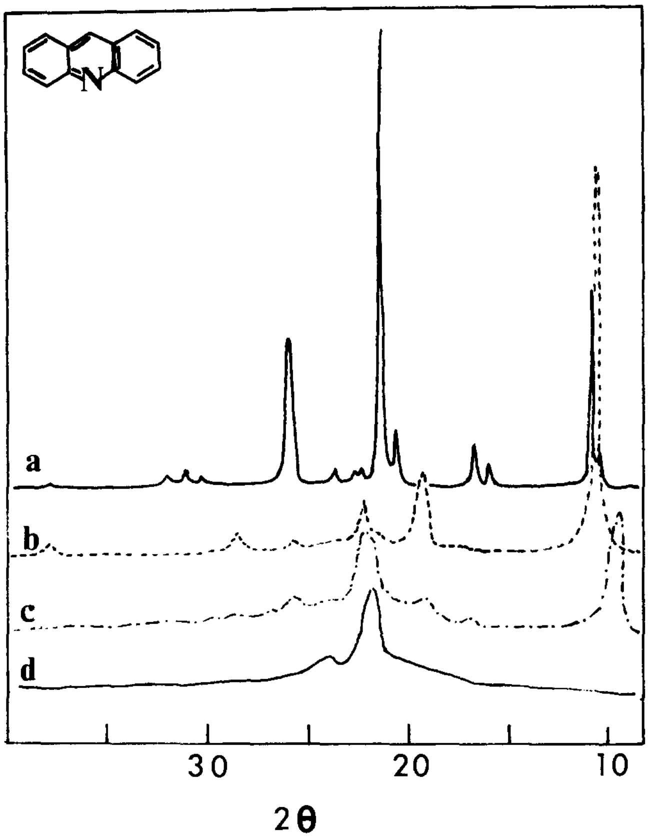

Figure 3 WAXS patterns at ambient temperature of (a) pure acridine, (b) 47% acridine–53% LDPE, (c) 34% acridine–66% LDPE, (d) pure LDPE

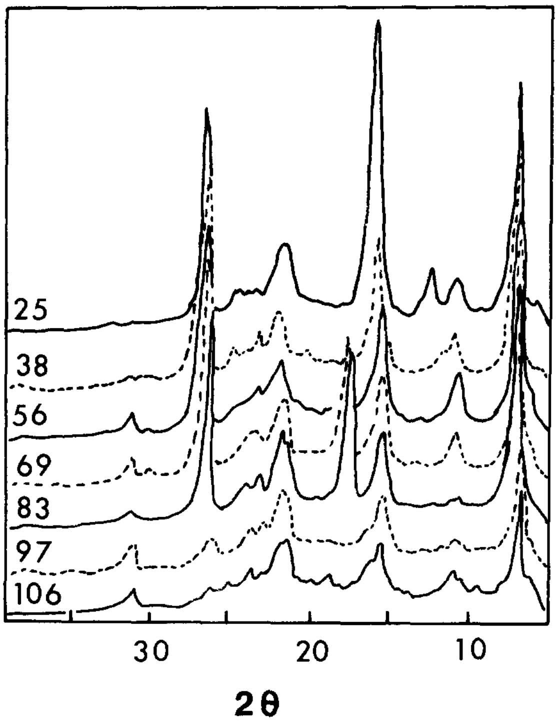

Figure 4 WAXS patterns of a mixture of 62.8% acridine and 37.8% LDPE as a function of temperature

has also been studied as a function of temperature (*Figure 6*). The phase diagram gives both compounds present below 104.9°C but only compound II above that temperature. Major changes again occur between 83.8 and 97.4°C. In particular the peak in the vicinity of 32° which disappears can be identified as one of the peaks typical of compound I. The 7° reflection of compound I was not seen in this experiment and all other major peaks are close to those of compound II. The diffraction pattern obtained at 106°C and characteristic of compound II alone is presented in *Figure 5*.

High-density polyethylene–phenazine

The melting point of high-density polyethylene was 131°C and that of phenazine 177°C. Cooling-rate effects were also observed here but they were not as important as in the LDPE–acridine system. The binary phase diagram obtained using a heating rate of 10°C min^{-1} is shown in *Figure 7*. There are two eutectic compositions at 12 and 34% (by weight) of phenazine. The eutectic temperatures are 129 and 128.5°C respectively. The lone compound occurs in the vicinity of 25% phenazine. X-ray diffraction studies were not as extensive for this system. X-ray

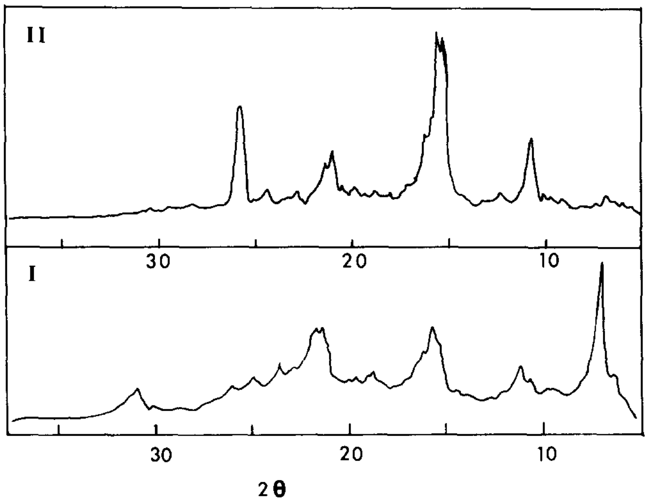

Figure 5 WAXS patterns of compound I and compound II at 106°C

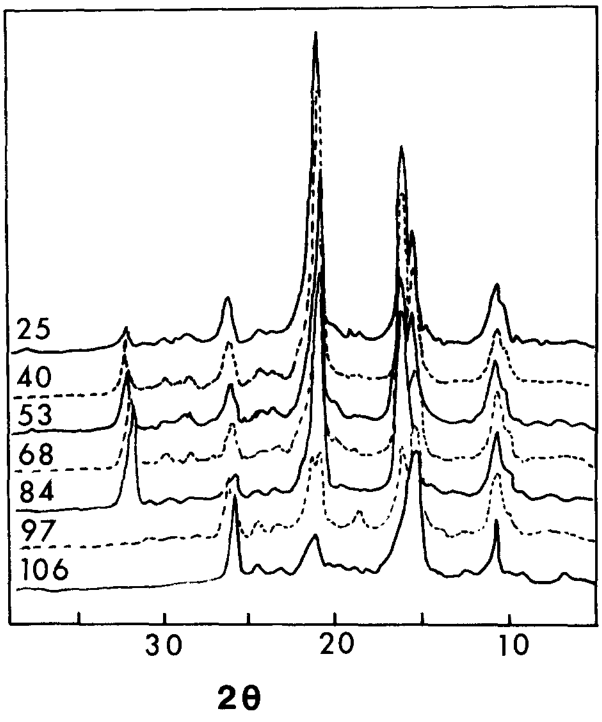

Figure 6 WAXS patterns of a mixture of 82.1% acridine and 19.9% LDPE as a function of temperature

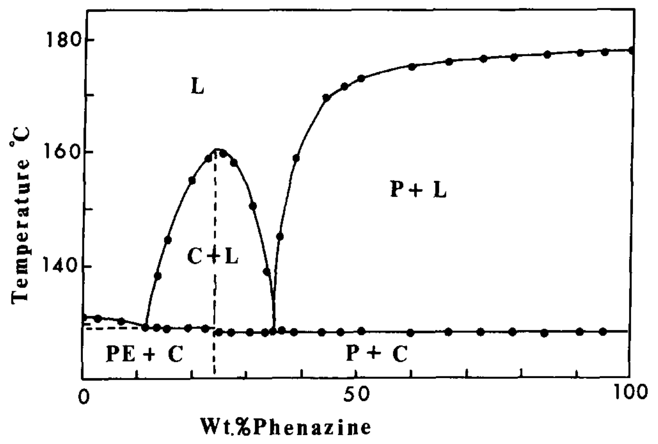

Figure 7 Phase diagram of phenazine and high-density polyethylene: PE, polyethylene crystals; L, liquid; C, compound; P, phenazine crystals

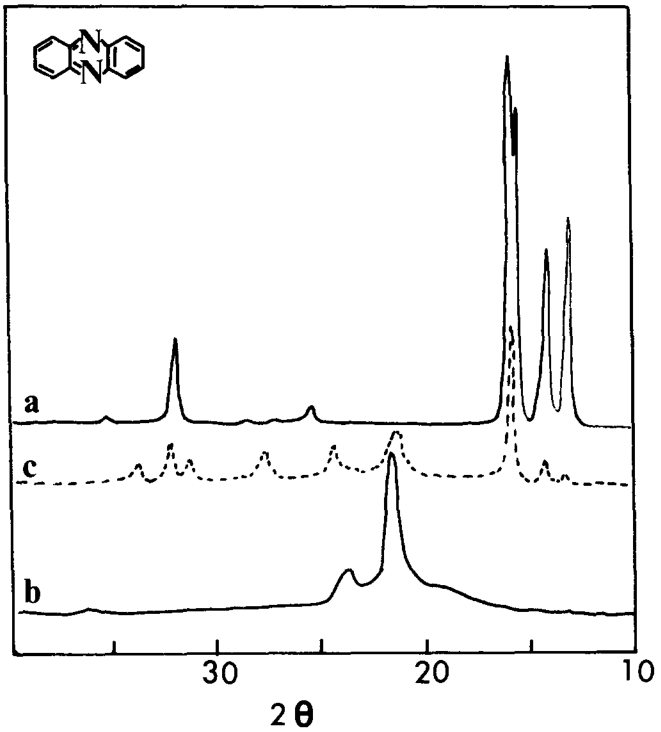

Figure 8 WAXS patterns of (a) pure phenazine, (b) pure HDPE, (c) 80% HDPE–20%phenazine

diffraction scans for pure phenazine, pure HDPE and an 80/20 HDPE–phenazine mixture are shown in *Figure 8*. Clearly in this case four new peaks can be observed. However, peaks typical of phenazine can also be seen whereas ideally only polyethylene and the compound should be present.

DISCUSSION

These studies clearly demonstrate the existence of complex phase diagrams involving compound formation in binaries of polyethylene with fused-ring aromatic molecules. Similar diagrams could not be obtained when the polyethylenes were reversed, i.e. the LDPE–phenazine and HDPE–acridine systems. In these cases the melting points of both components were unchanged from the separated states, suggesting immiscibility in the melt. The production of eutectic behaviour alone and compound formation appear to require that melting points be close to one another. In this respect the LDPE–acridine is ideal since the melting peaks are no more than 1°C apart. In all cases the polyethylene melting peak remains broad and, for high polyethylene concentrations, the eutectic peak is masked. The melting points of the compounds are, however, quite sharp and the eutectic temperatures could also be discerned for compositions greater than that of the first eutectic.

The sensitivity of the phase diagrams to cooling rate has been explored. Generally cooling rates in excess of 10°C min^{-1} resulted in a flattening of the compound I region of the LDPE–acridine system to 109°C (i.e. the melting points of the isolated components). Similarly the compound II region appeared only as a 109°C peak. However, both the 28.5 and 78% acridine eutectic points could be easily discerned along with the eutectic peaks at other compositions. The compound crystals therefore grow slowly and can be suppressed by quenching, a phenomenon that is quite common in metallic alloys.

The sensitivity of the phase diagram to heating rate has not been studied explicitly. However, the X-ray diffraction study was conducted slowly, thermal equilibrium being achieved at each temperature used. In the case of the LDPE–acridine system both specimens studied showed a eutectic temperature somewhere between 85 and 95°C, whereas in the differential scanning calorimetry conducted at 10°C min^{-1} the second eutectic temperature was in the vicinity of 104°C. Clearly a substantial but reproducible superheating was occurring. Since multiple melting peaks are often produced in single-component polymeric systems, due to annealing and recrystallization, the influence of heating rate on the d.s.c. curves could be extremely complex and has not been explored at this stage. It was simply ensured that the curves obtained were reproducible through the use of repetitive cooling and heating cycles. The phase diagrams are valid for 10°C min^{-1} cooling and heating rates but have not been extrapolated to zero heating rate at this time and so should not be regarded as equilibrium diagrams.

It should also be recognized that the X-ray diffraction scans may be sensitive to orientation effects in the thin films used. It is known from the extensive studies of Wittmann and Lotz[16] that epitaxial crystallization is an important effect in thin-film crystallization of polyethylene–fused-ring aromatic systems. Similar effects have also been observed in the LDPE–acridine system by our group[15]. The changes in intensity of the different peaks with temperature may be reflecting internal morphological rearrangements for temperatures below 83°C. The morphology of these systems has not yet been explored, but clearly such studies will be of considerable assistance in understanding currently available data.

Modelling studies of the crystals produced have not yet been conducted and will be a major task in themselves. It would, however, seem reasonable to assume that the lattice matches known to occur between the individual crystals of polyethylene and acridine[15] will be of relevance. Simple schemes involving alternating monolayers of each component may be appropriate, especially in view of the low-angle peaks present in the compounds, which may be symptomatic of superlattice formation.

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