On the lateral habits of polymer single crystals

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Single crystals of trans-1, 4-polyisoprene (TPIP) have been grown from dilute solutions in amyl acetate, n-heptane and n-butanol/n-heptane mixtures. Two samples of different molecular weights, and molecular-weight distribution have been used to demonstrate the effect of these molecular parameters on the shape of single crystals. The experiments suggested that crystallization of narrowly distributed polymer chains, irrespective of the molecular weight of the crystallizing species, will produce a hexagonal morphology. This narrow distribution of chains during crystallization can be achieved by starting with a sample of low polydispersity or using a solvent/non-solvent mixture for crystallization. If the chain-size distribution is not controlled, then at later stages of growth the heterogeneous mixture of chains will create a curvature on the $\{1\,1\,0\}$ faces and produce oval-shaped lamellar platelets. Further, the crystal habits in the present work were found to be related to the solvent, molecular weight and molecular-weight distribution, rather than to the crystallization temperature.

1. Introduction

Most of the knowledge about the molecular texture in the crystalline state of polymers has come from the study of their solution-grown lamellar single crystals wherein the randomizing effects are minimum. Direct electron microscopic observation of these single crystals and X-ray determination of the orientation of chain molecules therein led to the discovery of the chain-folding principle which became the basis for the evolution of kinetic theories of polymer crystallization. Generally, lamellar single crystals of polymers exhibit simple geometric lateral shapes with smooth well-defined growth faces. In many cases, a change in the lateral habits is found to result from changes in solvent, temperature and rate of crystallization; but these problems were never really addressed outside the context of solvent power. Thus lateral habits of polymer single crystals remained a matter of no more than peripheral interest. Khoury and Passaglia [1] gave specific attention to this problem and reviewed the cases in which the crystal periphery was rounded in shape and serrated on a fine scale. The profound implications of these rounded facets came to be realized when Sadler [2–4] pointed out that the curvature on the lateral faces of polyethylene single crystals could be due to a molecularly rough surface. Lateral habits of polyethylene and polyethylene oxide single crystals grown over a wide temperature range show good correspondence with the surface-roughening theory, according to which a rise in the crystallization temperature alone can account for the increase in curvature on the $\{1\,1\,0\}$ crystal faces. The theoretical predictions of Sadler are further supported by Organs and Keller [5] who have grown polyethylene (PE) crystals from hydrocarbon solvents of ascending or-

der. The boundaries of lamellar crystals were found to become increasingly curved with increasing crystallization temperature. If the surface roughening theory becomes applicable to polymer crystallization in general, the existing theories of kinetics of polymer crystallization may have to be reviewed [5].

Therefore, it is, tempting to analyse the crystal habits of other polymers because the morphological characteristics at early stages of growth may provide new insight into the mechanism of crystallization. *Trans*-1,4-polyisoprene (TPIP) is a linear hydrocarbon homopolymer but differs from polyethylene in regard to the structure of the backbone. This polymer exhibits a variety of single-crystal habits [6–8] some of which are similar to those of orthorhombic polyethylene. The objective of the present work was to identify the factors responsible and elucidate the mechanism for the development of curvature on the otherwise grown straight faces of the single crystals of this polymer.

2. Experimental procedure
2.1. Materials
Two samples of TPIP were used for crystallization: TPIP-1 was an unfractionated commercial sample containing 2% 3, 4 units (supplied by Polymer Corporation, Sarnia, Ontario, Canada, courtesy of Dr D. C. Edwards, under their trade name PIP); it was reprecipitated from benzene solution by adding ethanol; TPIP-2 was a low molecular weight sample prepared by fractionation of commercial sample, TPIP-1, using the benzene–ethanol system. Table I shows the molecular characteristics, and Fig. 1 shows

TABLE I Characterization of the samples

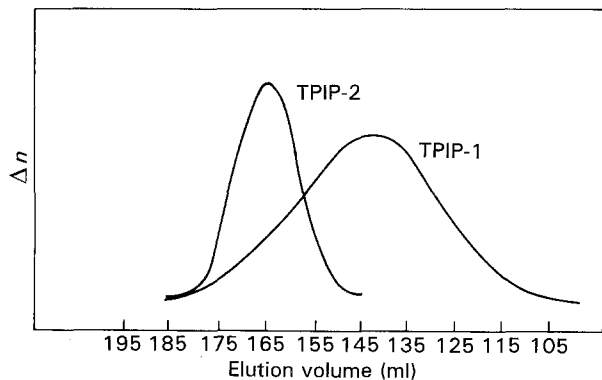| Sample	30 °C [η] benzene	$\bar{M}_w$ (gpc) × 10^{-4}	$\bar{M}_w/\bar{M}_n$ (gpc)
TPIP-1	2.60	64.0	9.4
TPIP-2	0.35	3.6	2.0

Figure 1 GPC traces of the two TPIP samples. GPC done in toluene at 30 °C.

the molecular-weight distribution (MWD) of the polymers obtained on a Waters — 200 GPC.

2.2. Solutions

Fractionally distilled solvents of analytical grade were used for preparing the solutions. Throughout the text, solution concentrations are expressed in wt/vol percentage. The polymers in the solutions were found to be highly prone to oxidative degradation. Flow time, taken in a Ubbelhode suspended level capillary viscometer for polymer solutions, decreased by as much as 20% within 3 days. Therefore, as far as possible, fresh solutions were used; and 2, 6-ditertiary butyl-p-cresol was added (0.5% wt/wt) in the polymer solutions to prevent degradation.

2.3. Sample preparation

Crystals were grown isothermally (± 0.5 K) from fresh dilute TPIP solutions on glass slides. 10 ml polymer solution was taken in 60–65 cm long glass tubes of 1–2 cm diameter. The tube was heated at 70 °C for 20 min, and transferred to an oven maintained at crystallization temperature. A glass slide in thermal equilibrium with the oven was dipped in the tube solution with the help of a string. After 10 min the slide was slowly drawn out with the help of a slow-speed motor and was kept hanging just above the solution surface for about 12 h. The dried slide containing crystals was coated with carbon and shadowed with chromium. The replica was detached in the usual manner by floating the carbon film on water and was viewed in a Philips EM-400 and in some cases in a Carl-Zeiss model EF4 transmission electron microscope. This method of polymer crystallization was developed by Patel and Patel [9], and was called the film formation method (FFM) by them. It has been

found to be very useful in growing various morphological stages of polymer crystals.

The procedure for crystallization from a solvent–non-solvent mixture was as follows: a definite quantity of the non-solvent was added dropwise to the polymer solution just to produce slight turbidity at the crystallization temperature. The turbidity was dissolved at 20–25 K higher temperature, and crystallization was carried out from this mixture by the above-mentioned FFM. In parallel experiments, crystals were grown on carbon-coated slides, and the carbon film containing crystals was used for taking electron diffraction patterns. The observed d-spacings, as calculated by Bragg's law, matched favourably with those reported earlier [10] for the β polymorph of TPIP.

3. Results and discussion

Fig. 2a shows oval-shaped lamellar crystals obtained from amyl acetate solution of the unfractionated poly-
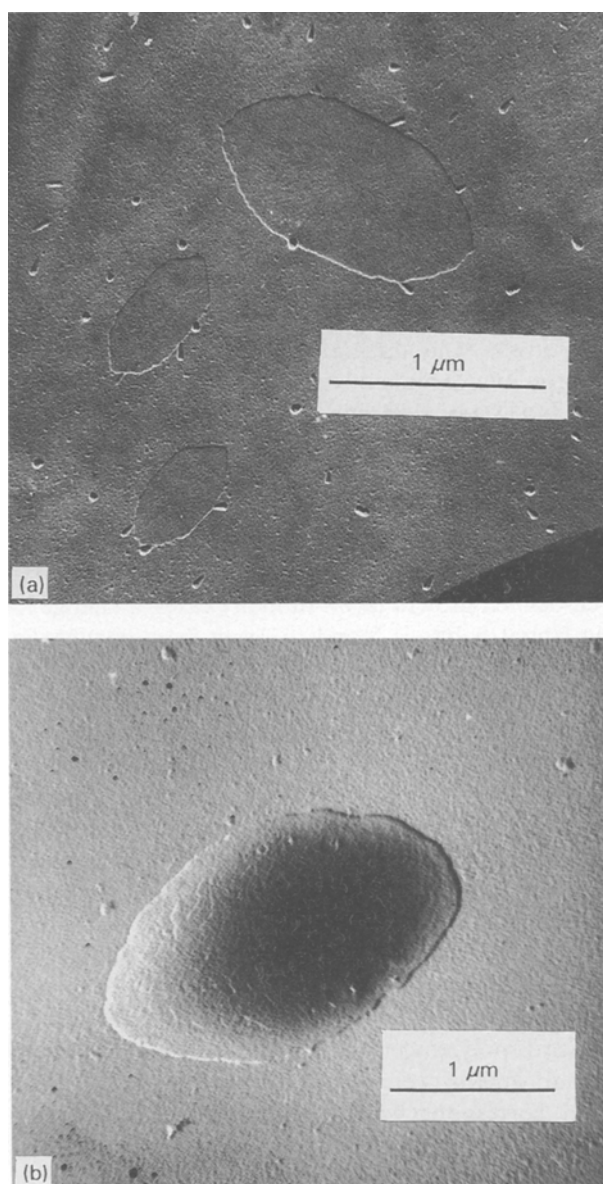

Figure 2 Oval shaped single platelets obtained from (a) 0.1% amyl acetate solution of TPIP-1 at 37.5 °C (note that some faces of smaller crystals are straight), (b) 0.4% n-heptane solution of TPIP-1 at 35 °C.

mer, TPIP-1. Similar crystals with curved boundaries were also obtained from n-heptane solution (Fig. 2b) of TPIP-1. The uneven size of the crystals indicates a time-dependent nucleation. A close scrutiny of Fig. 2a suggests that the initial stages of growth maintained perfect hexagonal shapes of the crystals. As the crystals advanced, at later stages a rounding of the boundaries started, which finally gave an oval-like appearance to the platelets. In fact, the prevailing conditions of crystal growth, such as a change in solution concentration or molecular-weight segregation, may lead to the modification of the growth mechanism towards the end of the process, and justify enquiry about the final shape of these objects during growth [11]. Therefore, the mechanism of overall development of the crystals is proposed as follows.

Under a given set of crystallization conditions, the more readily crystallizable molecules precipitate first in the crystal phase. It has been shown by Mehta and Wunderlich [12] that the precipitated crystals contain longer molecules leaving the mother solution enriched in shorter molecules. It follows that the beginning of crystallization is dictated by supersaturation as the driving force for the precipitation of the longest molecules. However, both theoretical and experimental evidence [12, 13] show that crystallization-induced fractionation should not be absolutely sharp in terms of molecular weight at any crystallization temperature. Therefore, later stages of crystallization must incorporate a certain amount of material of widely varying (preferably lower) chain length in order to account for the breadth (although small) of MWD in the precipitated crystals. Kawai and Keller [14] have deduced that when the concentration of the mother solution decreases to the extent of suppressing new nucleation, a second phase of the process starts in which crystallization becomes essentially diffusion-controlled. Further growth, therefore, can take place only by a secondary nucleation mechanism in which no new surface will be created. The shorter molecules which were rejected earlier during the course of primary nucleation and initial growth, will now diffuse on to the crystal growth fronts, because their diffusion ability will be more than that of larger ones. Under these conditions of slow growth, it is very likely that many new secondary nuclei will be formed on the crystal borders before the completion of the previous layer. Consequently, borders of crystals will become serrated, giving rise to further growth steps. The net result will be curvature on {1 1 0} faces, as seen in the bigger crystals throughout this investigation. Thus, conditions of slow growth and deposition (crystallization) of a heterogeneous mixture of chain lengths, are the two factors found to be responsible for the development of curvature on the crystal periphery.

Two different approaches were used to control the growth at later stages. In the first, a sample of relatively low polydispersity, TPIP-2, was used to grow crystals from amyl acetate solution, so that the size of the molecules in the entire sample does not vary much. As a result, the later stages of growth did not have to incorporate much material of widely varying length. The crystals, therefore, as observed in Fig. 3a, could
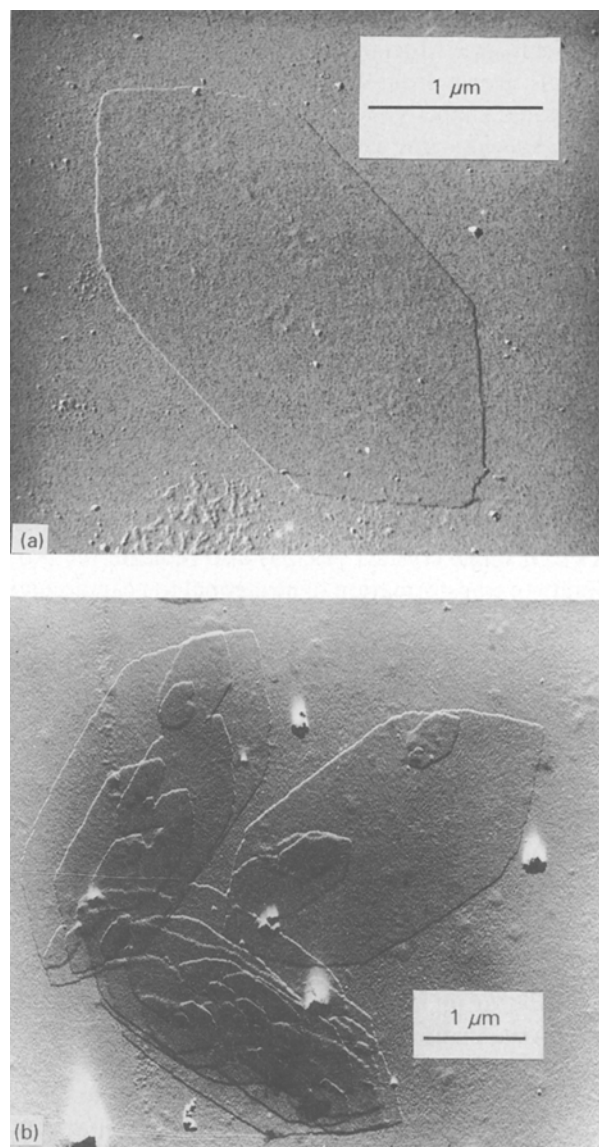

Figure 3 (a) Well-shaped hexagonal platelet obtained from 0.1% amyl acetate solution of TPIP-2 at 30 °C, (b) hexagonal twinned crystals obtained from 0.4% solution of TPIP-1 in n-heptane/n-butanol mixture at 35 °C.

maintain straight faces. In the second approach, a non-solvent, n-butanol, was added to the n-heptane solution of the unfractionated sample. The procedure was exactly that used in precipitation fractionation which promotes the precipitation of mostly selected molecules of highest average length. The supersaturation factor thus works for a longer time than that in earlier cases. The result, as seen in the crystals of Fig. 3b, is once again favourable. The distortion of crystal boundaries is much less compared to that in Fig. 2b. The difference in the growth mechanisms of the crystals of Figs 2a, b and 3a, b is that the latter did not have to incorporate a significant proportion of widely varying chain lengths, whereas in the former, although the growth started with molecules of uniform size, addition of broadly polydispersed material could not be avoided at later stages. Addition of the non-solvent to n-heptane solution of TPIP-2 produced a slight improvement (over crystals of Fig. 3b) in the hexagonal shapes. However, no further effect of fractionation on the morphology could be resolved.

Some of the other polymeric systems posing similar problems are isotactic polystyrene (iPS), in which crystals grown from a poor solvent were of simple hexagonal shapes [15], whereas crystals grown from good solvents (in which growth rates were much slower than that in poor solvent) showed somewhat rounded and a finely serrated periphery [15–17]. Thus the conditions of slow growth seem to be responsible for the rounding of crystal boundaries in case of iPS. Polychlorotrifluoroethylene (PCTFE) crystals grown in low molecular weight PCTFE oil showed a disc-like overall profile and finely serrated character of the periphery [18]. The possible reason for the rounded shapes could have been the participation of low molecular weight PCTFE species (supplied by the solvent) during crystal growth. The electron micrographs of trans-1,4-polybutadiene (TPBD) single crystals [19, 20] also indicate the possibility of transformation of hexagonal to near circular shapes, because the TPBD sample used for crystallization reportedly had a high heterogeneity [20].

The last stage of crystallization of smaller molecules which have thermodynamically poor crystallizability is exhibited in Fig. 4 in which irregularly shaped crystals have been deposited on the top of the basal lamella. This gives an idea of the type of irregularity which small molecules of uneven size, and lack of kinetic control in the diffusion-controlled portion of the crystallization, can impart on the crystal boundaries. If higher concentrations of the original solution are used, hedrites of the type shown in Fig. 5 will generate. Again, after the formation of parent lamella the crystallization could not produce regular multilayers. A large number of steps can be seen in both Figs 4 and 5. In contrast to this, crystallization of TPIP-2 did give such irregular structures, but only after forming a new regular layers on the parent lamella [7].

Despite some structural dissimilarities in orthorhombic PE and orthorhombic TPIP, nearly all the habits of PE crystals (summarized in [2]) can be found in TPIP [6–8] also under suitable conditions. A defin-
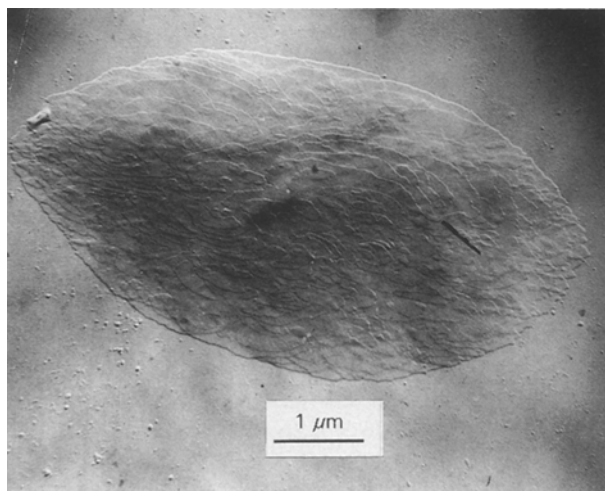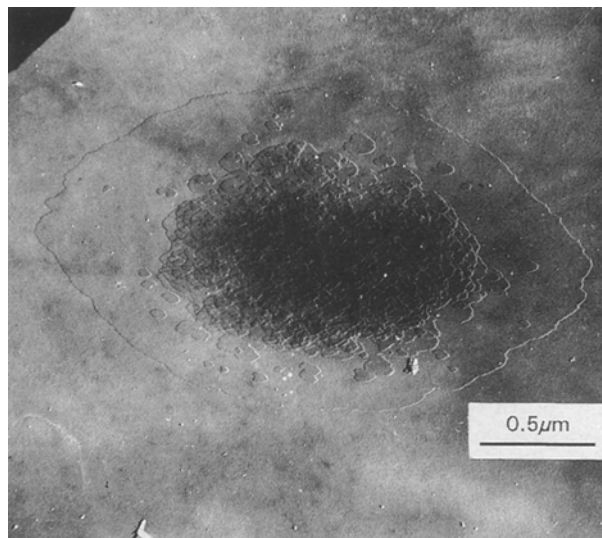

Figure 5 Oval-shaped hedrite structure showing advanced stage of the type of growth shown in Fig. 4a; obtained from 0.5% amyl acetate solution of TPIP-1 at 37.5 °C.

ite correlation of crystal shapes of PE with their crystallization temperature has been shown to exist [2], and further demonstrated by systematic experiments [5]. The surface-roughening theory, however, does not seem to be able to account for the morphological changes in TPIP because no change of temperature was found necessary for the development of curvature on the crystal boundaries (c.f. the conditions of Figs 2b and 3b). Other faceted crystals have also been found to grow at a single temperature [8]. Similarly the cases of iPS, PCTFE and TPBD cited earlier would need a separate explanation. The small change in temperature in the case of Figs 2a and 3a may apparently support Sadler's [2] view. But these temperatures were chosen for the convenience observed in the crystallization due to the difference in the dissolution temperatures of the solutions of two different molecular weight samples. It was, however, possible to grow crystals near 34 °C from both the samples in amyl acetate with the habits shown in the respective figures.

4. Conclusions

Besides supporting the validity of the above proposed mechanism for the change of habits, these experiments suggest that crystallization of narrowly distributed TPIP chains, irrespective of the molecular weight of the crystallizing species, will produce a hexagonal morphology. This narrow distribution of chains can be achieved by either of the above mentioned ways. Also, if the chain-size distribution is not controlled during the crystal growth, the heterogeneous mixture of chains will create a curvature on the {1 1 0} faces and produce oval-shaped lamellar crystals. Further, the crystal habits in this and the earlier communications [6–8] are found to be related to the solvent, molecular weight and molecular-weight distribution, rather than to the crystallization temperature.

A fresh look is required to be given to the cases of ill-defined or irregularly shaped crystals. Investiga-

Figure 4 Oval-shaped platelets showing irregular deposition of uneven sized molecules towards the end of crystallization; obtained from 0.2% amyl acetate solution of TPIP-1 at 37.5 °C.

tions on the latter stages of crystal growth could shed light on the possible reasons for the morphological complexities. Keith and Padden's [21] theory would probably account for the imperfections at the crystal edges. This subject will be discussed further in terms of conformational changes in a forthcoming paper on morphology–thermal property relation in TPIP.

Acknowledgement

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