

The gamma phase of high-molecular-weight polypropylene: 1. Morphological aspects

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A high-molecular-weight polypropylene ($M_w = 83\,000$, $M_w/M_n = 3.0$) has been crystallized isothermally as a function of pressure at a constant supercooling of 50°C . Wide-angle X-ray diffraction (WAXD) shows that the X-ray diffraction spectrum of the γ phase is identical to that reported for low-molecular-weight polymers, with the exception that the peaks are broader. Calculations of the γ content using WAXD show the nearly 100% γ phase is formed at 2 kbar, but a mixture of γ and α crystals are formed at lower crystallization pressures. Small-angle X-ray scattering (SAXS) studies show that γ lamellae are approximately one-half the thickness of α lamellae produced at an equivalent supercooling. Morphological studies conducted using transmission electron microscopy of carbon replicas of permanganically etched surfaces confirm the thin nature of the lamellae and demonstrate their inherent waviness. Unlike α crystals, γ lamellae do not form cross-hatched textures. A model is proposed, involving γ/α lamellae and epitaxy during the growth process, to account for all the observable morphological data.

(Keywords: polypropylene; gamma phase; morphology)

INTRODUCTION

Polypropylene is a morphologically complex polymer, forming three proven phases¹⁻⁵, which may have different appearances, and also a 'smectic' state. The molecule's ability to deposit epitaxially on α lamellae gives rise to branches inclined at a specific angle to the primary lamellae. This results in a unique low-birefringence cross-hatched texture. Polyethylene and related polymer crystals can grow epitaxially on polypropylene substrates⁶⁻⁸.

The most commonly observed crystal form is the low-birefringence monoclinic α form¹, followed by the high-birefringence β form. Until recently the γ form had only been produced at elevated pressures^{5,9} and its formation was believed to be enhanced in copolymers⁵. Its crystal structure was generally interpreted as triclinic^{5,10}, but was only slightly different from the monoclinic form. Recently, more accurate studies of molecules of molecular weight 5000-8000 have led to a reinterpretation of the crystal structure as orthorhombic^{11,12}. The proposed structure accounts for all the observed diffraction maxima in a more satisfying manner than the earlier triclinic interpretation. The structure is unique, in that, although it is composed of sheets of parallel molecules, the molecular orientation in adjacent sheets can be non-parallel. Pairs of sheets having molecular axes inclined to one another at 100° angles are

therefore the most characteristic feature of the crystal structure (*Figure 1*). Later independent studies by other researchers have supported the proposed structure¹³.

It is a simple matter to accept the proposed structure if the molecules are short and can form extended-chain crystals. Whether such a structure is possible in the folded-chain crystals of a high-molecular-weight polymer is another question.

All previous studies of high-pressure crystallization of polypropylene were conducted in the 1960s when it was not possible to control precisely the microstructure of the polymer. Atactic levels were relatively high and the materials were really copolymers. Now it is possible to control routinely the chemical microstructure during synthesis so that the molecules can be described as at least 99% isotactic. There is, therefore, a major need for the formation of the γ phase in polypropylene to be re-evaluated with advanced investigative techniques using the highest isotacticity now available. Such a comprehensive study has been completed and will now be presented in a series of papers, of which this is the first.

EXPERIMENTAL

The material used was supplied by Exxon Corporation and had M_n , M_w and M_z values of 27 000, 83 000 and 159 000, respectively. The tacticity is better than 99%, but not characterizable with greater precision¹⁴. All such characterizations were carried out by Exxon Corporation.

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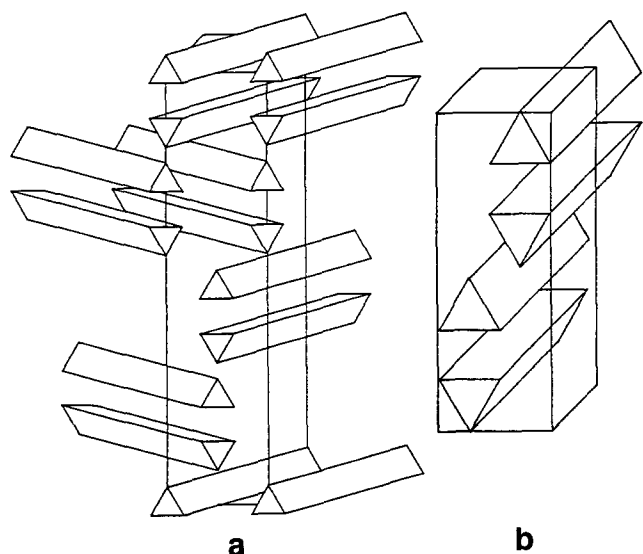


Figure 1 Schematics of chain-stem arrangements in the unit cells of (a) γ -polypropylene and (b) α -polypropylene

Samples with dimensions approximately 3 mm thick and 2.5 cm in diameter were cut from a sheet of isotactic polypropylene. They were placed in an elevated-pressure cell, melted at 190°C for 20 min and then the pressure applied rapidly to the desired value. The temperature was then adjusted to the desired isothermal crystallization temperature, which in each case corresponded to a supercooling of 50°C. The determination of the variation of the equilibrium melting point with pressure was conducted using standard methods of extrapolation and will be reported in detail in the second paper of this series. Following maintenance of the desired isobaric isothermal conditions for a time sufficient to complete the crystallization process, the temperature was reduced to room temperature, followed by the release of the pressure.

WAXD studies were carried out at atmospheric pressure using a Rigaku Denki diffractometer; additionally, WAXD images were recorded using a flat-plate camera. SAXS studies were conducted at the Center for Small Angle Scattering Research at Oak Ridge National Laboratories using a sample-to-detector distance of 5 m.

Specimens were prepared for electron microscopy by first microtoming a flat surface using a fresh knife at -20°C. The microtomed surface was then etched using the permanganic etching technique of Norton and Keller³. Specimens were then studied in two ways. Part of the specimen was coated with gold and studied using reflection optical microscopy. Carbon replicas were taken from the other part of the specimen and studied using transmission electron microscopy.

RESULTS

Wide-angle X-ray diffraction

Flat-plate X-ray pictures were taken first and they established that the specimens produced were unoriented. WAXD traces were then obtained from the pressure-crystallized specimens. The data for some representative pressures are shown in Figure 2. As can be seen from Figure 2, the atmospheric-pressure scan is typical of the α phase and correlates well with information in the literature. The diffractometer scan for the 200 MPa specimen correlates well with recent data for low-

molecular-weight materials and shows no evidence of any peaks characteristic of the α phase. It does differ from the published scans of the γ phase of low-molecular-weight materials in that the peaks are broader here. There may well be other minor differences that are not detectable at the level of resolution of the diffractometer used in these studies.

Specimens produced at all intermediate pressures show clear evidence of the presence of both phases, in agreement with the earlier data of Kardos *et al.*⁹. Many of the diffraction peaks of the α and γ crystals are the same or close to one another and cannot be used for estimates of the relative content of the two phases. The (1 3 0) peak of the α phase (18–19°) is unique as also is the (0 4 0) peak at 19–20° of the γ phase. In the absence of structure factors and any other corrective information, the ratio of the areas of these two peaks has been taken as indicative of the ratios of the two phases. Presented in Figure 3, the trend observed is similar to that reported by Kardos *et al.*⁹, although the exact shape of the curve was not defined by Kardos, nor was the pressure at which 100% γ phase could be produced precisely defined. It is important to note that, in a specimen that has less than 1% atactic content, there is still no specific transition as a function of pressure, at a constant supercooling, from one phase to the other. Both phases grow and apparently are stable; neither are there any major changes in crystallinity across the series; all are within a few per cent of 60%. It is interesting to note that the curve of Figure 3 shows an initial relatively linear slope of almost 10% per 10 MPa but that the rate of generation of the γ phase slows down and generates an asymptote.

Small-angle X-ray scattering

Following a study of the curves generated to ensure that there was a lack of orientation in the specimens,

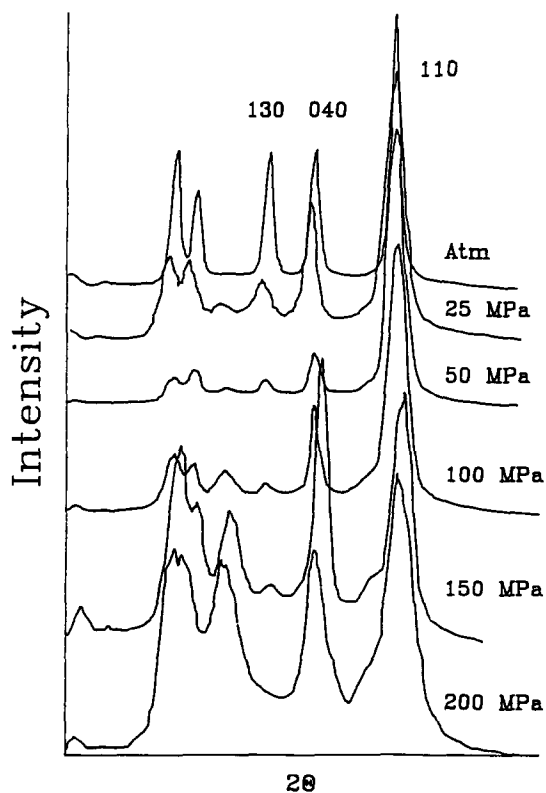


Figure 2 WAXD scans for samples crystallized at a constant supercooling of 50°C and various pressures

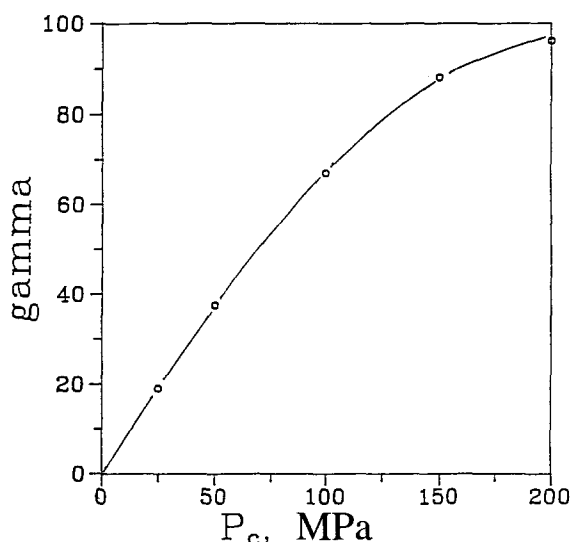


Figure 3 The γ content from WAXD as a function of crystallization pressure for a constant supercooling of 50°C

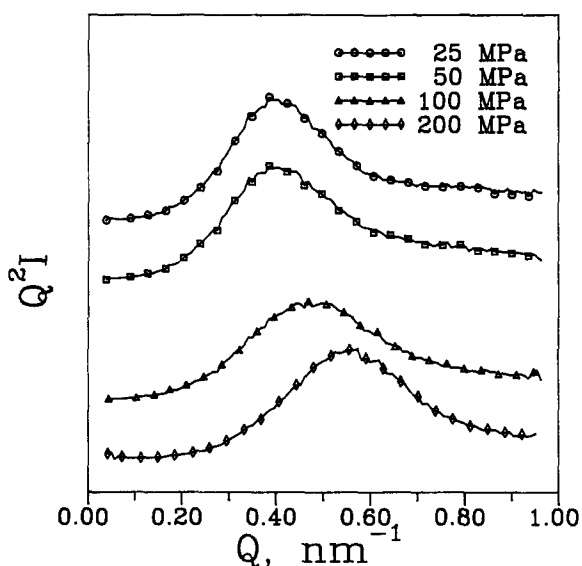


Figure 4 SAXS radially averaged data versus scattering vector as a function of crystallization pressure using Lorentz-corrected intensity

data were radially averaged for analysis. Most noticeable is a loss in intensity, compared to atmospheric-pressure crystallizations, for all pressure-crystallized materials. Specimens show single characteristic long-period peaks for all pressures of crystallization. There are changes in the position of the peak, compared to atmospheric pressure, even for the sample that was crystallized at the low pressure of 25 MPa. When Lorentz-corrected data are presented (Figure 4), the peak moves to higher scattering angles as the crystallization pressure is increased. This translation is a result of a continual decrease in the lamellar thickness with γ content.

Studies were also carried out of specimens crystallized at 100 and 200 MPa to verify that normal lamellar thickness–supercooling relationships were applicable to the γ crystals. This was found to be so, curves for 200 MPa crystallizations being presented in Figure 5. Clearly the long period is increasing with increasing crystallization temperature. Despite its unusual crystal structure involving non-parallel chains, the γ phase of polypropylene behaves in a conventional manner, the lamellar thickness being

about one-half of that of the α crystals produced at equivalent supercoolings.

Optical studies of microtomed sections

Spherulite size and density were similar for specimens crystallized at atmospheric pressure and at 25 MPa, both showing the birefringence typical of polypropylene crystallized at high supercoolings. Neither specimen showed any evidence of Maltese cross formation. Less than 10% of the material was in the γ form in the 25 MPa specimen. Hence, it can be assumed that the general form of lamellar organization is common to the specimens. For the 50 and 75 MPa specimens, no distinct Maltese crosses could be found, but there was less mixed birefringence. The 100 MPa crystallized specimen showed a clear Maltese cross (Figure 6a); this specimen contained 60% γ form. There was no evidence of two types of spherulites being present. Hence, it was concluded that both crystal forms occupy the same spherulites. The sample crystallized at 200 MPa, which was better than 95% γ phase, gave a quite different appearance. The spherulites were much less distinct in terms of internal structure and there was no Maltese cross present (Figure 6b).

Optical and electron microscope studies of etched specimens

There were clear changes in the behaviour of specimens towards permanganic etching as the γ/α ratio changed with crystallization pressure, despite the fact that the Keller–Norton optimized etchant³ was used. The difference in reactivity between the crystalline and amorphous phases, on which resolution depends, was found to decrease significantly with increasing γ content. Specimens with higher γ content also tended to generate more artefacts. This behaviour may be caused by the thinner lamellae of the γ phase being completely etched away more easily, or by some inherent difference in the reactivity of the folded surfaces due to some major structural change caused by the need for non-parallel chains.

Reflection optical microscopy of gold-coated etched surfaces provides an excellent way of observing the

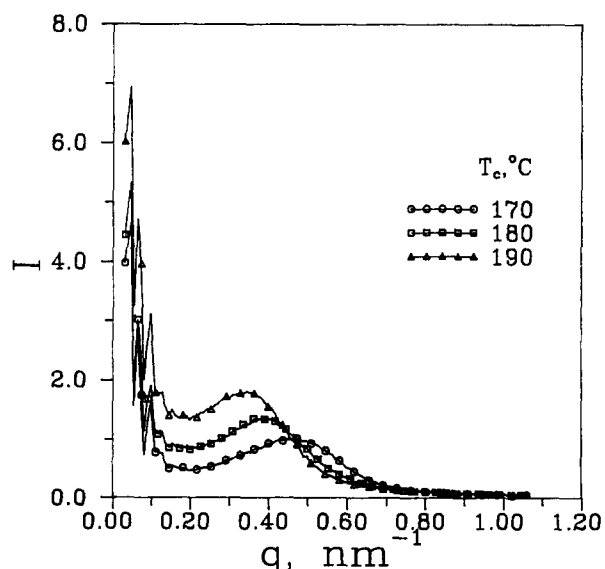


Figure 5 SAXS one-dimensional radially averaged intensity as a function of crystallization temperature for a crystallization pressure of 200 MPa

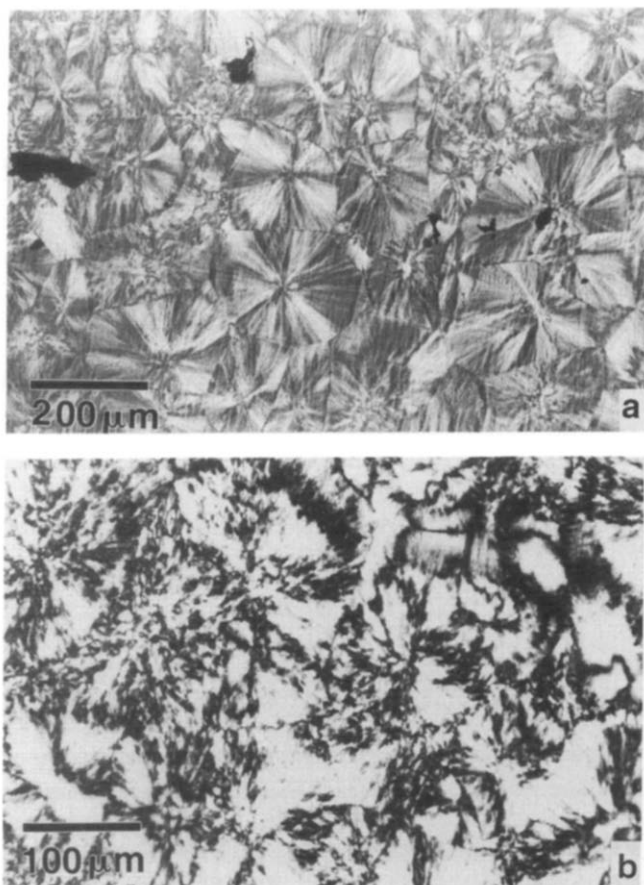


Figure 6 Spherulites in microtomed sections of polypropylene crystallized at 50°C supercooling and (a) 100 MPa, (b) 200 MPa

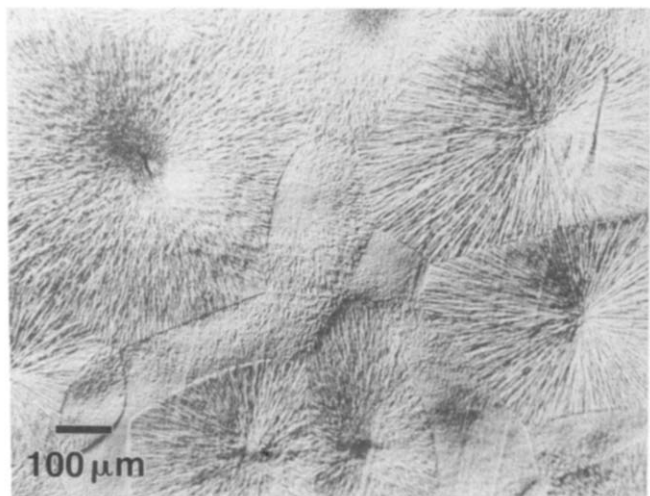


Figure 7 Reflection optical micrograph of lamellae in polypropylene crystallized at 25 MPa and 50°C supercooling

spherulitic structure and even some details of internal lamellar arrangements. It is much easier to carry out than scanning electron microscopy and can generate lower-magnification pictures with ease. To the best of our knowledge this is the first report of the use of this technique. Typical photomicrographs of α spherulites present in atmospheric and 25 MPa crystallized specimens are shown in Figure 7. Micrographs typical of pressure crystallization at 100 and 200 MPa are shown in Figure 8. Spherulites are observed for all pressures of crystallization, but changes in the internal texture are discernible, even at this level of magnification.

The TEM studies of carbon replicas of the same specimens just described provide considerable detail on the lamellar thickness variations and the general behaviour of the lamellae. At 25 MPa the lamellar structure is similar to that observed in atmospheric pressure crystallizations (Figure 9), as might be expected as the γ content is only 10%. The lamellar packing is not as uniform as observed in atmospheric-pressure specimens, but two different lamellar populations cannot be discerned. For a 50 MPa specimen, the same lamellar structure is present and tangential lamellae can still be found. An important observation is that many of the branches are found at angles significantly less than the 80° typical of cross-hatching. Behaviour at 75 MPa is similar to 50 MPa, but etch damage becomes more pronounced (Figure 10). Lamellar organization is much less ordered than at atmospheric pressure and the lamellae have a tendency to be curved. The latter behaviour is similar to that routinely observed in the ubiquitously thin lamellae of *cis*-polyisoprene¹⁵. For higher crystallization pressures the degree of difficulty in obtaining acceptable resolution becomes worse and the level of etch damage increases. A typical view of a 100 MPa specimen is shown in Figure 11, where the lamellae can still be seen faintly. Their appearance is complicated by the presence of spherical artefacts of radii similar in value to the lamellar thickness. Whereas the use of reflection optical microscopy with the same

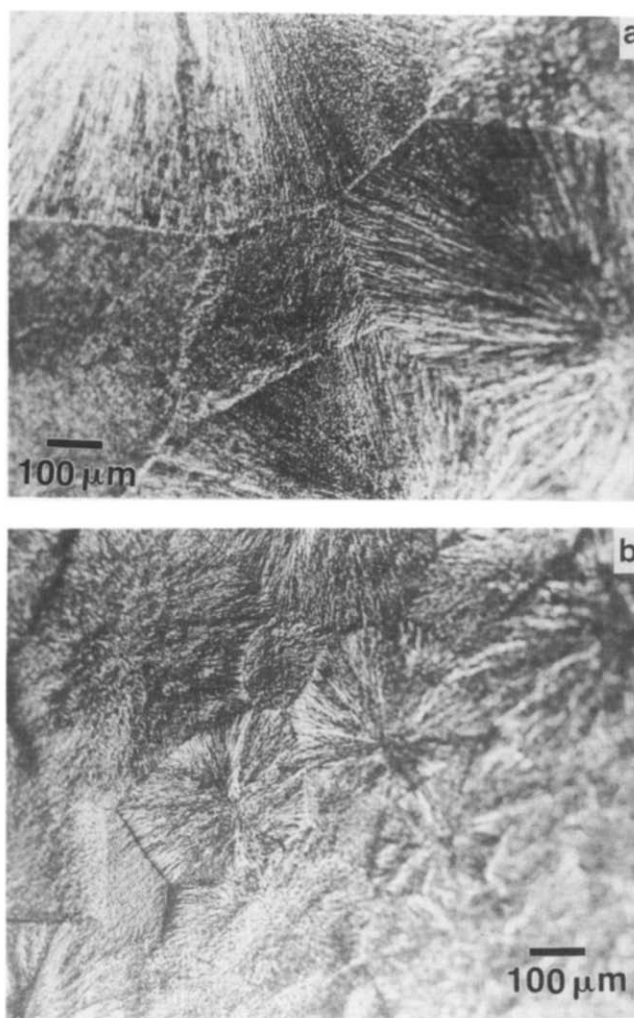


Figure 8 Reflection optical micrographs of coated permanganically etched polypropylene, crystallized at (a) 100 MPa and (b) 200 MPa

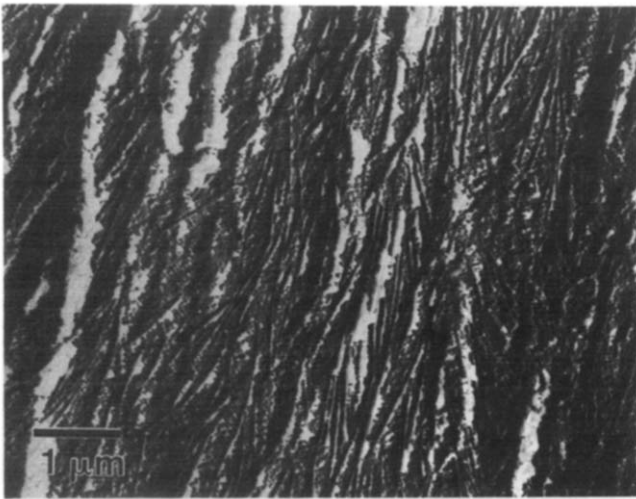


Figure 9 TEM micrograph of a carbon replica of etched polypropylene crystallized at 25 MPa and 50°C supercooling

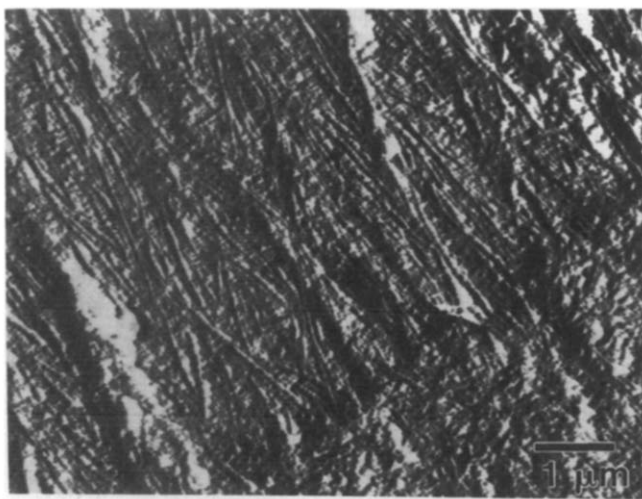


Figure 10 TEM micrograph of a carbon replica of etched polypropylene crystallized at 75 MPa and 50°C supercooling

specimen gave well resolved structures with some indication of the internal texture, the TEM studies gave no really useful additional information. It should also be noted that cross-hatching is eliminated by 100 MPa, perhaps due to the observable lamellae being γ phase. In studies of low-molecular-weight degraded polypropylenes, Lotz *et al.*¹³ concluded that α lamellae could not generally grow from γ lamellae, but occasionally do so. Our observations are in accord with this conclusion.

DISCUSSION

This study has confirmed the conclusions of research conducted 25 years ago on specimens of lower isotactic content and less well controlled molecular-weight distributions. It has also uncovered new facts on the lamellar thickness of the γ crystals and on the organization of γ spherulites as well as demonstrating the existence of spherulites containing both α and γ lamellae.

First, the study has confirmed the coexistence and concurrent growth of α and γ lamellae at the same temperature and pressure. This observation is important since it demonstrates that the coexistence is a fundamental

property of the system and not simply caused by microstructural impurity variations. It should be recalled that Turner-Jones *et al.*⁵ reported that the γ phase was formed more easily in copolymers than in homopolymers. If this were a general effect, then it would be expected that tacticity variation should produce a similar effect and perhaps a γ phase produced only by molecular regions of abnormally low isotacticity. The fact that the γ phase could be produced easily in a polymer, that is to all intents and purposes completely isotactic, demonstrates that the γ phase formation is an essential property of the polypropylene chain.

It is also important to recognize that the diffraction patterns obtained are in all essentials the same as those reported for the low-molecular-weight polymers studied by other workers. The polymer was not degraded in any way, and could reproduce the α form when the γ form was melted and then recrystallized at atmospheric pressure. This fact demonstrates that the formation of the γ phase is not unique to low-molecular-weight extended-chain crystals. It must therefore be recognized that this form is consistent with chain folding. Because of surface packing problems when chain folds are considered to cross from one stem to another tilted at 80° to the first, it seems most likely that the folds would be restricted to sheets of a common parallel tilt angle (Figure 12). This restriction places considerable constraints on the growth faces of the γ crystals. It is unfortunate that the growing tips of the lamellae could not be observed in the γ form because of the etching problems.

When the long periods obtained from the SAXS experiments are converted into lamellar thicknesses, it can be seen clearly that there is a continual decrease of lamellar thickness with γ content (Figure 13). It should be noted that the long periods have been determined using two methods. The peak of the Lorentz-corrected curves has been used in the conventional manner, as also has the uncorrected curve (Table 1). Data from the corrected curves have been used for the lamellar thickness calculations, which used the standard method of multiplying the long period by the crystallinity. Essentially the specimen containing only γ crystals has a lamellar thickness close to half of that of α crystals generated at atmospheric pressure and the same supercooling.

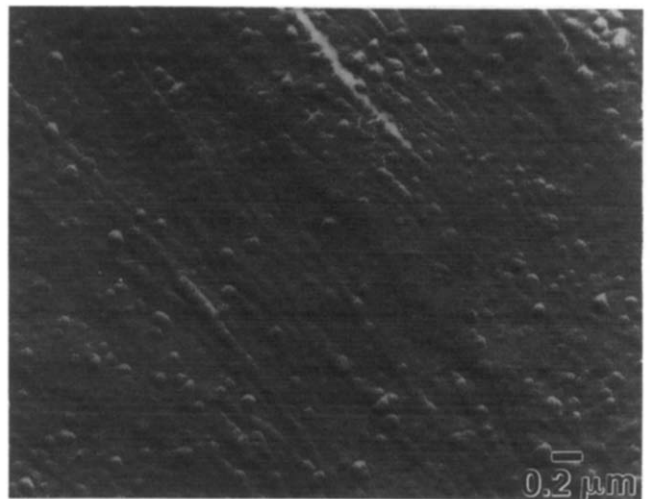


Figure 11 TEM micrograph of a carbon replica of etched polypropylene crystallized at 100 MPa

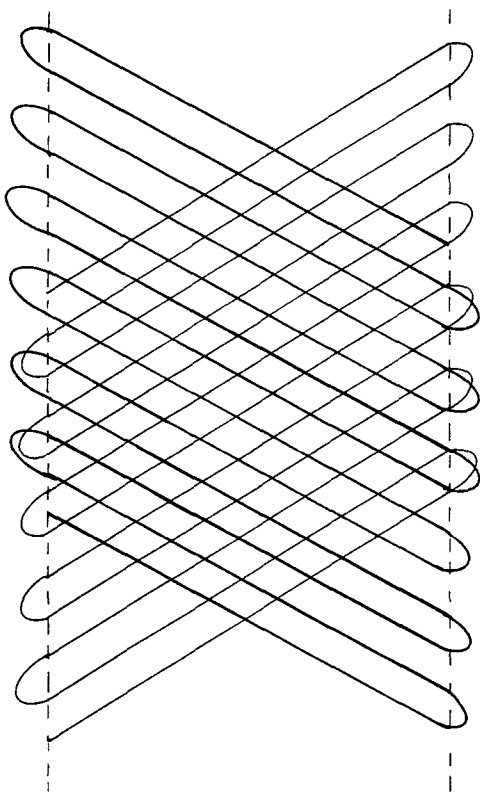


Figure 12 Schematic diagram of adjacent re-entry folding in γ -polypropylene

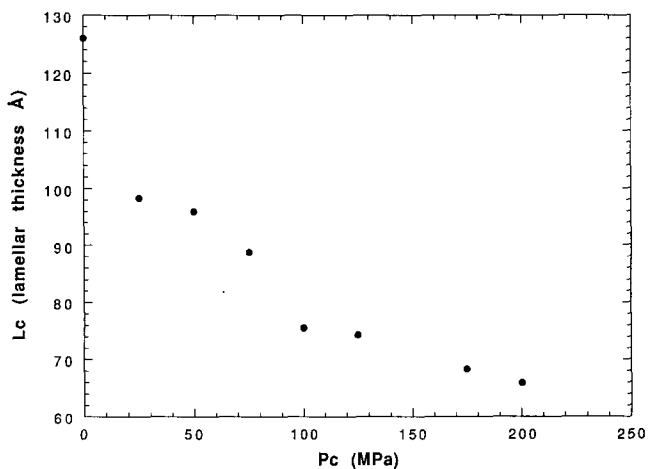


Figure 13 Plot of lamellar thickness versus crystallization pressure for a constant supercooling of 50°C

Accepting that the chains are inclined to the lamellar normal at a steep angle, as suggested by the model of Figure 12, permits an estimate to be made of the stem length. This angle could be either 40° or 50° relative to the lamellar normal. When allowance for this inclination is made, then it is found that the stem lengths of the γ and α phases are close to one another. This is a very important observation since it suggests that the fold structures of the phases are similar in structure. This further suggests that the folds are restricted to sheets of parallel chains having a common tilt angle.

A thornier problem is the lack of any evidence for a bimodal population of lamellar thicknesses in the SAXS experimentation or in the electron microscopy. If the specimens simply contain lamellar populations of 60 and 120 Å thicknesses in proportion to the observed WAXD

intensities, then the bimodal character should be quite evident in specimens crystallized between 50 and 100 MPa. Not only was a single peak observed, but also there was no hint of anything else in correlation function analyses. At the very least, this evidence indicates that the α and γ lamellae do not exist in identifiable separate stacks. It was noted earlier that there was no evidence for two separate lamellar populations in the electron micrographs, although there does exist the distinct possibility that the thinner γ lamellae might have been etched away. However, there were no discernible gaps that they could have occupied, such as were observed in studies of crosslinked low-density polyethylene¹⁶.

In the work of Lotz *et al.*¹³ on low-molecular-weight extended-chain crystals it was noted that γ lamellae tend to form stacks of lamellae branched off the α lamellae. This led to a situation in which the α lamellae existed in a relatively isolated fashion. However, it has to be recognized that the situation could be very different here for a high-molecular-weight polymer where chain folding is necessarily present. The need for folds to be deposited at the lamellar surface of the substrate crystal for minimum energy during the secondary nucleation process may result in a quite different morphological relationship. If such a situation were occurring here, then it could conceivably cause only the γ lamellae to be detected in SAXS experiments. Whereas this does seem to be a plausible explanation for the high γ content specimens observed at the highest pressures, it does not appear to be consistent with the linear growth kinetics, which indicate that the γ crystals are the dominant lamellae at pressures of 100 MPa and above¹⁷. Such an explanation also seems unreasonable for the low γ content specimens observed at low pressures. The fact that the γ content is a continuous function of increasing pressure tends to be in conflict with such a generalized explanation in which the amount of γ phase generated would be a function of random branch generation. Additionally, the drastic reduction of the lamellar thickness occurring at a pressure as low as 25 MPa where only 10% of the material is in the γ form makes such an explanation untenable here also. It is noted that the lamellar thicknesses at 25 and 50 MPa are consistent with α crystals having a uniform 40° tilt relative to the lamellar normal. Also those at 100 and 125 MPa are consistent with a uniform 50° tilt relative to the lamellar normal. These two angles are precisely those possible in the γ crystal. However, considerably more SAXS studies of specimens produced at intervening pressures would be necessary before any definitive statements could be made on whether or not

Table 1 Long periods from SAXS data for isotactic polypropylene crystallized isothermally at various pressures, with a constant supercooling of 50°C

Pressure (MPa)	Observed intensity		Lorentz-corrected	
	Q (nm ⁻¹)	L (Å)	Q (nm ⁻¹)	L (Å)
atm	0.263	238	0.300	210
25	0.342	184	0.385	164
50	0.342	184	0.385	160
75	0.360	174	0.425	148
100	0.385	164	0.496	126
125	0.427	148	0.500	124
175	0.473	132	0.555	114
200	0.480	130	0.572	110

the lamellar thickness–pressure curve is quantized into tilt regions.

One possible interpretation for the studies reported here could be that both crystal forms are present in each lamella, rather than existing as separate lamellae within the same spherulite. Such a possibility is not unreasonable if the orthorhombic crystal structure is studied (Figure 1), especially in the light of the projected fold structure of Figure 12. It contains a pair of sheets of parallel chains which are then followed by a pair of sheets with chains at 80° to those of the first pair. In many ways the difference between the α and γ crystals is analogous to the difference between f.c.c. and h.c.p. crystals, which is simply caused by two distinguishable ways of stacking hexagonally packed sheets. Stacking faults are very common in such crystals and it should be quite easy for a set of three or four or more sheets to be formed, instead of the alternating pairs required by the γ crystal. Such an anomalous set would correspond to an α crystal of the correct stem length, but having an abnormal angle of inclination to the lamellar normal. There is no inherent reason to prevent such an event from occurring; indeed, it is a generally accepted fact that polyethylene forms similar steep angles of inclination when crystallized under the most ideal conditions. The process would in fact correspond to a situation of continual epitaxial competition and deposition between the two crystal forms. As will be demonstrated in a later paper in this series, the kinetics of lamellar growth are best interpreted in terms of a competition between the two crystal forms during secondary nucleation.

Such a model of crystallization is consistent with the observed similar stem lengths in the γ and α crystals when formed at equivalent supercoolings, and with the inference that this is a direct result of virtually identical fold surfaces. It is also consistent with the very clear demonstration that the cross-hatching in α spherulites is a direct result of the deposition of single sheets of chains at 80° , followed by α crystallization in the branches generated, but with a lower than usual lamellar thickness¹⁸.

If the deposition of 80° inclined sheets on an α substrate is regarded as a generation of stacking faults, then any situation intermediate between the pure α crystal and the pure γ crystal is going to be a higher-energy crystal. As such, its formation could be predicted by thermodynamics. There would be a maximum number of stacking faults per unit volume of crystal that could be incorporated at any given pressure. However, since the γ crystal is intrinsically more dense, its formation will be favoured by the application of pressure. Presumably also, this would lead to an increasingly higher limiting concentration of stacking faults with increasing pressure. Hence, it is possible that the transition from α to γ crystal could be regarded as occurring through a pressure-induced solubility effect. In some ways, it is analogous to a continuous series of solid solutions in a metallic alloy, such as the copper–nickel system. However, the major difference is that it is necessary to think in terms of the stacking of sheets rather than the packing of different-sized spheres. It is suggested that a theory could be developed to describe the behaviour, based on the thermodynamics and kinetics of solid solution formation. Such a development is currently in progress and will be reported at a later date if successfully derived.

Should this model be correct, then the lamellar

thicknesses at intermediate pressures may be an average of the individual crystal thicknesses developed by microsections of γ and α crystals resident in the same lamellae. It is possible that they could be of the 60 and 120 Å thicknesses determined in the pure crystals. It is also possible that the thicknesses of the α and γ crystals would be similar, but only if the α sections were tilted with respect to the lamellar normal. The SAXS studies would not be sensitive to such effects since it is the long period that generates the scattering curves. It is suggested that evidence might be present in the line broadenings of the wide-angle X-ray diffraction lines. The WAXD studies reported here are not of the precision necessary to investigate this point.

CONCLUSIONS

The γ phase of polypropylene is an intrinsic form, not restricted to low-molecular-weight fractions or to copolymers. It is formed in such a way that there appears to be an equilibrium concentration of both α and γ crystals present at a given pressure of crystallization. The percentage of γ crystal generated increases in a smooth fashion, reaching a 100% asymptote in the vicinity of 200 MPa.

Only one long period is detectable in SAXS experimentation, and analysis demonstrates that the lamellar thickness of the γ form is about a half of that characteristic of the α form at the same supercooling. Analyses demonstrate that the stem length, and presumably also the fold structure, of the α and γ crystals are similar at an equivalent supercooling. The crystals of the α and γ forms are present in the same spherulites and also appear to be present in the same lamellae.

Cross-hatching is eliminated from the spherulites when a small percentage of the γ crystals are present. The phenomenon may be caused by continual epitaxial competition resulting from alternative stacking sequences of folded-chain sheets of similar energies.

ACKNOWLEDGEMENTS

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