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γ-Phase in propylene copolymers at atmospheric pressure

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Crystallization studies have been conducted on three copolymers of propylene with ethylene as a function of supercooling at atmospheric pressure. The results confirm the conclusions reached almost 30 years ago that copolymerization causes the γ-phase to be generated at atmospheric pressure for high molecular weight polymers. The greater the amount of comonomer, the greater the ease of formation of the γ-phase. The γ/α ratio is inversely proportional to supercooling, as has been found for isobaric crystallization at elevated pressures. It has been found that the equilibrium melting point decreases with ethylene content in a significant manner.

(Keywords: propylene–ethylene copolymers; γ-phase; supercooling)

INTRODUCTION

The γ-phase of polypropylene was first noted during the 1960s[1–3] and was generated largely by crystallization at elevated pressures. It was identified first as triclinic, but recent studies of a form generated at atmospheric pressure from low molecular weight polymer led to a reassignment of the structure as orthorhombic[4,5]. The new structure accounts for the diffraction pattern in a more satisfying manner than the earlier structure. The new structure is unique, in that it contains sheets of parallel molecules, but the molecular orientation between adjacent sheets becomes non-parallel every two sheets. Early studies had associated the formation of the γ-phase with chemical heterogeneity in the polypropylene chain caused by atacticity or by copolymerization[6]. More recent studies[7] have demonstrated that the γ-phase is produced at elevated pressures from high molecular weight homopolymer and that it has the same diffraction pattern as the low molecular weight polymer. This study has also confirmed that the γ-phase is not the result of some unexpected degradation reaction at elevated pressures.

The study of Turner-Jones[6] considered some copolymers of propylene with ethylene (as well as other comonomers) and found that the presence of a comonomer enhanced the formation of the γ-phase. The polymers that were available for study at that time contained atactic material, and there was no way, a priori, of separating the effects of atacticity from the effects of copolymerization, which would be complementary. Polymers available now have >99% isotacticity and so the effects of the microstructural variables can be separated. The copolymers are synthesized using a slurry-based Zeigler–Natta type of catalyst, similar to those used in the production of linear low density polyethylenes (LLDPEs)[8,9]. Such catalysts tend to produce a mixture of almost linear homopolymers with branched copolymers of lower molecular weight. This effect results from the porous nature of the surfaces of the slurry particles and is related to the differences in diffusional behaviour of the two comonomers into pores. In LLDPEs such as ethylene–octene copolymers[10,11], the bimodality in the copolymer content–molecular weight relationship is major, and materials are close to 50% near-linear molecules and 50% copolymer. There is a variation of copolymer content with molecular weight for those molecules that do contain significant amounts of comonomer. Under these circumstances crystallization of the near-linear molecules occurs first, and the occurrence of very significant amounts of fractionation according to both copolymer content and molecular weight is well established. In propylene copolymers the effect is much less significant because of the smaller size difference between the propylene and ethylene comonomers. In Turner-Jones' study of propylene copolymers[6] the melting curves observed were very complicated and were regarded as indicative of fractionation occurring due to major copolymer composition effects. Some studies were also carried out on fractions produced by solvent extraction. In newer polypropylenes the heterogeneity is much lower. As will be seen, the melting curves of our specimens are much less complicated. As a preliminary to the study of fractionated materials of narrower copolymer content distributions, we have conducted a study of three unfractionated copolymers. There are three reasons for doing this. First, the comprehensive studies of Turner-Jones[6] were also on unfractionated materials, and it is important to determine if the behaviour could be duplicated in similar materials not having an atacticity problem, and also a less extreme copolymer heterogeneity problem. Second, when compared with fractions at a later date, the studies will allow us to infer the changes generated by blending of copolymers of different comonomer contents. Third, a later study will consider the crystallization of copolymers at elevated pressures, and many of the essential studies

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*To whom correspondence should be addressed will necessitate use of the unfractionated materials, because of the volume of specimen needed.

As will be seen from this study, the γ-phase can be generated easily in these copolymers at atmospheric pressure, unlike the homopolymer.

EXPERIMENTAL

The copolymers were provided by Exxon Corporation who also carried out all molecular characterization studies, details of which are provided in *Table 1*. Specimens for wide angle X-ray diffraction (WAXD) studies were prepared by isothermal crystallization in a Mettler hot stage.

Differential scanning calorimetry (d.s.c.) was conducted on a Perkin–Elmer DSC 7 at 10°C min^{-1}. The calibration of the calorimeter was checked every 3 to 4 h to ensure that the accuracy was better than 0.02°C. WAXD studies used a Rigaku Denki diffractometer, and hot stage microscopy used a Mettler hot stage mounted on either a Nikon or an Olympus microscope.

All samples were prepared under a flow of nitrogen gas during melting and crystallization to prevent degradation of the polymers. A more detailed crystallization and melting analysis has been given earlier[12].

RESULTS AND DISCUSSION

First, d.s.c. experiments were conducted using the cooling mode to determine the crystallization ranges of the three copolymers. Experiments conducted thereafter were aimed at determining the amount of γ-crystal generated in each of the three copolymers at a selected number of isothermal temperatures. Each of the α-, β- and γ-crystal forms has its own distinctive peak in the WAXD plot. These characteristic peaks are found in the 2Θ plot between the angles 18–19°, 15–16° and 19.2–20.5° for α-, β- and γ-crystals, respectively. The presence or absence of each peak means the existence or absence of its form. The results for the 0.5% ethylene copolymer (*Figure 1*) show an absence of γ-crystals at both 120 and 136°C, but some β-crystals in addition to α-crystals at 120°C. Both the 3% and 5% ethylene copolymers show substantial amounts of γ-crystals (*Figures 2* and *3*). As in previous studies[6], the γ/α ratio is calculated using the X-ray peaks that can be uniquely assigned to each of the α- and γ-phases. These are the (1 3 0) peak of the α-phase (18–19°) and the (0 4 0) peak of the γ-phase (19.2–20.5°).

Table 1 Sample identification

Sample	Ethylene content (wt%)	$M_w \times 10^3$	Melt flow rate
iPPH	0.0	257	3.9
iPPC0.5%	0.5	268	3.9
iPPC3%	3.0	300	4.0
iPPC5%	5.0	300	2.7

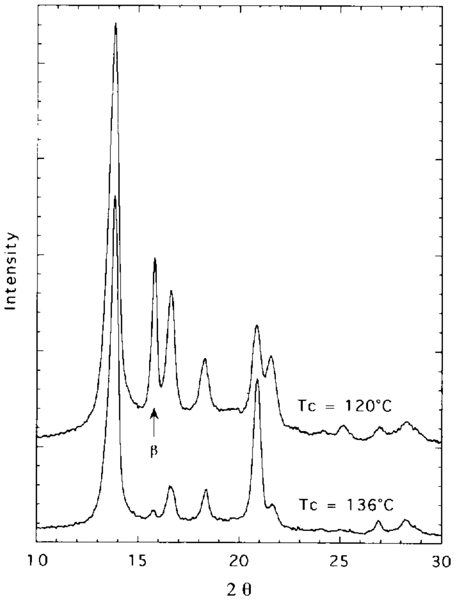

Figure 1 WAXD intensity *versus* scattering angle for 0.5% ethylene copolymer isothermally crystallized at the indicated temperatures

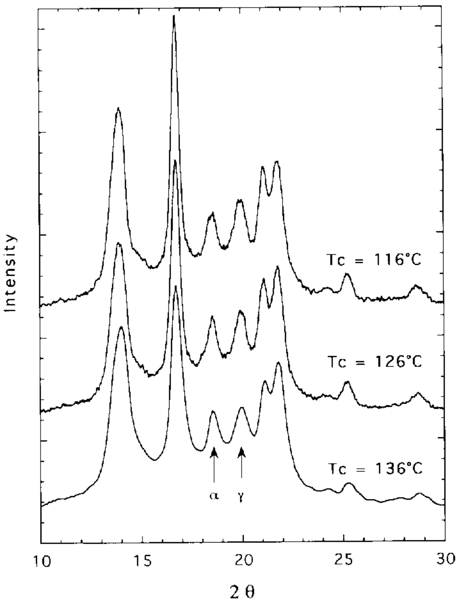

Figure 2 WAXD intensity *versus* scattering angle for 3% ethylene copolymer isothermally crystallized at the indicated temperatures

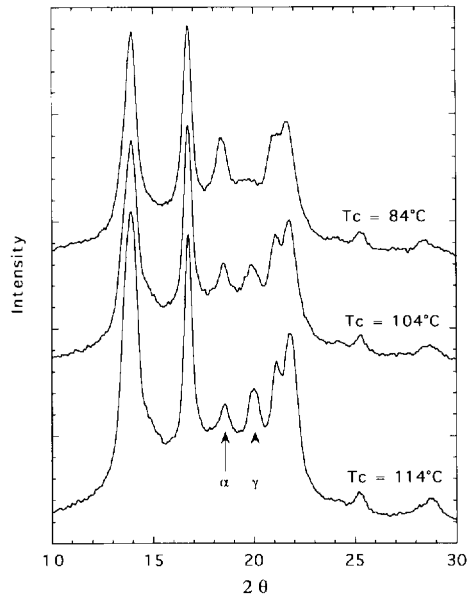

Figure 3 WAXD intensity *versus* scattering angle for 5% ethylene copolymer isothermally crystallized at the indicated temperatures

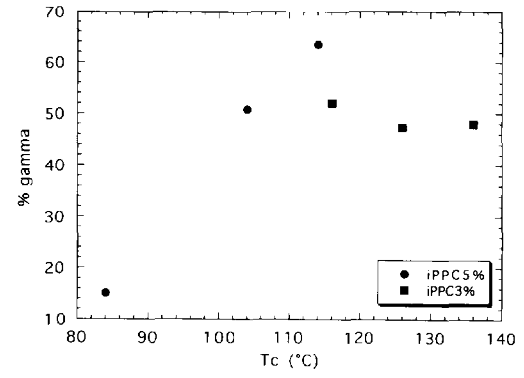

Figure 4 Percentage of γ-phase present as a function of crystallization temperature for the 3% and 5% ethylene copolymers

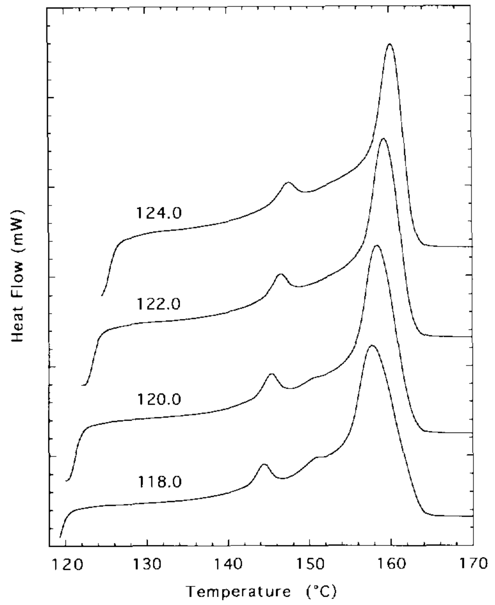

Figure 5 D.s.c. plots of 0.5% copolymer at different isothermal crystallization temperatures, which are indicated on each curve

In the absence of structure factors and other corrective information, the ratio of the areas of these two peaks has been taken as indicative of the ratios of the two phases.

The percentage of γ-phase produced at different crystallization temperatures for the 3% and 5% copolymers is shown in *Figure 4*. As can be seen from the curve, there appears to be a maximization of γ-content in the vicinity of 110°C and, for crystallization temperatures above 110°C, the content is relatively constant. These data are similar to those obtained in isobaric experiments[13] as a function of supercooling on propylene homopolymer, where the γ-content is maximized at the lowest supercoolings. Here, however, the maximum level achieved is 65%, whereas for the homopolymer at elevated pressure, levels of close to 100% result. It is not yet known whether higher levels of γ-content can be achieved at elevated pressures for the copolymers; however, such experiments are to be conducted at a later stage.

It is well known from studies at elevated pressures[12] that the original explanation of Turner-Jones[1,6] – that microstructural heterogeneities are solely responsible for the formation of γ-crystals – is untenable, since the γ-phase is formed from homopolymers with >99% isotacticity. Additional studies[13] have shown that the equilibrium melting point of the γ-phase at atmospheric pressure is slightly higher than that of the α-phase. Hence the γ-phase should be slightly more stable, in a thermodynamic sense, than the α-phase. It does, however, still appear to be correct to infer that the presence of microstructural heterogeneities encourages the phase's formation. For instance, it is shown in this study that the γ-phase is formed more easily in the 5% copolymer than in the 3% copolymer. Indeed, in all our studies we have failed to generate the γ-phase in a high molecular weight homopolymer of >99% isotacticity at atmospheric pressure under any conditions tried so far.

D.s.c. plots are shown in *Figures 5*, *6* and *7* for the copolymer contents of 0.5, 3 and 5%, respectively. The 0.5% propylene–ethylene copolymer shows, in *Figure 5*, a small peak in the region 142–148°C followed by a strong peak in the region 155–165°C. These two peaks represent

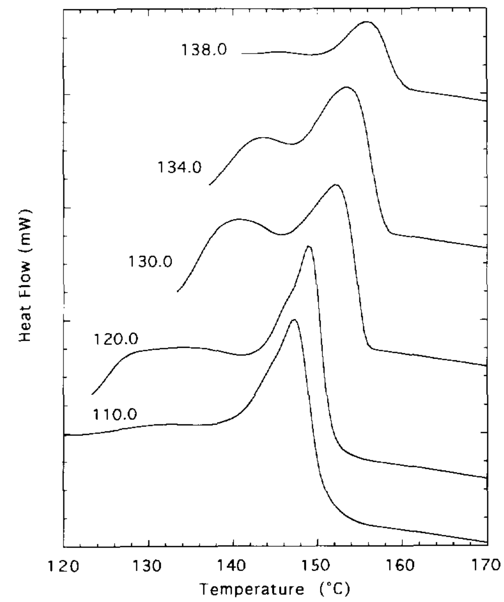

Figure 6 D.s.c. plots of 3% copolymer at different isothermal crystallization temperatures, which are indicated on each curve

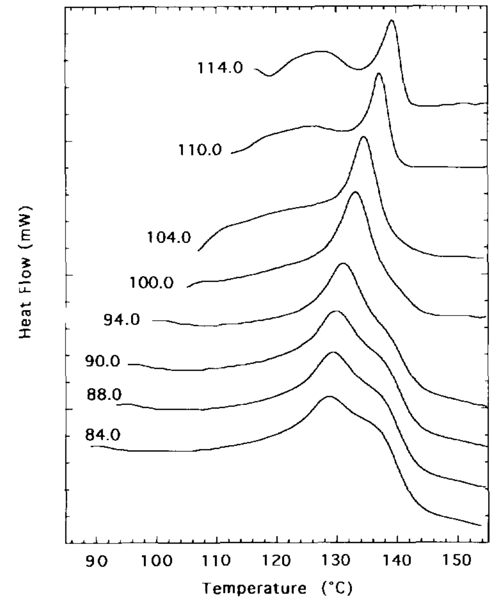

Figure 7 D.s.c. plots of 5% copolymer at different isothermal crystallization temperatures, which are indicated on each curve

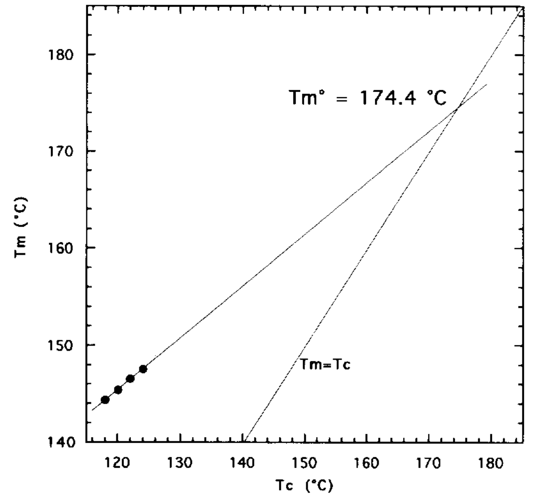

Figure 8 Equilibrium melting point of the *β*-form. The data points represent the small d.s.c. peaks of *Figure 5*, in the range of 142–148°C, which represent the melting of the *β*-form. (The coefficient of determination, R^2, of the line fit is 0.999)

the melting of the *β*-form and the α-form, respectively. It has been reported in the literature[1,14] that the melting temperature of the *β*-form is observed around 145–150°C. It seems that the 0.5% ethylene content enhances the formation of the *β*-form. When the melting peak of the *β*-form is plotted *versus* the corresponding crystallization temperature, a straight line can be fitted to determine the equilibrium melting point of 174.4°C (*Figure 8*).

The melting curves of the 3% ethylene copolymer (*Figure 6*) are quite different from those of the 0.5% copolymer. For crystallization temperatures near 110°C, the d.s.c. curves show a very small hump followed by a large peak. When the crystallization temperature is close to 120°C, the hump becomes more obvious and very broad. As the crystallization temperature is increased to 130°C, the hump becomes larger and sharper whereas the peak becomes wider. Above 134°C the hump starts to decrease in intensity whereas the peak continues to broaden. There are two possible hypotheses for this occurrence: (A) the hump and the peak represent different crystal forms, α and γ; (B) different peaks represent different stem lengths. In hypothesis B, the broad hump would characterize the melting of short stems and the large peak would describe the melting of larger stems.

The disappearance of the hump at high supercoolings (110°C) with a high γ-content indicates that the hump cannot be γ-crystals. Also, according to Pae[15], the γ to α transformation occurs very slowly and cannot be detected by d.s.c. run at 10°C min^{-1}.

There are three possible explanations if hypothesis B is correct: (i) the two crystal forms grow together; (ii) the γ-form grows first followed by the α-form; (iii) the α-form grows first followed by the γ-form. Epitaxial growth of the γ-form on the α-form or the α-form on the γ-form has been well explained by Lotz and co-workers for the two different unit cells of the γ-form[16,17]. Turner-Jones[6] showed that the development of the γ-form is preferred when the samples are not totally melted and then very slowly cooled. She explained that observation as being due to a preferred epitaxial growth of the γ-form. However, an alternative explanation could be that the γ-form is preferred at lower supercoolings (*Figure 4*), as nucleation only starts at a high temperature if the sample is not totally molten. The last curve of *Figure 6*, which represents the melting at $T_c = 138$°C for 40 min of crystallization, has a very small hump.

In short, the likely reason for the formation of the hump is due to differences in stem length. This reasoning can be most easily developed in terms of some α-form epitaxially growing on the γ-form. The latter crystal has an orthorhombic unit cell with non-parallel chains of adjacent planes and the difference in the stem length would be about 0.766 (cos(40)), i.e. the stems of the α-form would be about 76% of the stem lengths of the γ-form. So although both α- and γ-forms may be melting concurrently in the main peak, it appears that thinner α-crystals epitaxially grown on the γ-crystals may be responsible for the hump. This hypothesis will be tested in future work, through the use of WAXD studies as a function of temperature.

The melting of the 5% ethylene copolymer is represented in *Figure 7* for different crystallization temperatures. The plots can be divided into two groups. The first group is composed of samples crystallized in the range of 84 to 94°C. All of them show a decrease of the melting curve from the crystallization temperature until about 110°C and then a peak followed by a shoulder. The second group, composed of samples crystallized in the temperature range of 104 to 114°C, exhibits a shape similar to that described earlier for the 3% ethylene content. It should be recalled that the samples are not totally crystalline, so materials produced at high supercoolings can crystallize further during melting. That growth is represented by a slight drop of the d.s.c. curve. The melting of these crystals, which are more stable, is characterized by a shoulder above the main melting peak.

The subject of the true equilibrium melting point of polypropylene has been discussed previously[12], as have the complications that result from the peculiar thickening behaviour of polypropylene and its influence on equilibrium melting point extrapolations. Plots of melting point *versus* crystallization temperature for the 0.5% copolymer are shown in *Figure 9*, where both the return-to-baseline and the peak temperatures have been used. For reasons discussed earlier[12], the latter is to be preferred for this polymer. As can be seen from the plots,

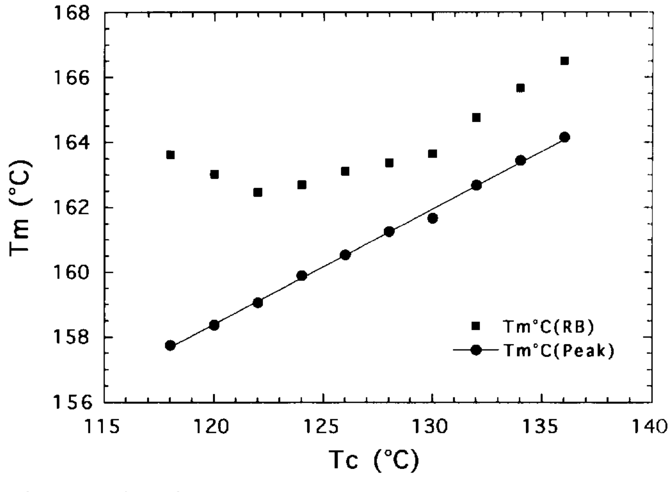

Figure 9 Plots of melting point *versus* crystallization temperature for the 0.5% ethylene copolymer using both return-to-baseline (RB) and peak temperatures

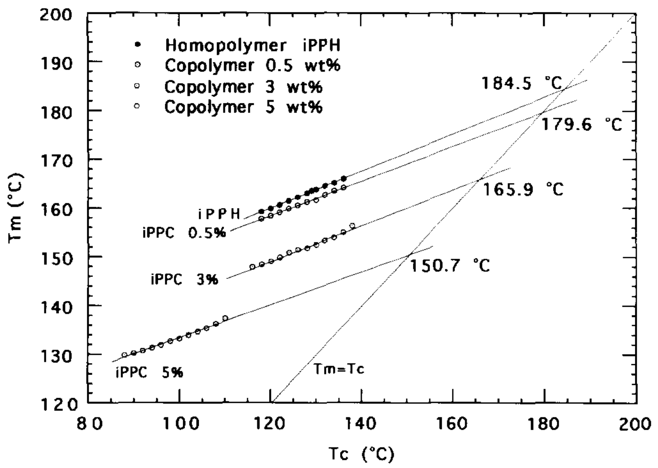

Figure 10 Hoffman–Weeks plots for all three copolymers and the homopolymer using the peak temperatures. (The coefficient of determination values, R^2, of the line fits are 0.998 for homopolymer, 0.998 for 0.5%, 0.989 for 3%, and 0.991 for 5% copolymers)

the return-to-baseline shows a strong upturn at low supercoolings and, if used, would lead to abnormally high extrapolations of equilibrium melting point. Hoffman–Weeks plots[18] for all three copolymers and the homopolymer are shown in *Figure 10*, using the peak temperatures. All give relatively good straight line fits and extrapolate to values of equilibrium melting point which show a strong trend downwards with increasing comonomer content. Since the specimens show varying γ/α ratios, it would have been expected that the curves would show different slopes when the specimens were predominantly α-crystals or predominantly γ-crystals. However, most of the data have been obtained at low supercoolings where the γ-phase predominates for the higher ethylene content copolymers and so the single slope is observed.

In the earlier work of Turner-Jones[6], considerable stress was placed on the shape and complexity of the melting curves and of their relation to the molecular fractionation effects that were believed to occur at the growth front. The reported melting curves were strongly reminiscent of those characteristic of LLDPEs, where molecular fractionation arising from copolymer content distributions is universally recognized as occurring. Many of Turner-Jones' experiments were carried out using slow cooling and others involved a combination of slow cooling and isothermal treatments. Our studies have considered only isothermal crystallizations, following rapid cooling to the crystallization temperature, and the d.s.c. plots are relatively simple. Because of differences between our treatments and those of Turner-Jones, the two sets of data are not strictly comparable. It should also be remembered that there have been significant improvements in d.s.c. equipment during the past 25 years. It is, however, very clear that the use of currently available propylene copolymers, which have much less heterogeneity than the earlier ones, considerably simplifies the behaviour, and explanations of the behaviour are easier to generate.

CONCLUSIONS

The results confirm that copolymerization causes the γ-phase to be generated at atmospheric pressure for high molecular weight polypropylene. The greater the amount of comonomer present in the polymer, the easier the formation of the γ-form. Furthermore, WAXD analysis proves that the γ-form is preferred at low supercoolings. D.s.c. studies have permitted a determination of the equilibrium melting points of the copolymers' crystals. The results show that the melting point of the γ-form is close to that of the α-form.

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