Crystalline Structure of Propylene–Ethylene Copolymer Fractions

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ABSTRACT: Crystalline structure were studied on both block and random propylene–ethylene copolymer fractions, which were obtained by temperature rising elution fractionation. The peak characteristic of α-polypropylene (PP) was observed for all fractions, except the fraction eluted at room temperature. A characteristic peak of polyethylene crystals [i.e., (200) planes] was observed in some fractions, indicating the existence of long ethylene sequence in these fractions. This is in accordance with the analysis from Fourier transform infrared spectroscopy and ^{13}C-NMR. The γ-form crystal of PP was observed in these copolymer fractions at atmospheric pressure. It is suggested that the insertion of comonomer into the isotactic PP chain makes the crystallizable sequences sufficiently short and produces the γ-form crystal. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 68: 381–386, 1998

Key words: propylene–ethylene copolymer fractions; TREF; crystalline structure; γ-form crystal of PP

INTRODUCTION

Since 1958, when isotactic polypropylene (i-PP) became commercially available, the crystalline architecture and crystallization of i-PP from the melt and solution have been topics of interest. Industrial applications have also been developed for copolymers of propylene. Each i-PP chain molecule possesses a chain conformation with a 2×3-1 helix. Because the presence of the asymmetrically substituted methyl groups causes rotation around the backbone bonds to be direction-dependent, both right-handed and left-handed helices with stereoisomer configurations of d and l result.[1] Combination of these possibilities leads to four distinguishable chain conformations. The intramolecular interaction energies of all four types of helices are identical. Their intermolecular interactions with each other in the crystal packing, however, depend upon packing geometry. Best packing is frequently achieved when the nearest neighbours of right-handed helices are the enantiomorphic left-handed helices and vice-versa. Different packing geometries lead to four well-known crystal structures (polymorphs): the monoclinic (α) form,[2] the hexagonal (β) form,[3] the triclinic (γ) form,[4] and the quenched form.[2] Some reports have also proposed the existence of a δ form.[5] Among these crystal structures, the monoclinic (α) form is by far the most common, being formed in normal melt-crystallized and solution-crystallized i-PP samples.

Copolymers of propylene have a very broad compositional variation. At least two different categories can be identified based on chemical composition. One is a series of ethylene–propylene (E-P) copolymers in which the ethylene comonomer unit is rich component.[6,7] This category, and E-P copolymers in particular, has attracted the most attention in both academic and industrial re-

search because of their possible range of applications. Although the propylene comonomer units may be included in the polyethylene (PE) crystals as defects, the mole percentage of the comonomer units critically affects the crystal structure. Another is the propylene-rich copolymers with ethylene and other short branch comonomer units.[8,9] These copolymers have been studied much less than the previous category. Nevertheless, research activities in these copolymers are gaining strength. The second category was less well recognized for a number of years, compared with the previous category, because these copolymers are basically the result of stereoregularity, namely, i-PP with copolymer units having methyl groups positioned in different directions.[10]

In the present work, crystalline characteristic of block and random propylene–ethylene copolymer fractions, which were obtained from temperature rising elution fractionation (TREF), will be studied in terms of sequence content and sequence distribution.

EXPERIMENTAL

Materials

TREF was conducted on low ethylene content propylene–ethylene copolymers provided by SOLVAY. The grade number of block and random copolymers were RV210 and KV202; ethylene content was about 8% and 5%, respectively. The fractionation procedure and results can be seen elsewhere.[11]

Apparatus

The wide angle X-ray diffraction (WAXD) experiments were conducted on a powder method using a Phillip Sie-122 X-ray diffractometer using CuK$_\alpha$ radiation having a wavelength of 1.54 Å at ambient temperature. Scattered intensities were measured over 2θ values between 5 and 50° in steps of 0.05°.
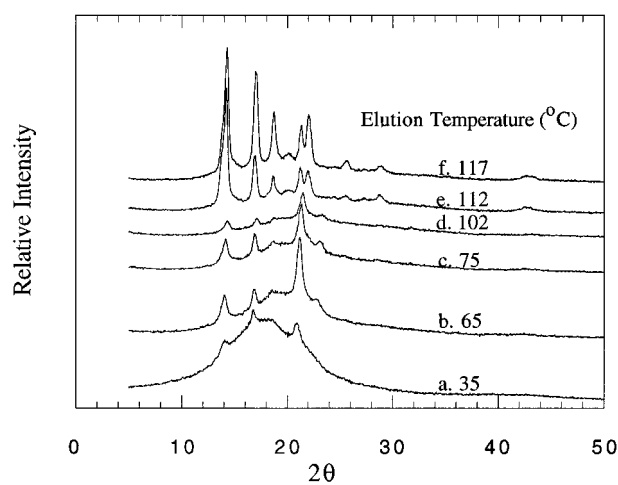
RESULTS AND DISCUSSION

Effect of Compositions on the Characteristics of Crystal Structure

WAXD studies have been used extensively to study partially crystalline polymers. Typical diffraction patterns of an amorphous polymer ex-
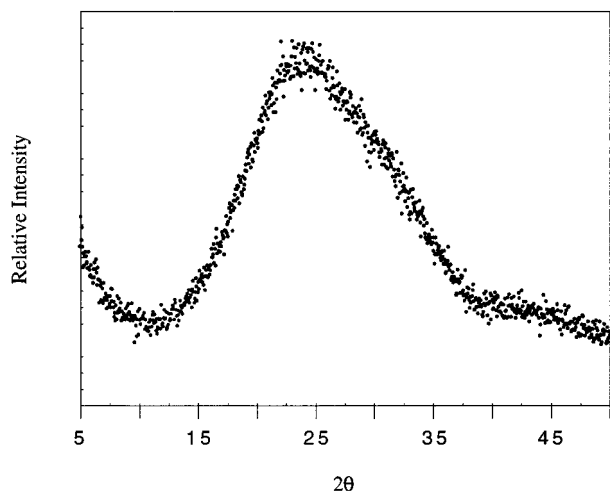
(a) Eluted at 24°C

(b)

Figure 1 WAXD diffractogram of block copolymer fractions eluted at different temperatures.

hibit only broad diffuse halos. The X-ray diffraction curve for partially crystalline polymers is that of "sharp peaks" due to scattering from the crystalline regions superimposed on this broad diffuse scattering from the amorphous phase.

Figure 1 shows typical WAXD diffractographs of the block copolymer fractions. From the curve in Figure 1(a), it can be seen that the fraction that was eluted at room temperature showed a broad amorphous halo with no crystalline reflections, whereas fractions eluted at progressively higher temperatures show progressively sharper crystalline peaks [Figure 1(b)]. This indicated an increase in both the quantity and quality of crystallinity.

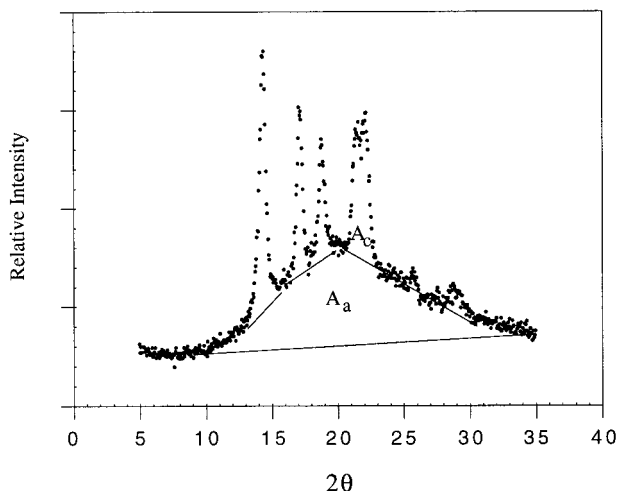From curves b–d in Figure 1b, it can be seen

Figure 2 Calculation method for crystallinity by WAXD diffractogram.

that the characteristic peaks of α-polypropylene (PP) at $2\theta = 14.15, 16.75, 18.6, 21.2,$ and $21.9°$ represent the (110), (040), (130), (111), (131), and (041) diffraction planes. There is a peak at $2\theta = 23.4°$ that is characteristic of the PE crystalline (200) plane. This indicated that, at these eluting temperatures, there are ethylene sequences that are sufficiently long to crystallize in the fractions. For curve a, eluted at 35°C (B2), there is no PE crystalline peak. This result is in agreement with the Fourier transform infrared spectroscopy and ^{13}C-NMR spectroscopic analysis,[11] where confirmed fractions eluted above room temperature to 100°C can be assigned to PP copolymer containing some ethylene units. Fractions eluted from 100 to 110°C are mainly composed of long propylene sequences and long ethylene sequences. Fractions eluted from 110 to 123°C are mainly composed of propylene long sequence or PP homopolymer.

Curves e and f exhibit a small peak at $2\theta = 20°$. By comparison with the WAXD diffractogram of α-PP, β-PP, and γ-PP,[3] this is characteristic of the (140) and (130) planes of γ-PP. The diffractogram is similar to that of an i-PP, containing a mixture of γ- and α-form crystals obtained generally by slow cooling or by crystallizing under pressure.[12] From the experiment, it can be seen that γ- and α-form crystals can coexist in the block copolymer fractions.

With the random copolymer, even at a low elution temperature, the PE crystal line was not present. This indicated that there cannot be ethylene sequences long enough to crystallize in the random copolymer. The ^{13}C-NMR analysis showed triad con-

tent of ethylene [EEE] in random copolymer fractions near 0.[11] The γ-form of i-PP was not observed either in the random fractions at this crystallization condition.

WAXD can be used to measure the crystallinity X_c from the ratio of the areas under the crystalline and amorphous reflections, A_c and A_a (Fig. 2)[13]:

$$X_c = [1 + (K_a A_a / K_c A_c)]^{-1} \qquad (1)$$

where K_a and K_c are constants normally assumed to be equal.

X_c was calculated in each case using the above equation and assuming $K_a = K_c$. The accuracy of these results is limited by difficulties in estimating the contribution of the amorphous background.

Figure 3 shows the relationship between crystallinity and eluting temperature for the block copolymer. With increasing eluting temperature, the crystallinity increased for the block copolymer fractions. This result, as expected, confirmed that the TREF fractionation of the block and random copolymers is based on the ability of crystallization. For random copolymer fractions, we observed the same trend.

γ-Phase in PE Copolymer Fractions

The γ-phase of PP was first noted during the 1960s[3,4] and was generated largely by crystallization at elevated pressures. It was identified first as triclinic. Early studies had associated the formation of the γ-phase with chemical heterogeneity in the PP chain caused by atacticity or by copo-
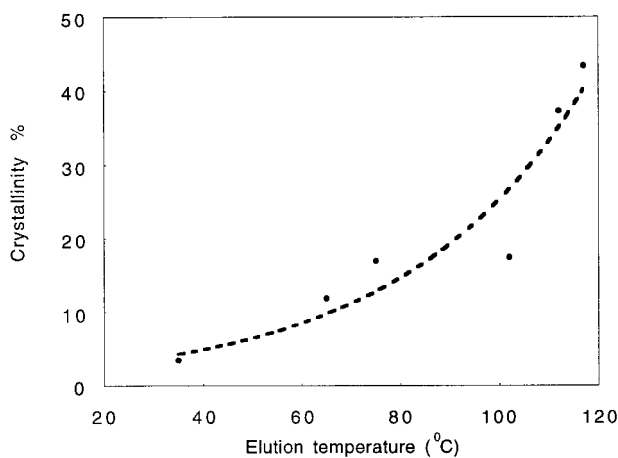

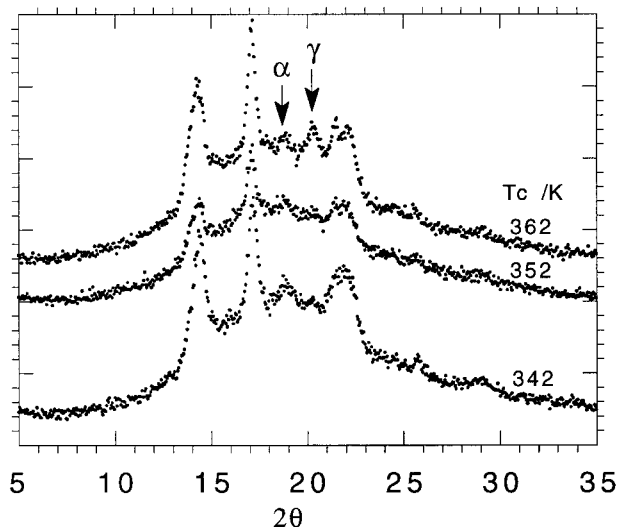**Figure 3** Variation of crystallinity with elution temperature.

Figure 4 WAXD patterns of a random copolymer fraction (eluted at 80°C) crystallized at different T_c.

lymerization.[14] More recent studies[15] have demonstrated that the γ-phase is produced at elevated pressures for high molecular weight homopolymer and that it has the same diffraction pattern as the low molecular weight polymer. This study also confirmed that the γ-phase is not the result of some unexpected degradation reaction at elevated pressures.

The study of Turner-Jones[14] 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 materials, and there was no way, *a priori,* of separating the effects of atacticity from the effects of copolymerization that could be complementary. Polymers currently available have > 99% isotactivity, and the effects of the microstructural variables can be separated.

In the Turner-Jones study of PP copolymers, 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 conducted on fractions produced by solvent extraction.

In the present study, the γ-phase was studied both in the unfractionated and fractionated block PP and random PP copolymers.

The X-ray diffraction patterns of the α- and γ-forms had been described 30 years ago.[3] They were similar in many respects, but the third strong reflection at d-spacing 4.77 Å from the α-form is absent in the γ-form and is replaced by a line at 4.42 Å. These characteristic peaks are found in the 2θ plot between the angles 18–19°, 15–16°, and 19.2–20.5° for the α-, β-, and γ-crystals, respectively. The presence or absence of each peak means the existence or absence of its form.

Figures 4 and 5 show the WAXD patterns for R4 and R6 (eluted at 80 and 95°C, respectively) crystallized at different T_c. The relative contribution of α and γ to the total crystallinity (not of the total sample) was calculated using the X-ray peaks that could be uniquely assigned to each of the α- and γ-phases. The (130) peak of the α-phase (18–19°) and the (040) peak of the γ-phase (19.2–20.5°) were used for this purpose. In the absence of structure factors and other corrective information, the ratio of the intensity of these two peaks was taken as a measure of the two phases.

Figure 6 shows the percentage of γ-phase produced at different crystallization temperatures for random PP fractions. It can be seen that the proportion of γ-form increases with increasing crystallization temperature and comonomer contents. Its development is ascribed to the interruption in the i-PP sequences caused by the other monomer.

Figure 7 shows the effect of the comonomer content on the γ-crystal content for block PP. It can be seen that, when the ethylene content is about 15%, the γ-content is a maximum.

For fractions cooled naturally in air, it was found that some block copolymer fractions can form the γ-phase, whereas no γ-phase can be observed in random copolymer fractions. The result is accor-
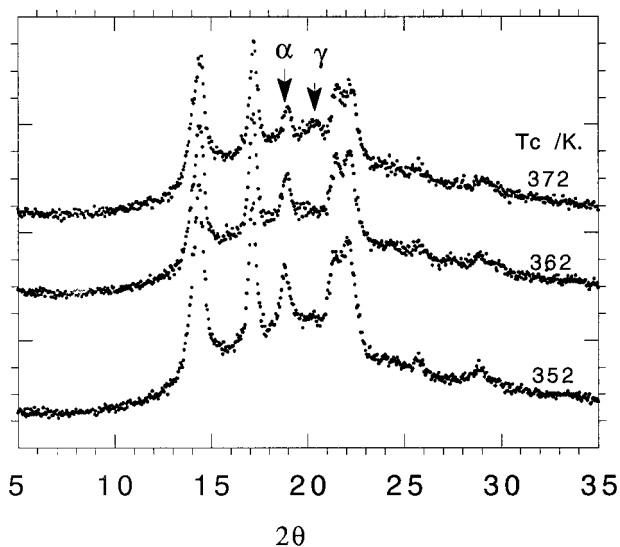

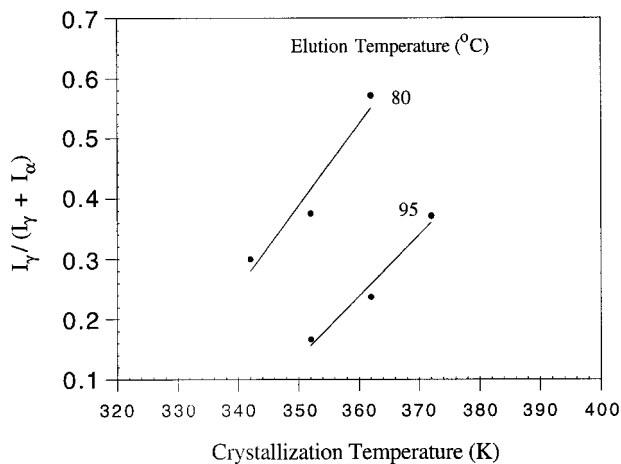**Figure 5** WAXD patterns of a random fraction (eluted at 95°C) crystallized at different T_c.

Figure 6 Variation of γ-phase content to T_c for random fractions.

Figure 8 WAXD patterns of bulk PP copolymer crystallized at different pressure.

dance with that reported before.[3] The γ-phase is formed in the bulk block copolymer at elevated pressure crystallization. Figure 8 showed that the γ-phase content increased with increasing pressure.

Conclusively, the PP γ-crystal can be formed by isothermal crystallization close to T_m, very slow cooling, and elevated pressure in block and random copolymers. The insertion of comonomer units into an i-PP chain make the crystallizable sequence shorter, resulting in an easy formation of the γ-form crystal.

CONCLUSIONS

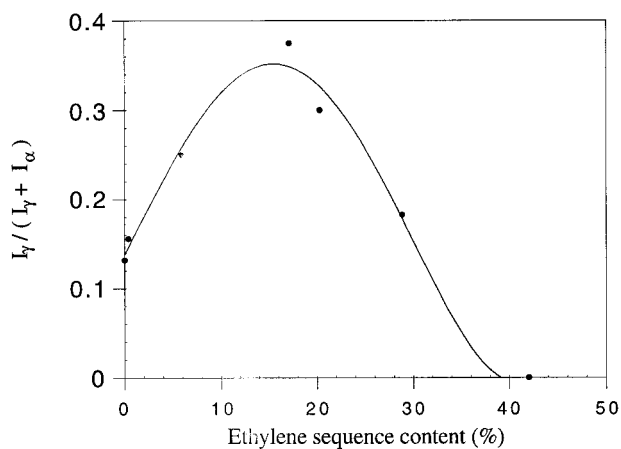The crystal structures of block and random copolymer fractions, which were obtained from TREF

Figure 7 Effect of ethylene sequence content on the content of γ-phase in block PP fractions.
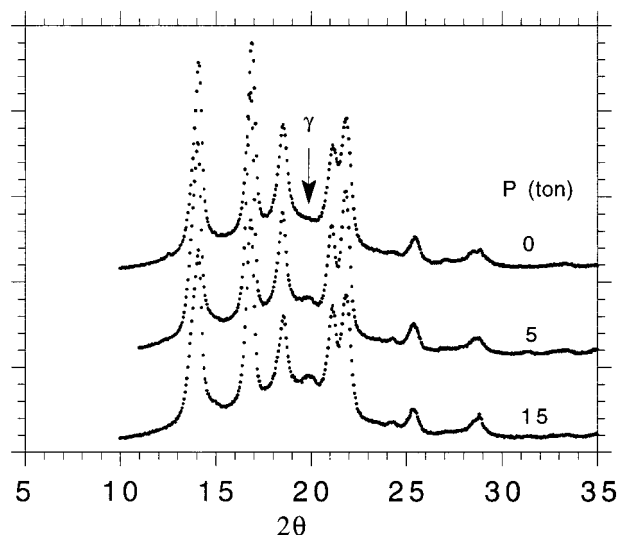
fractionation, were studied by WAXD. The peak characteristic of α-PP was observed for all fractions, except the amorphous fractions. For B4, B5, and B10, a characteristic peak of PE crystals [i.e., (200) planes] was observed, thus indicating the existence of long sequences of ethylene units in these fractions. On the other hand, no peak characteristic of PE was found for the other block fractions eluted below 65°C and above 110°C and all of the random fractions, indicating there is no long ethylene sequences in these fractions. This result is in agreement with the Fourier transform infrared spectroscopy and ^{13}C-NMR spectroscopic analysis.

The results show that the crystallinity of the fractions increase with increasing elution temperature for both block and random copolymer fractions. This confirms that the TREF fractionation occurs by separation of the molecules by their crystallizability.

The γ-form crystal of PP was observed in these copolymer fractions at atmospheric pressure. It was found that ethylene sequence content had some influence on the formation of γ-phase. For block fractions, the γ-phase content achieved a maximum at the ethylene sequence content about 15%. It is suggested that the insertion of comonomer into an i-PP chain makes the crystallizable sequences sufficiently short and produces the γ-form crystal. The proportion of γ-form increases with increasing crystallization temperature.

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