Macromolecules **2003,** *36,* 5623−5636

Formation of the α and γ Polymorphs in Random Metallocene−Propylene Copolymers. Effect of Concentration and Type of Comonomer

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Received March 5, 2003; Revised Manuscript Received May 19, 2003

ABSTRACT: Four sets of random propylene-based copolymers with 1−10 mol % of ethylene, 1-butene, 1-hexene, or 1-octene as co-units, synthesized with the same metallocene catalyst, were investigated by differential scanning calorimetry and wide-angle X-ray scattering following rapid and isothermal crystallization. Parameters related to defect concentration, defect type, and microstructure and thermodynamic and kinetic factors were evaluated as to their role in developing the γ polymorph. The effect of the comonomer in enhancing the fractional content of the γ polymorph is akin to the role of defects in the homo-poly(propylene) chain. However, differences in the partitioning of the comonomer between the crystalline and noncrystalline regions leads to contents of the γ phase that differ among the copolymers at any given crystallization temperature. Qualitatively, these differences can be used to assess the degree to which a counit participates in the crystallite. The experimental results suggest that there is no discrimination of the defects that enter the crystal lattice (stereo, regio, ethylene, or butylene units) between the α or γ crystallites. The results with copolymers establish that the bases that lead to the formation of the γ polymorph are the same for homo-poly(propylene) and its copolymers.

Introduction

Isotactic poly(propylenes) are important materials from both commercial and technical standpoints and have interesting and, in some aspects, not yet well-known crystallographic features. The properties of these materials can be varied from strong and rigid to elastomeric behavior by virtue of copolymerization. Understanding the effect of chain microstructure on the morphology and crystallization behavior of poly(propylene) and its copolymers is the key to applying these materials to an ever-diversifying range of applications from household articles to engineering materials. Ethylene- and 1-butene-based propylene copolymers are widely used for film applications, often as one of the components of multilayered co-extruded films. A major advance in expanding the properties of poly(propylenes) and their range of applications was the advent of metallocene catalysts,[1,2] which afforded incorporation of large contents of comonomer,[2,3] copolymerization of cyclic and other comonomer types that are not easily incorporated with classical Ziegler−Natta (ZN) catalysts, and excellent control of stereoregularity. In addition, metallocene catalysts may yield copolymers with a truly random comonomer distribution, uniform intermolecular distribution of the comonomer content, and narrow molecular weight distribution, leading to a new class of random polyolefins, which are inaccessible through conventional heterogeneous Ziegler−Natta catalysts.[4] To date, metallocene-based propylene copolymers have been synthesized with a variety of comonomers of the linear 1-alkene type, from ethylene to 1-hexadecane,[5−12] and comonomers leading to branched side chains such as 4-methyl-1-pentene,[13] giving a wide range of interesting materials. Despite this success, many of the studies reported in the literature concentrate on ZN-based copolymers,[14−26] the large majority with ethylene as comonomer.[16,18,19,21−26] The properties of metallocene-catalyzed propylene copolymers are only recently surfacing.[5−12]

Inherent to the isotactic poly(propylene) chain, formed either with a ZN or a metallocene catalyst, is the presence of structural irregularities of the chemical (regio defects or comonomer units) or stereo type. Previous detailed studies of homopolymers have found a close correlation between the concentration of these irregularities and the maximum content of γ polymorph that the chain develops.[27] Concentrations of the γ polymorph exceeding 80% can be developed in metallocene-type polypropylenes at conditions approaching those used in industrial processes, lending new significance to the properties conferred by this crystallographic form beyond the laboratory and scientific interest. The orthorhombic unit cell of the γ polymorph, made of nonparallel bilayers, is unprecedented for polymeric systems. There has been some interest in understanding the role of chain defects in enhancing the formation of this uncommon crystallographic phase.[27−33] In the γ polymorph each bilayer is made of parallel chains with opposite hand helices, and adjacent bilayers are tilted at 81° with respect to each other.[34−37] The α polymorph has a more classical chain packing with parallel chains of alternating right- and left-hand 3/1 helices also arranged in bilayers. A series of metallocene poly(propylenes) with a random distribution of defects crystallized from the isotropic melt enabled the effects of both molecular mass and defects on the formation of these polymorphs to be systematically investigated. While molecular mass (in a range of 40 000−300 000

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10.1021/ma030157m CCC: $25.00

g/mol) has only a minor effect on the formation of the γ polymorph, the concentration of defects has a major effect, increasing the content of this polymorph.[27] The γ phase is also favored with increasing crystallization temperature (T_{cryst}) up to a point where the kinetics of the crystallization of this phase, based on structural requirements, become very slow, and this leads to a local maximum in the γ content. It was found that the T_{cryst} at which the maximum content of γ phase is obtained increases from 120 to 150 °C for defect content decreasing from 4.4 to 0.41 mol %, respectively.[27] Local maxima were confirmed in subsequent works with similar metallocene type homo-poly(propylenes).[30,31] The presence of the maxima suggests that two competing factors affect the formation of this polymorph. On one hand, packing energy calculations suggest that the γ form would be slightly more stable than the α phase.[38] Hence, it is favored over the α phase with increasing temperature. On the other hand, defects, and therefore short isotactic sequences, favor the γ polymorph. However, the concentration of short sequences available for crystallization decreases with increasing T_{cryst}. The result is a maximum in the concentration of the γ form with T_{cryst}. Stereo (mrrm) and regio defects predominantly of the head-to-head type were found to lead to the same content of γ phase.[27,30]

Polypropylenes produced with a ZN-type catalyst have a broad distribution of defects from chain to chain and a distribution of defects intramolecularly that deviates strongly from the random behavior. The defects are more concentrated in the molecules with the lowest molar mass.[36] Since the presence of short isotactic sequences is a requirement for the formation of the γ polymorph, it is not surprising that ZN poly(propylenes), homopolymers, or copolymers, unfractionated or fractions, lead to insignificant[17,19,27,30,39,40] or much lower contents of crystallites of the γ form than those synthesized with a metallocene catalyst with the same overall concentration of defects.

Central to the present study is to investigate if the irregularity conferred by the comonomer to the polypropylene chain affects the formation of the γ polymorph in a manner akin to that given by stereo and regio defects and to what extent the type of comonomer influences the crystallographic polymorphs. Crystallographic, thermodynamic, and structural studies of propylene copolymers have been carried out previously in broad copolymers of the Ziegler–Natta type[21,22] or on fractions obtained from heterogeneous propylene–ethylene[23–25] and propylene–1-hexene copolymers.[17] Only a few reports on crystallization, melting, and some physical properties of metallocene-type propylene copolymers are available.[5–12] It is also difficult to extract from these works the effect of the comonomer type on properties because different catalysts were used in each study. Different catalysts may lead to significantly different concentrations of stereo and regio types of defects, which were not determined in these previous studies and may affect in different degrees the formation of the polymorphs.

This work presents a systematic study of the effect of type and concentration of comonomer on the formation of the α and γ polymorph of series of metallocene-type random propylene copolymers synthesized with the same type of catalyst. This ensures uniformity in the content and distribution of stereo and regio defects, which are also present in the chain and are known to affect the ratio of the crystallographic polymorphs, in addition to the comonomer effect. Two structural variables are studied independently of each other, comonomer content (up to ~10 mol %) and type of comonomer including ethylene, l-butene, l-hexene, and l-octene under rapid and isothermal crystallization. The role of the "punctual" defects found in the homopolymer vs comonomer units, in the formation of the γ polymorph, is evaluated from an analysis of the experimental data. These fundamental studies serve as background properties that can be used in ascertaining the degree to which any other propylene copolymer deviates from the random behavior. For example, in two recent studies, the concentration of the γ polymorph was used as an indirect measure to determine the stereoblock character of polypropylenes catalyzed with ZN[39] and with unbridged metallocene systems.[41]

Studies of the crystalline regions by solid-state ^{13}C NMR of the same copolymers have shown direct evidence of the inclusion of ethylene and l-butene units in this region.[10,11] These results were recently confirmed by acid etching followed by solution NMR.[7] Moreover, similar spectra of propylene-l–hexene and propylene–l-octene copolymers showed no evidence of inclusion in the crystal of butyl and longer branches.[42] The crystallographic parameters measured by Turner-Jones[14] and more recently by Marega et al.[20] also suggest that a significant proportion of l-butene can be incorporated into the crystal lattice. As will be shown in this and forthcoming works, the differences in comonomer partitioning between the crystalline and noncrystalline regions are reflected in the concentration of the γ polymorph and the spherulitic lamellar morphology developed by these copolymers.

Experimental Section

Materials. The copolymers studied are experimental samples obtained with a bridged Exxpol metallocene catalyst.[1,2] Their molecular characterization is given in Table 1. The designation encodes the type of comonomer and the total defect content. Also listed in the table is a homopolymer (M170K1.70) synthesized with the same catalyst under the same experimental conditions. This sample, previously studied,[27] is included to ascertain the effect of stereo and regio irregularities in the formation of the γ polymorph independent from the comonomer effect. The molecular mass and concentration of stereo- and regio-type defects are very similar for all the copolymers studied and can be considered constants. Properties within the series can be analyzed as a function of comonomer concentration and type as the only variables. Listed in separate columns in Table 1 are molar concentrations of the comonomer, head-to-head misinsertions of the erythro type and concentration of stereo defects. Defects caused by hydrogen abstraction (1,3 type) were absent in these samples. The total concentration of all types of defects added to the concentration of comonomer is also listed in this table. The analysis of experimental data throughout the text is referred to this value.

A range of comonomer content was available in both the ethylene and l-hexene series, which allows a systematic study of the effect of increasing comonomer, for fixed stereo and regio defects, on the formation of the crystallographic polymorphs. In addition, propylene copolymers with ethylene, l-butene, l-hexene, or l-octene as comonomer are available containing approximately 3.3 mol % total defects. Data from this series allowed the study of the effect of comonomer type on the properties of these copolymers. The molecular mass and its distribution were determined by standard gel permeation chromatography.[43] Calibration was performed with polystyrene standards. The type and fractional content of all the defects was obtained from the solution-state ^{13}C NMR spectra.[44–47]

Table 1. Molecular Characterization of Metallocene Homopolymer and Metallocene Propylene Copolymers

sample	comonomer type	comonomer (mol %)	regio (mol %)	stereo (mol %)	total defects (mol %)	M_w (g/mol)	M_w/M_n
M170K1.70		0.0	0.8	0.9	1.7	169 800	1.80
PE1.8	ethylene	0.8	0.4	0.6	1.8	233 100	1.98
PE2.8	ethylene	1.7	0.4	0.7	2.8	221 300	1.81
PE3.3	ethylene	2.1	0.5	0.7	3.3	210 000	1.77
PE3.4	ethylene	2.2	0.5	0.7	3.4	214 800	1.75
PE5.8	ethylene	4.6	0.4	0.8	5.8	251 000	2.12
PE8.2	ethylene	7.0	0.5	0.7	8.2	185 300	1.86
PE8.7	ethylene	7.5	0.4	0.8	8.7	188 000	1.71
PB3.4	1-butene	1.7	0.8	0.9	3.4	216 500	1.70
PB4.8	1-butene	3.2	0.7	0.9	4.8	~210 000	1.85
PH2.0	1-hexene	0.3	0.7	1.0	2.0	245 000	1.83
PH2.2	1-hexene	0.6	0.7	0.9	2.2	~230 000	
PH3.2	1-hexene	1.6	0.7	0.9	3.2	~210 000	
PH3.5	1-hexene	1.8	0.7	1.0	3.5	206 800	1.71
PH4.3	1-hexene	2.7	0.7	0.9	4.3	217 000	2.53
PO2.9	1-octene	1.3	0.7	0.9	2.9	202 300	1.76

Crystallization Procedures. All samples were either isothermally crystallized from the melt at temperatures between 60 and 138 °C or quenched from the melt directly into tap water at 25 ± 1 °C. The following crystallization times at the isothermal temperatures were used: $T_c = 100$ °C (24 h), $T_c = 110$ °C (3 days), $T_c = 120$ °C (1 week), $T_c = 125$ °C (2 weeks), $T_c = 130$ °C (3−4 weeks), $T_c = 138$ °C (> 4 weeks). These times were sufficiently long so that all but the highest defect content copolymers crystallized to completion. Complete extent of transformation was verified by the absence of a low-temperature melting peak corresponding to crystallites formed subsequently on quenching.

Plaques approximately 20 mm long, 13 mm wide, and 0.5 mm thick were initially sandwiched between thin aluminum plates and molded in a laboratory Carver press. All isothermal crystallizations were carried out in two oil baths, one held at 180 °C (±1 °C) for melting the specimens (20 min) and the other at the required crystallization temperature. The typical accuracy of the crystallization bath was better than ±0.2 °C. To prevent degradation and contamination of the samples with the silicone oil used in the baths, melting and crystallizations were carried out in evacuated glass tubes, which were suspended in the oil baths. Following crystallization the tubes were quenched in tap water and the samples removed when the temperature reached ambient conditions. Selected samples were melted in the press between aluminum foils to provide a seal and then inserted directly into the oil bath for crystallization. Following crystallization, these samples were quenched in tap water and then washed in a strong detergent solution to remove the silicone oil prior to their removal from the mold. No discrepancies were observed in the melting behavior between the two methods of crystallization.

Wide-Angle X-ray Scattering (WAXS). Room temperature WAXS diffractograms were obtained using a slit collimated Siemens D-500 diffractometer in a 2θ range between 5° and 45° with a step size of 0.02°. The instrument was calibrated for d spacing with a standard polished piece of polycrystalline quartz, and the film thickness was offset using shims. Filtered Cu Kα radiation was used as source. Diffraction patterns obtained above room temperature were recorded using a Siemens D500 $\theta-\theta$ diffractometer with an attached Anton Paar HTK high-temperature head. Temperature calibration was carried out with benzil (diphenylethanedione, mp 95 °C). Both diffractometers operated at 30 mA and 40 kV.

Peak assignments for the γ and α phases followed previous designations by Brückner and Meille[34] and Turner-Jones.[48] The fraction of crystals in the γ polymorph was obtained following the method of Turner-Jones[14] from the height of the (117) reflection at $2\theta = 20.1°$, characteristic of the γ form, and the (130) reflection at $2\theta = 18.8°$, typical of the α polymorph,[27] as $H\gamma/(H\gamma + H\alpha)$.

Differential Scanning Calorimetry. Melting and crystallization behavior were followed using a Perkin-Elmer differential scanning calorimeter DSC-7 under nitrogen flow. Melting was carried out at a scanning rate of 10 K/min. When dual endotherms were present, the peaks were manually deconvoluted and the areas correlated with the γ and α polymorphs. Temperature calibration was carried out with indium as a standard.

The crystallization kinetics of each polymorph was followed by the variation of the heat of melting of the γ and α peaks with crystallization time. Each sample was initially melted at 180 °C for 3 min and cooled at 40 K/min to the required crystallization temperature. After the required crystallization time had elapsed, the specimens were melted at 10 K/min, starting from the crystallization temperature. This procedure was used to avoid any additional contributions of crystallites that may be formed during cooling or quenching the samples prior to scanning. A sequence of increasing times and temperatures was used for each material, up to a maximum crystallization time determined by that required for no further increase in melting enthalpy.

Results and Discussion

Polymorphs and Melting Behavior. Isotactic poly(propylenes) crystallized in a mixture of the γ and α phases usually melt in two peaks; the lower melting peak is associated with the γ form and the higher with the α.[27,30,49] Both α and γ polymorphs have characteristic WAXS reflections, and it was shown that those corresponding to the γ form disappear in the diffractograms obtained at temperatures between both endotherms, whereas only reflections of the α form are generally present at temperatures at the peak of the highest melting endotherm.[27,30] Thus, the content of each phase can be obtained either from X-ray diffractograms or from the thermal data. Previous works in homo-poly(propylenes) have established a good correspondence between the content of the γ polymorph obtained by WAXS and the content calculated from differential scanning calorimetry by deconvolution of the melting peaks.[27,30,49] The same features are observed in the copolymers studied in this work.

The homopolymer and all the copolymers listed in Table 1 yielded either broad endotherms (for quenched materials) or double melting when isothermally crystallized. One example is shown in Figure 1a for PE1.8 crystallized at 120 °C. At this temperature the copolymer develops 55% of crystallites in the γ polymorph. Correspondingly, two well-defined endotherms with very similar heat of fusion are observed. As discussed in other works,[30] crystallites formed isothermally do not reorganize to any significant extent on heating, and both meltings are associated with two types of crystallites with different thermal behavior. Figure 1b shows WAXS diffractograms of the same sample obtained at temper-

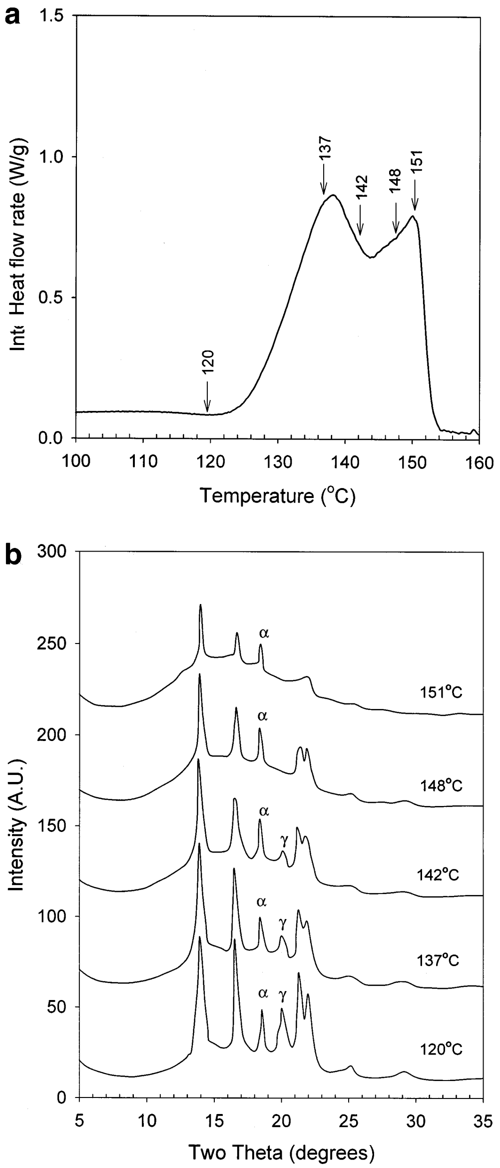

Figure 1. (a) DSC melting of sample PE1.8 crystallized at 120 °C. (b) Diffractograms taken at the temperatures indicated by the arrows in the thermogram. Reflections corresponding to the α and γ polymorphs are indicated.

atures indicated by the arrows in the thermogram of Figure 1a. There are no significant differences between the WAXS pattern obtained at room temperature and the pattern obtained at 120 °C, i.e., before any significant melting occurs. The content of γ phase up to this temperature is 55%, the same as that measured at room temperature. As the temperature is raised to 137 °C, near the peak of the lowest endotherm, the 117 reflection ($2\theta = 20.1$ °C) characteristic of the γ polymorph starts to decrease while the reflection corresponding to the α phase ($2\theta = 18.8$ °C) remains unchanged. Clearly only γ crystallites are melting in this temperature range. At 142 °C, a temperature between both endotherms, the γ peak is still observed albeit with low intensity and disappears at 148 °C, just below the highest temperature endotherm peak. It is therefore evident that, in agreement with the behavior of the homopolymer, the crystallites formed in the α and γ polymorphs from the copolymer melt at significantly different temperatures. The low melting endotherm is associated with melting of γ crystallites, and the high temperature corresponds to the α polymorph. As seen in Figure 1b, at temperatures just above the high-temperature melting peak (151 °C), only a small content of α crystallites remained unmelted. Thus, in addition to determining the γ content of the copolymers by WAXS, the fraction of this polymorph was also obtained from the DSC endotherms after peak deconvolution and analysis of the area of both peaks. The data from both methods are compared in Figure 2. A good correlation between the WAXS and DSC data was obtained for the homopolymer and copolymers crystallized in a range of temperatures between 100 and 130 °C, as seen by their proximity to the straight line with slope one drawn in the figure. The data for quenched samples is not included because the γ content in most of these samples was negligible, and the small crystallites formed on quenching reorganize to some extent during melting.[50] In addition, lower temperature maxima of copolymers with $< 40\%$ γ are poorly defined, leading to a greater scattering of the data in this region.

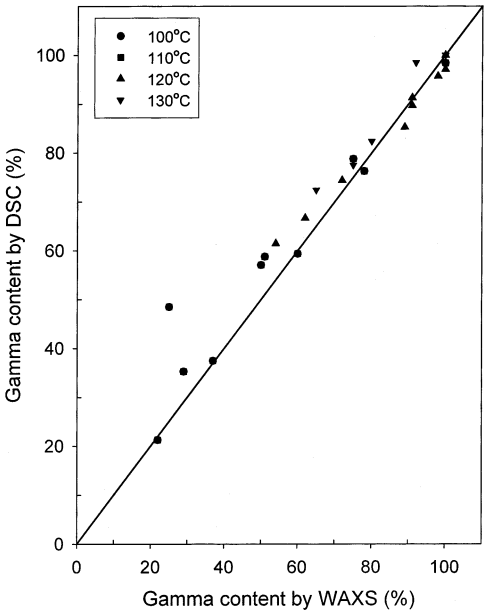

Figure 2. Content of γ phase calculated by DSC against γ phase obtained from WAXS. Solid line corresponds to line of slope one.

γ Content as a Function of Crystallization Temperature and Concentration of Comonomer. The effect of increasing comonomer concentration on the formation of the γ polymorph was studied in the series of propylene−ethylene and propylene−1-hexene copolymers crystallized in a range of temperatures between 25 and 138 °C. Representative diffractograms and meltings after isothermal crystallization in the temperature range between 25 and 120 °C are given in Figure 3a,b for PE2.8 and in Figure 4a,b for PH3.5. All the copolymers develop γ phase whose content increases with crystallization temperature. At the highest crystallization temperatures, propylene copolymers with total defect content higher than ∼3 mol % crystallize almost exclusively in the γ form, as shown in the WAXS patterns of PH3.5 crystallized at temperatures ≥120 °C. In this diffractogram the α reflection is negligible. For a constant crystallization temperature the concentration of the γ polymorph increases with increasing comonomer concentration. Rapid crystallization at 25 °C of all the copolymers, except the ones with the highest defect contents, led to the formation of α crystallites. Under these quenching conditions propylene copolymers with ∼7 mol % ethylene develop 34% of the crystallinity in the γ phase. The smectic phase, which develops under rapid quenching in films whose thicknesses are less than about 25 μm,[27] did not form in the thicker films used in the present study. Slower heat transfer in these films led to primarily α crystallites even after rapid crystallizations. As the temperature is raised above 50 °C, the reflection at 20.1° corresponding to the γ phase begins to develop and increases with temperature in any copolymer at the expense of the α.

The relative changes in the low- and high-temperature endotherms with increasing crystallization temperature (Figures 3b and 4b) parallel the changes in the WAXS reflections associated with the α and γ phases. As the concentration of the γ phase increases with increasing temperature, the magnitude of the low-temperature endotherm also increases at the expense of the high-temperature one. This feature is general for any of the copolymers in each series as shown in the examples provided in Figures 3b and 4b. The good correlation between the double melting and the content of each polymorph is indicated by the proximity of the experimental data to the straight line with a slope of one in Figure 2. All copolymers melt over a broad temperature range; this feature is characteristic of semicrystalline random copolymers in which the concentration of the counit is not uniform between the crystalline and noncrystalline regions and follows from basic thermodynamic equilibrium theory.[51] During melting the defect concentration in the melt decreases, and the remaining crystals melt at increasingly higher temperatures. Hence, the observed broad melting of the propylene copolymers in Figures 3b and 4b is a natural consequence of their copolymeric nature.

The variation of the γ content with temperature is given in Figure 5 for the propylene−ethylene series and in Figure 6 for propylene−1-hexenes. In Figure 5 data for PE8.2 have been removed for clarity and because its behavior is identical to that of PE8.7 (shown). Both series display similar behavior. Up to ∼130 °C the content of γ phase increases rapidly with temperature in any copolymer. At a fixed crystallization temperature the content of γ phase increases with increasing total defect content. It reaches values close to 100% at the highest concentration of defects even for relatively low crystallization temperatures, as seen by the data of PE8.7 crystallized at 100 °C. The form of these figures is very similar to that adopted for homo-poly(propylenes) with increasing concentration of stereo and regio defects.[27,30] A local maximum in the content of γ phase with temperature is also observed for the propylene−ethylene copolymer with the lowest defect content. Before describing the maximum in more detail and its implications on the mechanism of formation of the γ polymorph, experiments were carried out to ensure that the data plotted in Figures 5 and 6 correspond to the concentration of the γ polymorph developed at the crystallization temperature. In the high-temperature range the crystallization rate is slow, and the copolymers developed additional crystallinity when transferred to room temperature. Therefore, it is important to determine the crystal form of the quenched crystallites for a correct determination of the concentration of the γ polymorph. As also found in homopolymers, WAXS experiments indicated that the copolymer crystallites formed on quenching, after high isothermal T_{cryst}, are

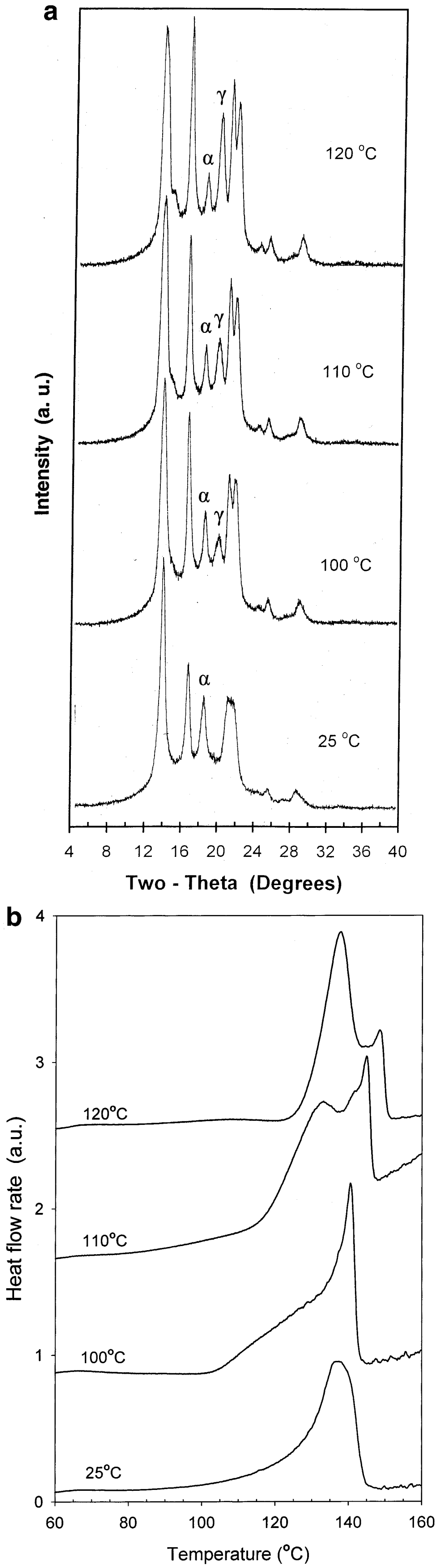

Figure 3. (a) Room temperature WAXS diffractograms and (b) DSC meltings of PE2.8 crystallized at the temperatures indicated.

of the γ phase, confirming the local maximum displayed in Figure 5. When a quenching peak was found in the

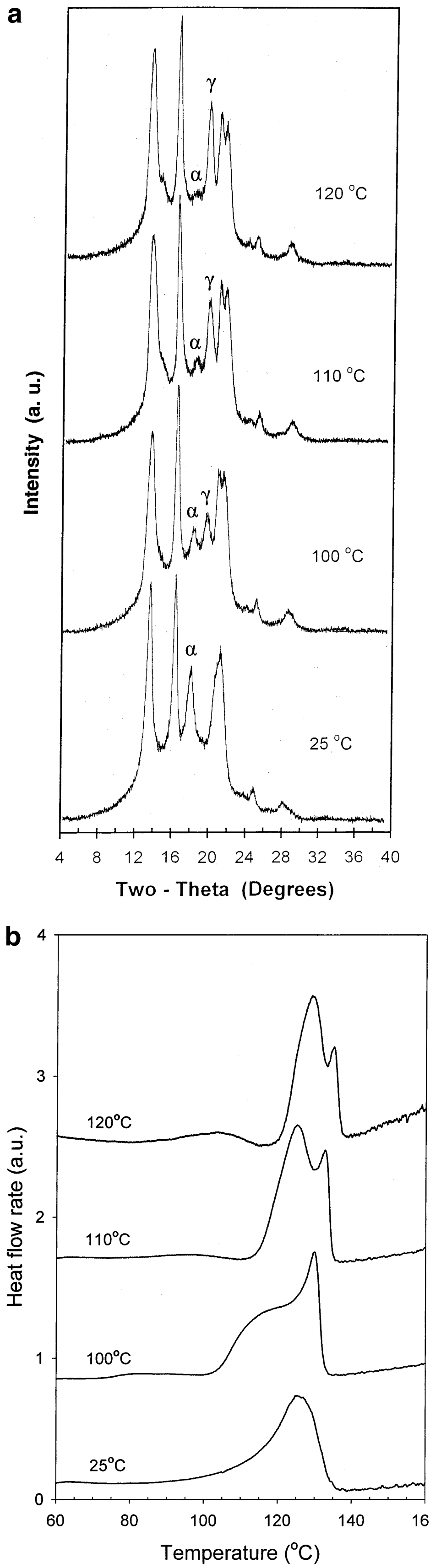

Figure 4. (a) Room temperature WAXS diffractograms and (b) DSC meltings of PH3.5 crystallized at the temperatures indicated.

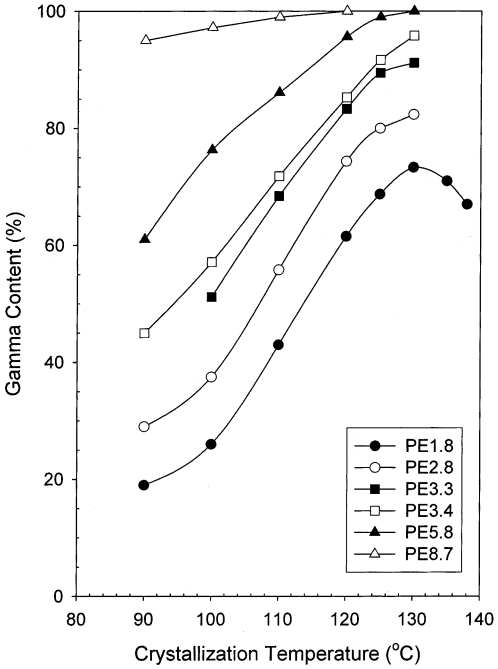

Figure 5. Percentage of γ phase as a function of crystallization temperature for propylene–ethylene copolymers with ethylene content increasing from 0.8 to 7.5 mol %.

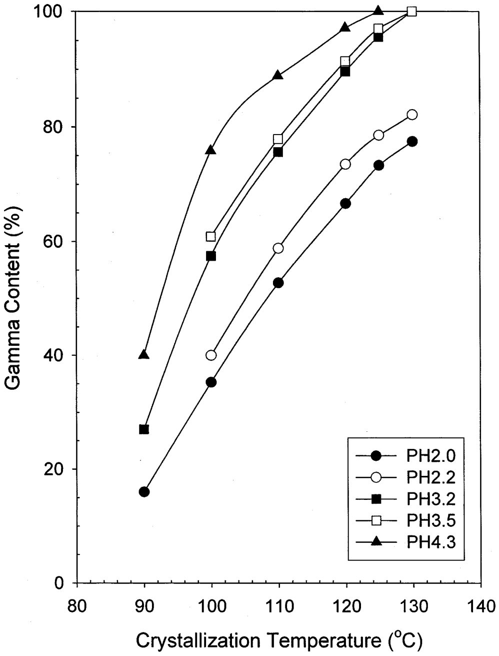

Figure 6. Percentage of γ phase as a function of crystallization temperature for propylene–1-hexene copolymers with 1-hexene content increasing from 0.3 to 2.7 mol %.

melting data, its heat of fusion was used to correct the fractional content of γ calculated from WAXS. A maximum is not observed in the least defective propylene–1-hexene copolymer (2.0 mol %) or in any of the other copolymers analyzed here due to the unduly long crystallization kinetics at temperatures above 130 °C and depletion of long crystallizable sequences that form the α phase. This aspect will be analyzed in more detail in the Kinetics section.

The similarity of behavior between homopolymers and copolymers when the comonomer is added as an additional structural irregularity in the iPP chain, suggests that the mechanism of formation of the γ polymorph in the homo-poly(propylene) is also operative for its random copolymers. The requirements for the formation of this polymorph were described in detail in our previous work.[27] They involve the need of molecules with short or relatively short crystallizable sequences, such as those with randomly distributed structural irregularities (comonomers and other types of defects), and a structure in the crystal−amorphous interfacial region that prevents folding and requires tilted ordered chains to propagate a lamellar crystallite. While the formation of the γ phase is favored with increasing T_{cryst}, the number of short crystallizable sequences is depleted at the highest T_{cryst}, leading to the observed local maximum as a function of temperature. Regarding the formation of the γ phase, the data of Figures 5 and 6 suggest that the comonomer acts as any other defect would in the poly(propylene) chain.

A more detailed analysis of Figures 5 and 6 reveals that, for any given total defect content, the propylene−l-hexene series develop a concentration of the γ phase about 10% higher than their propylene−ethylene analogues. This point will be discussed in the next section where four different comonomers are analyzed for the same total defect concentration.

γ Content as a Function of Comonomer Type. Diffractograms and melting thermograms for propylene−ethylene (PE3.4), propylene−l-butene (PB3.4), propylene−l-hexene (PH3.5), and propylene−l-octene (PO2.9), all with ∼3.3 mol % total defects and crystallized at 120 °C, are given in parts a and b of Figure 7, respectively. Both WAXS patterns and melting behavior show significant differences between the four copolymers. The 1-butene units lead to a more prominent reflection and melting peak corresponding to the α phase, followed by the ethylene units and then by the 1-hexene and 1-octene units. The ability of crystallization of each copolymer type in the γ form is evaluated in Figure 8, where the content of this polymorph is plotted as a function of T_{cryst} for the four copolymers. As expected from the reasonably high defect content, these copolymers developed a content of γ phase in excess of 50% in the range of T_{cryst} between 100 and 130 °C. The data for propylene−l-hexene and propylene−l-octene share a common curve and have the highest concentration of γ phase with values changing from ∼60% to 100% with increasing T_{cryst}. Propylene−ethylene develops slightly lower contents of γ phase at most temperatures. Propylene−1-butene is the copolymer with the lowest concentration of γ phase at any temperature; the values change from ∼45% to 80% in the same T_{cryst} range.

Differences in the content of γ phase for homo-poly(propylenes) with the same average concentration of defects were attributed to differences in the intramolecular distribution of defects.[39,41] A more blocky distribution of defects leads to significantly lower contents of this polymorph. This, however, is not the case for the copolymers studied. The use of the same type of metallocene catalyst led to the same random distribution in the comonomer and same content of regio and stereo defects.[2,39] The concentration of diads or triads of the comonomer, calculated from the solution ^{13}C NMR spectra of these copolymers, was very close to the predicted Bernoullian distribution.[52] Differences in the observed concentration of the γ phase at any T_{cryst} are consistent with a different ability of cocrystallization of each type of comonomer with the propylene units.

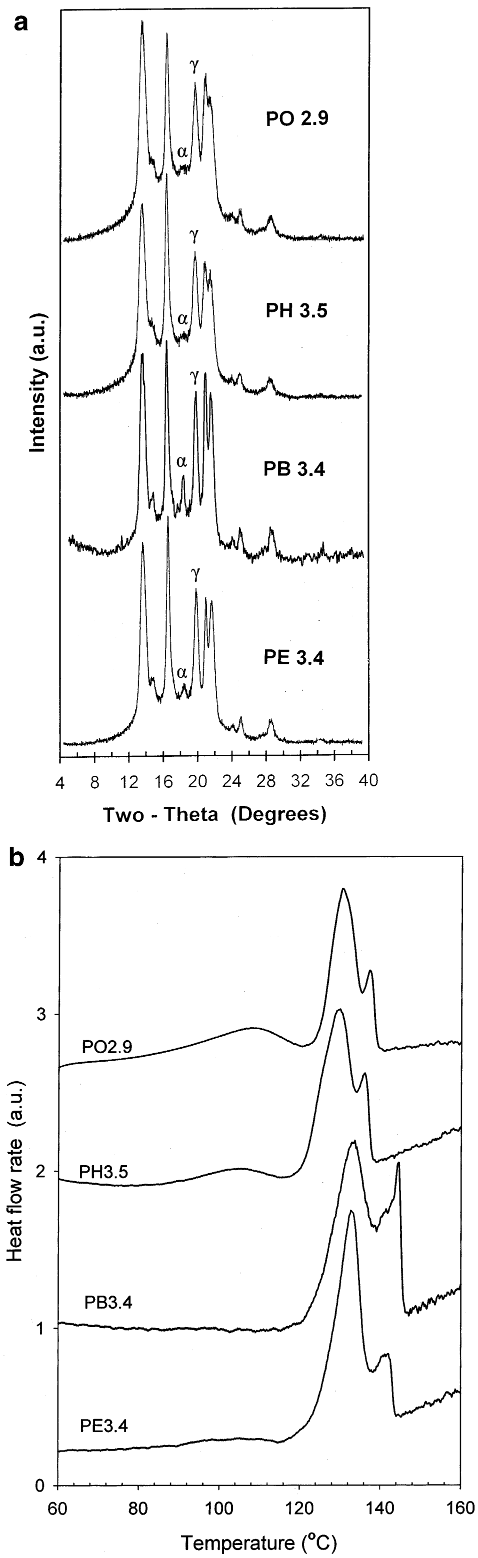

Figure 7. (a) Room temperature WAXS diffractograms and (b) DSC meltings of propylene−ethylene (PE3.4), propylene−1-butene (PB3.4), propylene−1-hexene (PH3.5), and propylene−1-octene (PO2.9) crystallized at 120 °C. All copolymers with ∼3.3 mol % defects.

It was shown by direct analysis of the crystalline regions by solid-state ^{13}C NMR of the same copolymers that ethylene and 1-butene units are partially included in the crystalline phase. However, spectra of the crystalline regions of propylene−l-hexenes and propylene−l-octenes showed no evidence of resonances associated with the methyl or methylene groups of the branch of

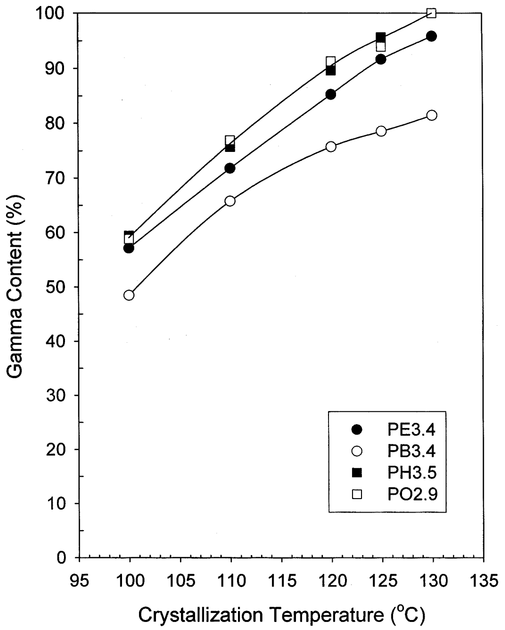

Figure 8. Percentage of γ phase as a function of crystallization temperature for propylene copolymers with ~3.3 mol % defects.

these comonomers.[10,11,42] At the same average concentration of comonomer in the chain, the concentration of l-butene units in the crystalline regions, calculated from the NMR data, was higher than the concentration of ethylene units. The data suggest that the 1-butene units are better incorporated into the poly(propylene) lattice than the smaller ethylene units. This difference in partitioning of the counits also explains the melting behavior. As recently reported[7] and shown in Figure 7b, propylene−1-butene has the highest final melting temperature followed by propylene−ethylene. Copolymers with 1-hexene and 1-octene units show negligible melting differences. With a higher probability of 1-butene units to enter the crystalline lattice, the average crystallizable sequence length in this copolymer is longer than in the propylene−l-hexene or propylene−l-octene chains and may account for the observed higher melting temperature.

The results of Figure 7 are also consistent with the differences in partitioning of the counit (ethylene, l-butene, l-hexene, or l-octene) between the crystalline and noncrystalline regions, in regards to chain structural requirements to form the γ polymorph. Described in previous works in homopolymers[27] was the premise that short sequences of crystallizable units favor the formation of this polymorph. At the same total concentration of defects, the average crystallizable sequence length of propylene−l-hexenes and propylene−l-octenes is shorter than for propylene−ethylenes and propylene−l-butenes; hence, higher contents of the γ polymorph are predicted in the former copolymers. The experimental data from Figures 5, 6, and 8 follow these predictions. They suggest that the concentration of the γ polymorph developed by a given propylene copolymer could be used as a qualitative assessment of the degree of partitioning of the comonomer unit upon crystallization. The higher the concentration of the γ phase, the more excluded the comonomer unit is from the crystalline lattice. Note that the last statement only applies to a series of copolymers with the same content of stereo and regio defects and the same content and distribution of comonomer units.

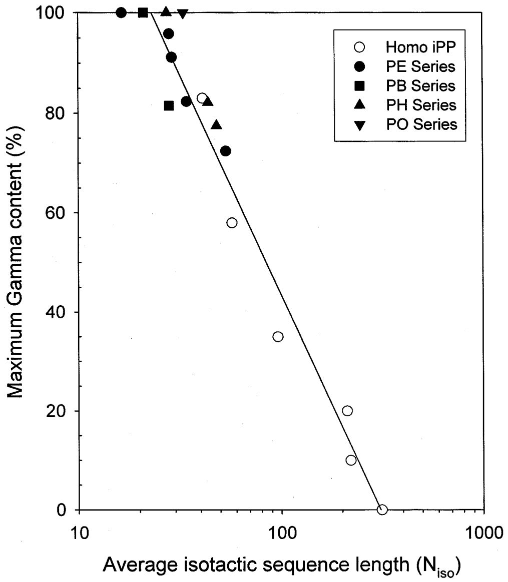

Figure 9. Maximum percentage of γ phase as a function of the average length of isotactic sequences. Open circles are data for homopolymers from ref 27.

The average length of isotactic sequences, N_{iso} (calculated as $1/\Sigma$fractional content of all defects), was found to scale with the maximum fractional content of the γ polymorph developed in homo-poly(propylenes).[27] The maximum fraction of the γ polymorph obtained for all copolymers at the optimum temperature (or at the highest temperature at which crystallization was experimentally feasible) is plotted against N_{iso} in Figure 9. Following suggestions by De Rosa et al.,[41] a semilogarithmic plot is presented. The open symbols are data previously reported for homopolymers obtained with a metallocene catalyst,[27] and the continuous line is a linear regression over these data. The data for propylene−ethylenes fall on the homopolymer line while the γ content of the two propylene−1-butenes is shifted to lower values. To develop the same 80% of γ crystallites requires a higher concentration of l-butene than of ethylene or than a combined stereo (of the mrrm type) and 2,1 regio defects in a homopolymer. The data for propylene−1-octene and propylene−1-hexene (closed triangles in the figure) are slightly shifted to the right of the homopolymer reference line, in agreement with an enhanced ability to crystallize in the γ form. We find from this figure that average sequence lengths of 33 units would yield pure γ crystallites in propylene−l-hexene and propylene−l-octene copolymers while this number is reduced to 25 for homopolymers and propylene−ethylenes and to ~20 for propylene−1-butene copolymers.

A subject of interest concerning defects, such as isolated rr triads, regio 2,1 erythro defects, and ethyl and l-butene comonomers, all found to enter the crystalline lattice at different levels,[7,10,11,42,53] is the possibility of a preferential partitioning of these defects in one of the polymorphs. In this context it was recently suggested that isolated rr triads are more easily accommodated in the γ than in the α crystallites.[30] In this latter work the diffractogram of homo-poly(propylenes) that crystallize in a mixture of the α and γ polymorphs was modeled by mixtures of a purely α diffraction pattern and a disordered γ pattern. The assumption of equal thickness for α and γ crystallites was made. The degree of disorder needed to account for the experimental pattern was found to increase with decreasing T_{cryst}, and it was associated with the experimental lower melting temperatures and broader endotherms of the γ crystallites formed at progressively lower T_{cryst}. Following this model of α/γ structural disorder, the conclusion was made that stereo mrrm defects are preferentially included in the γ polymorph while the α phase remains basically free of defects. While the presence of α/γ structural disorder of the type described by Auriemma et al.[30] may be found to some extent in poly(propylene) crystallites, the correlation with a preferential segregation of these mrrm stereo and possibly other "punctual" defects in the γ crystallites is not supported by previous NMR observations or by the data from the present work. For example, a homo-poly(propylene) with only stereo defects (predominantly of the mrrm type) that was slowly cooled or isothermally crystallized led to pure α crystallites.[53] However, analysis of the ^{13}C NMR spectrum of the crystalline regions indicated that a fraction of the stereo defects were included in the α crystallites. In an additional experiment, copolymer PE3.4 crystallized at 1 °C/min developed ~40% of the γ phase and negligible contents after rapid cooling in air. Solid-state NMR analysis gave the same concentration of ethylene units in the crystal in both samples.[10] If the defects were preferentially segregated to the γ form as speculated by Auriemma et al.,[30] poly(propylenes) crystallized in the α phase would have shown insignificant fractions or an absence of resonances associated with these types of defects in the spectra corresponding to the crystalline phase. It is, thus, concluded that the defects, stereo, regio, or ethylene units, must enter both polymorphs with roughly the same probability. Lower meltings of γ crystals are observed whether or not the chain structural irregularities enter the crystalline lattice, suggesting that γ crystals are thinner than α and not necessarily more defected.

The content of the γ phase developed by a homopolymer and two of the copolymers all with approximately the same total defect content (~1.8 mol %) is plotted against T_{cryst} in Figure 10. The γ contents of the homopolymer, M170K1.70 in Table 1, are extracted from the previous work,[27] and the data of the copolymers correspond to PE1.8 and PH2.0. Up to temperatures of ~130 °C, the homopolymer with defects of the stereo (mrrm) and regio (2,1) type and the propylene−ethylene copolymer with about half of the total defect content as ethylene units develop very similar concentrations of the γ polymorph. These data suggest a similar average defect partitioning in both polymers. The level at which ethylene units enter the crystalline lattice was found to be very similar to the average level at which stereo and regio defects enter the crystal;[54] hence, a similar behavior of these units is expected with regards to the formation of the γ polymorph.

At the highest T_{cryst}, the propylene−ethylene copolymer develops higher contents of the γ phase and shows significantly reduced crystallization rates than the homopolymer. For example, while complete crystallization of the homopolymer at 135 °C took ~24 h, it required over 2 weeks in the propylene−ethylene copolymer. These data suggest differences in the rate of partitioning of the ethylene and stereo groups as a function of T_{cryst}. Following the experimental data of Figure 10, one could predict slower kinetics for the accommodation in the crystalline regions of the ethylene units than those required to accommodate the stereo defect groups. One consequence of a partitioning of stereo and ethylene units subject to thermal history would be a significant difference in crystallization rates, as observed between the homopolymer and the copolymer for T_{cryst} above 130 °C.

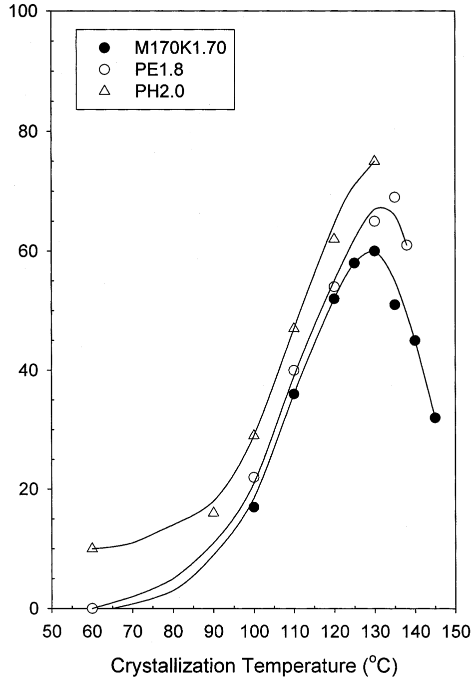

Figure 10. Percentage of γ phase as a function of isothermal crystallization temperature for homo-poly(propylene), propylene−ethylene PE1.8, and propylene−1-hexene PH2.0. The total concentration of defects is about the same in the three polymers.

As seen in Figure 10, the content of γ phase developed by propylene−l-hexene is, in the whole range of T_{cryst}, ~10% higher than the data obtained in the homopolymer and propylene−ethylene copolymer with about the same concentration of defects. These results follow the pattern of the 3.3 mol % series shown in Figure 8 and reinforce the NMR results obtained in propylene−l-hexene copolymers, which were consistent with the rejection of this comonomer from the lattice.[42]

Previous extensive data in homopolymers and the present data in copolymers all reveal that the main structural requirement in the formation of the γ polymorph is the presence in the chain of short crystallizable sequences. Units that can cocrystallize with the propylene units increase the average length of crystallizable sequences and, thus, reduce the ability to develop the γ polymorph. The degree of cocrystallizability of stereo regio, ethylene, butene, hexene, and octene units with propylene, obtained by NMR is in excellent qualitative agreement with the fractions of the γ phase obtained in a series with a matched content of defects.

Kinetics of the Formation of the γ Polymorph in Random Propylene Copolymers. In this section we first describe the general features for the formation of the γ and α polymorphs with time. This leads to a universal behavior in homo-poly(propylenes) and their copolymers. An independent analysis of the effect of concentration and type of defect on the kinetics follows.

The development, with time, of the α and γ polymorphs of selected copolymers was followed by WAXS at fixed T_{cryst}. In addition, the heat of fusion of the low- and high-temperature endotherms was monitored as a

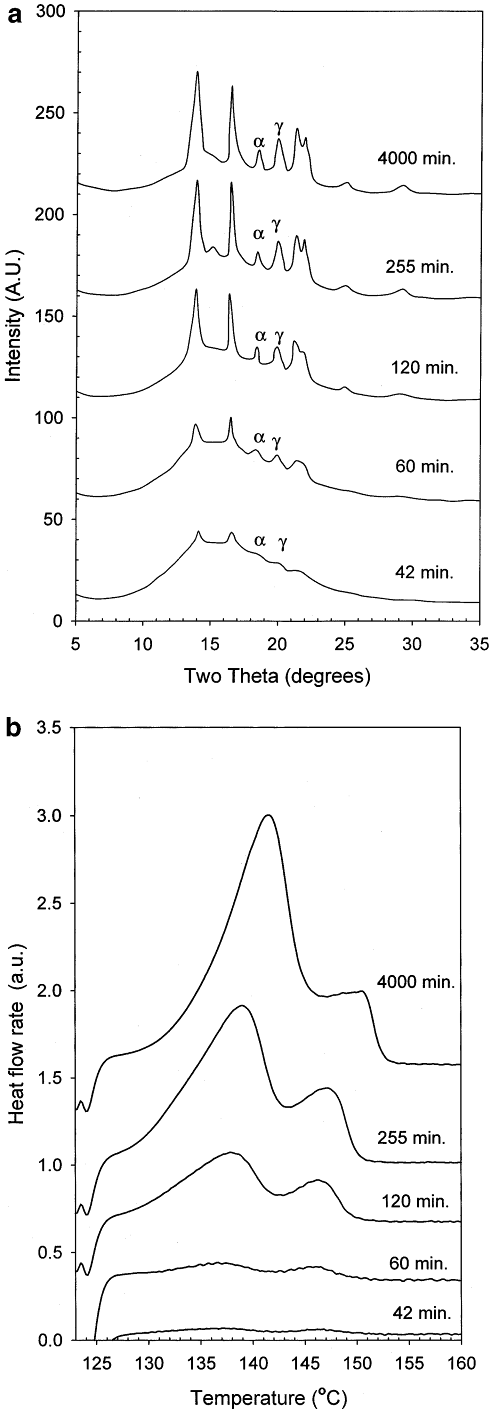

Figure 11. (a) WAXS diffractograms of PE2.8 obtained during crystallization at 123 °C at the times indicated. (b) DSC meltings started from the crystallization temperature.

function of crystallization time. Of interest is assessing whether the independent temporal development of the α and γ phases in copolymers follows that of the homopolymers.[27] If so, it would be suggestive of the same formation mechanisms.

Representative WAXS patterns of copolymer PE2.8 during crystallization at 123 °C are given in Figure 11a as a function of time. As was found during crystallization of homopolymers,[27,49] both polymorphs are observed at the very earliest detection of crystallinity. The (117)γ and (130)α reflections show the same increase in intensity during the initial 60 min of the crystallization. With further time the intensity of the α reflection remains constant while the γ reflection increases continuously. The relative variation of the intensities of both polymorphs depends on the specific copolymer and the crystallization temperature. However, the simultaneous appearance of both polymorphs in the initial stages of the crystallization is a common feature of the copolymers and homopolymers studied. Corresponding meltings are shown in Figure 11b, which corroborates the simultaneous formation of both polymorphs observed by WAXS. Two small endotherms with a similar area are obtained after crystallization for ~60 min. As crystallization proceeds, the area of the high-temperature melting, corresponding to the α phase, remains constant while the lower melting peak associated with the γ crystallites continues to increase. The sigmoidal variation of both endotherms with time is shown in Figure 12a for the same copolymer crystallized at T_{cryst} between 115 and 127 °C. These plots allow independent analysis of the development of both polymorphs. The α crystallinity quickly reaches a constant value that decreases with increasing T_{cryst}. On the other hand, the γ crystallinity continues to increase with time at any T_{cryst}. The highest value of the γ crystallinity first increases with T_{cryst}, reaches a maximum value, and then decreases with further increase in T_{cryst}.

The effect of increasing concentration of comonomer in the development of both polymorphs is shown in Figure 12b–d for three propylene–1-hexene copolymers. Independent of the type and concentration of comonomer, all of the copolymers display kinetics with similar characteristics. The development of both the α and γ polymorphs with time follows a sigmoidal function typical of the nucleation and growth processes in the crystallization of polymers. A large negative temperature coefficient of the crystallization, which is observed for all of the copolymers, is consistent with the importance of nucleation and, thus, undercooling to the crystallization process. At any fixed T_{cryst}, crystallization takes place at lower undercoolings with increasing concentration of 1-hexene. Thus, the crystallization kinetics become slower, and the range of T_{cryst} for experimental observation shifts to lower values, as is shown in Figure 12b–d. Data in Figure 12, and similar studies in homopolymers, make it evident that, independent of the type of defect in the poly(propylene) chain, the α and γ polymorphs appear simultaneously, suggesting that both have the same initial crystallization rates. Thus, WAXS and DSC kinetic data for the copolymers confirm that this behavior is universal for the crystallization of this polymorph in any type of homo-poly(propylene) or random propylene copolymer.

The kinetics of the combined heat of fusion of the α and γ peaks for copolymers with ~3.3 mol % of defects crystallized at 115 °C are given in Figure 13. These data allow evaluation of the effect of a different partitioning of the comonomer, between crystal and amorphous phases, on the crystallization rate at a fixed T_{cryst}. For example, to obtain an enthalpy of melting of 20 J/g, only 15 min of crystallization is needed for propylene–l-butene, while this time increases to 25 min for propylene–ethylene and to ~70 min for both propylene–l-hexene and propylene–l-octene. These times are directly related to the overall crystallization rates. They can be correlated with the NMR results that described the partitioning of the comonomer between the crystalline and amorphous phases. Comonomers that are excluded from the crystalline lattice, such as l-hexene and l-

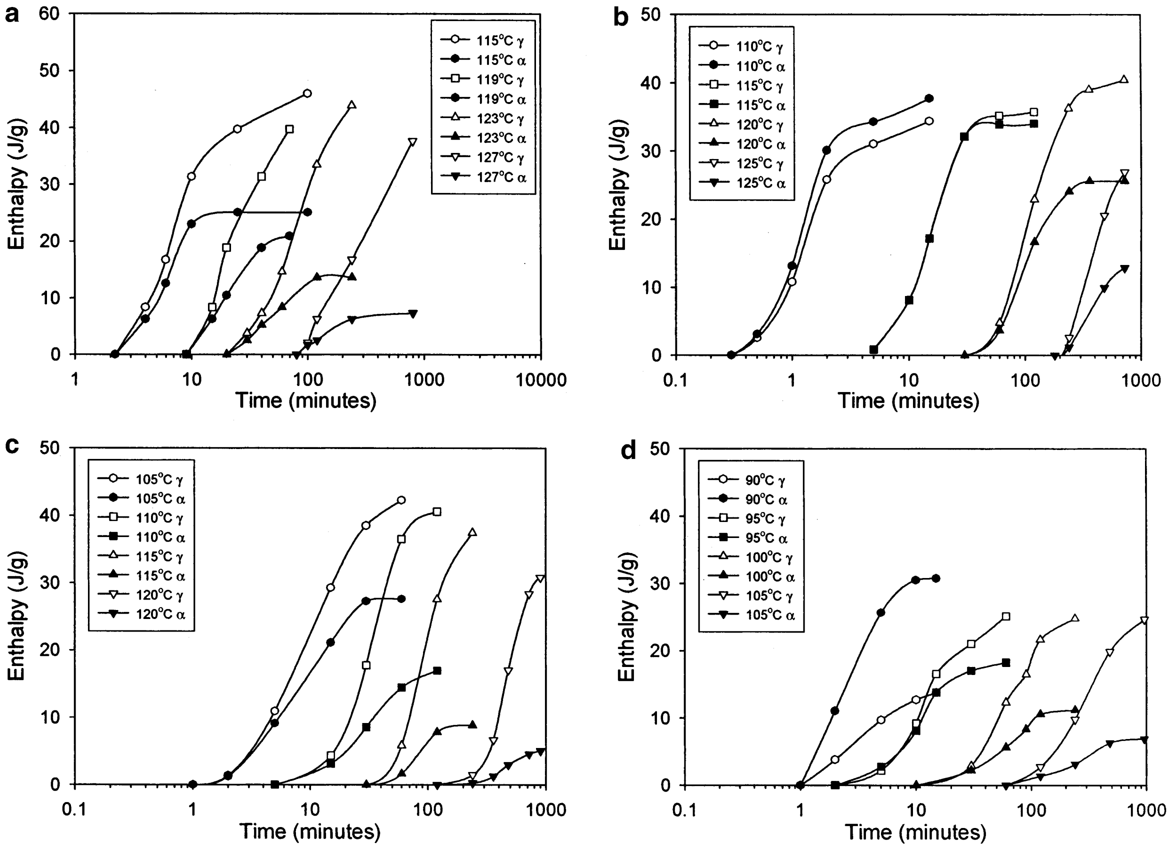

Figure 12. Sigmoidal development of α (filled symbols) and γ (open symbols) crystallinities with time at the indicated temperatures for the following copolymers: (a) PE2.8, (b) PH2.0, (c) PH3.5, and (d) PH4.3.

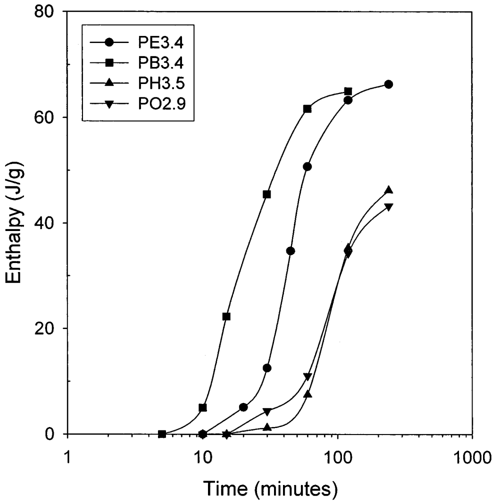

Figure 13. Sigmoidal variation of the total crystallinity for propylene−ethylene (PE3.4), propylene−1-butene (PB3.4), propylene−1-hexene (PH3.5), and propylene−1-octene (PO2.9) crystallized at 115 °C. All copolymers with ∼3.3 mol % defects.

octene, have lower values for the sequence propagation probability of the crystallizable units, and, thus, slower crystallization than copolymers with counits that participate in the crystallization such as the l-butene and ethylene groups. In the latter group the 1-butene copolymer crystallizes faster than the ethylene one, reflecting the greater partitioning of the 1-butene comonomer. Differences in crystallization rates affect the relative values of α and γ crystallinities and, thus, the observed fractional content of the γ form.

For any given copolymer with a total defect content higher than 2 mol % the concentration of γ phase increases systematically with increasing T_{cryst} (see data in Figures 5 and 6). Thus, it would be desirable to compare the crystallization kinetics of each copolymer crystallized at 115 °C in Figure 13, at constant undercooling and γ content. This can only be properly accomplished if the equilibrium melting temperature for each copolymer with 3.3 mol % defects is known. At the present time these values are unknown.

It is instructive to evaluate the total heat of fusion obtained at high levels of transformation, as well as the independent heat of fusion for the γ and α crystallites, with increasing crystallization temperatures as was done with the homopolymers.[27] Representative examples are given in Figure 14 for three propylene−ethylenes copolymers with increasing ethylene content. The series of propylene−l-hexenes, −l-butenes, and −l-octene copolymers display similar characteristics. The data of Figure 14 are for crystallites formed at the T_{cryst}; i.e., the melting was started at the T_{cryst} without previous cooling. Typical for crystallization of random copolymers, we find that the total heat of fusion decreases with increasing T_{cryst}. This result is a consequence of the decrease in the number of crystallizable sequences of sufficient length to form a stable crystallite with decreasing undercooling in any random copolymer.[55] At a fixed T_{cryst} the heat of fusion decreases with increasing concentration of comonomer and reflects the overall inhibition of the crystallization process imposed by the ethylene units despite their partial inclusion in the lattice. For example, based on a heat of fusion of the pure crystallite of 209 J/g,[56] crystallization at 130 °C leads to crystallinity levels of 43%, 24%, and ∼2.5% as the concentration of ethylene increases from 0.8 to 4.6 mol % in Figure 14.

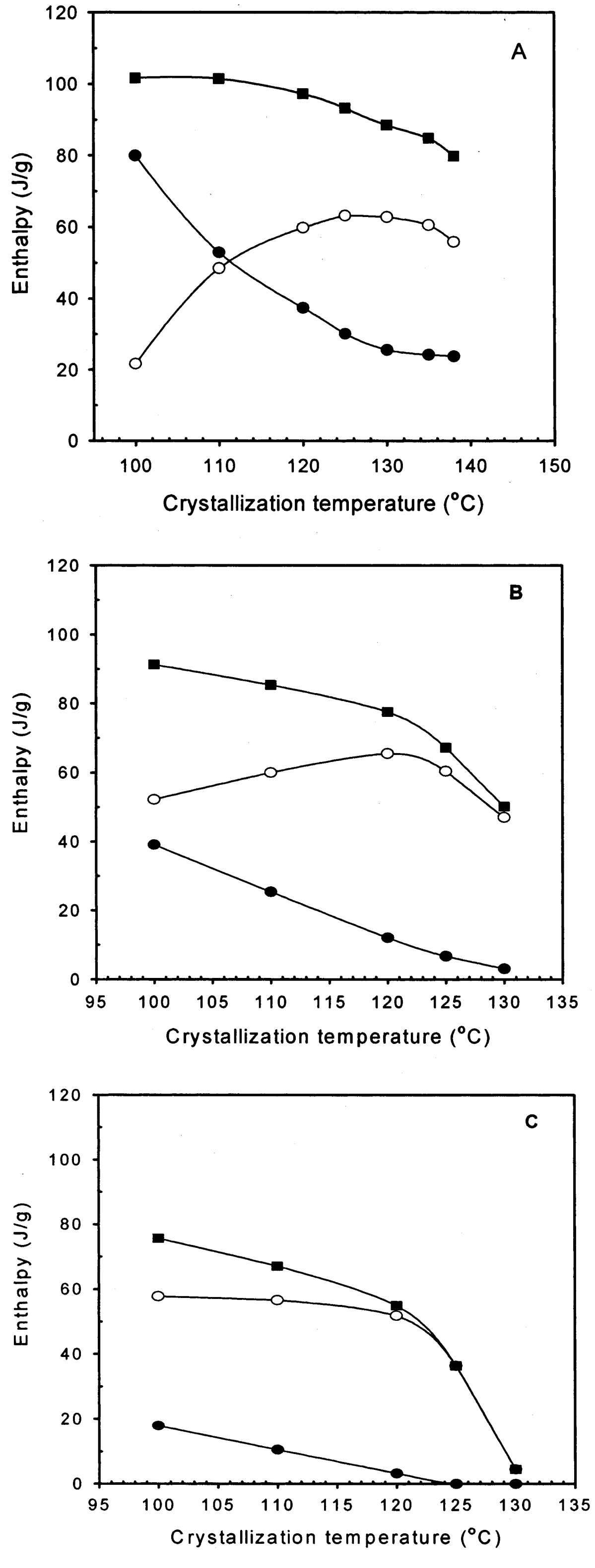

Figure 14. Variation of the independent heat of fusion of α (closed circles) and γ (open circles) crystallites, as well as the combined heat of fusion (closed squares), as a function of crystallization temperature for the following propylene copolymers: (A) PE1.8, (B) PE3.4, and (C) PE5.8.

The heat of fusion corresponding to the α crystallites decreases continuously with T_{cryst} following the expected trend for random copolymers. The heat of fusion of the γ crystallites first increases with temperature, reaches a maximum value, and then decreases with further increase in T_{cryst}. This behavior is universal for the crystallization of homo-poly(propylenes)[27] or for all random propylene copolymers. A maximum in γ crystallinity with T_{cryst} reflects that two competing mechanisms are involved in the formation of this polymorph. Hence, it is the relative variation in α and γ crystallinities with T_{cryst} which accounts for the observed maximum of the concentration of γ with T_{cryst} (Figure 5). For ethylene and (presumably) 1-butene copolymers with less than ~2 mol % defects, the relative fraction of the γ polymorph, calculated from heat of fusion, leads to a local maximum with temperature in agreement with the data of Figure 5. The maximum is not observed in propylene−1-hexenes with matched concentration of defects because of the slower kinetics. The temperatures at which α crystallites are no longer formed can be estimated from data such as those of Figure 14. These temperatures are experimentally attained at total defect concentrations >~3.5 mol % for propylene−ethylenes and at >~3 mol % for propylene−l-hexenes. For the copolymers studied they can be as low as 110 °C for the most defective propylene−ethylene (PE8.7) or above 130 °C. Crystallization at these and higher temperatures take place only in the γ polymorph.

Role of Structural Irregularities and Crystallization Kinetics in the Mechanism of Formation of the γ Polymorph. The experimental data of the formation of the γ polymorph in homopolymers were mechanistically reconciled from two major considerations:[27] (1) the partitioning by sequence length that isolated structural irregularities randomly introduced in a chain impose on the molecular structure[32,48] and (2) the role of very different crystal−amorphous interphases propagating either an α or γ type lamellar crystallite.[57]

Within any given series of copolymers of the same comonomer type, the fraction of γ polymorph that is obtained as a function of increasing comonomer content or increasing T_{cryst} follows an identical behavior to that observed by increasing defects in the homopolymer chain. The γ content increases with increasing the fractional content of any type of defects or comonomer as illustrated by the data in Figures 5 and 6. Thus, mechanistically, both homopolymers and copolymers follow the same initial requirement, the need of chains whose microstructure leads to thin crystallites, i.e., the presence of short crystallizable sequences in the chain.

The role of a different interface was reconciled with the experimental observation that the γ polymorph is favored in molecules with shorter average continuous isotactic sequences and at higher crystallization temperatures. It was suggested that the α polymorph is formed from the longest sequences through some type of folding while the molecular tilt, required to dissipate the ordered chain flux emanating from the crystalline regions, allows the propagation of γ crystallites from the short sequences without the need of folding.[27,32,34,57−59] This situation is a special case for polypropylene and of this particular polymorph because tilted chains in the unit cell represent a low-energy structure.

The maximum in the γ crystallinity with temperature is associated with two competing processes based on the availability of crystallizable sequences. The copolymer behavior sets a random sequence distribution, which combined with nucleation theory can be used to estimate the change in concentration of crystallizable sequences with T_{cryst} and mol % defects in the chain. This concentration is directly related to the isotactic sequence length required to form a nucleus of critical size, given in Figure 17 of ref 27. At the lowest T_{cryst} the required length to form a stable nucleus (as primary step in the crystallization) is very small; thus, most crystallizable sequences may fold and lead to α crystallites. With increasing temperature, a larger number of crystallizable sequences approach in exact length the nucleation requirements. These sequences can crystallize in γ crystallites without folding. However, at higher temperatures the length requirements to form a stable crystallite become much higher. The availability of long sequences for crystallization is reduced; thus, the fraction of units that crystallize in the γ phase decreases at these high temperatures, in agreement with the experimental variation of the heat of fusion with temperature given in Figure 14.

Packing energy calculations suggested a slightly higher stability of the γ phase.[38] On this basis, one would have expected higher melting temperatures for γ crystallites. The observed melting points are, however, lower than those for the α phase, suggesting thinner γ crystallites, as also pointed out in a previous work.[58] As indicated earlier, the present experimental data do not suggest that a higher concentration of defects is included in the γ crystallites.

The formation of the γ phase in each series of random copolymers is adequately explained using the same qualitative arguments used in homopolymers with randomly distributed defects. However, when comparing the behavior for different comonomer types, important and systematic differences are identified in relation with differences in comonomer partitioning between the crystalline and noncrystalline regions. Propylene−1-butenes crystallize with lower concentrations of the γ polymorph than any of the other copolymers studied. This experimental observation confirms the NMR findings that the 1-butene units are included in the crystal at the highest level.[7,54] The 1-hexene and 1-octene units, rejected from the crystal, lead to the highest contents of the γ polymorph at any temperature. Qualitatively, the concentration of the γ polymorph gives a measure of the degree of incorporation of the comonomer in the crystalline regions of propylene random copolymers.

Acknowledgment. Funding of this work by the National Science Foundation, Grant DMR-0094485, is gratefully acknowledged. The assistance of Dr. J. Chatterjee and Mr. S. Doyle with collection of DSC data is also acknowledged.

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MA030157M