Polymorphic Transformation in Isotactic 1-Butene/Ethylene Copolymers

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ABSTRACT: The effect of molecular weight, composition, and aging temperature on the kinetics of the tetragonal-to-hexagonal polymorphic transformation in isotactic (*it*) 1-butene/ethylene random copolymers has been investigated by differential scanning calorimetry and wide-angle X-ray diffraction. It has been found that, as it occurs in *it* poly(1-butene) homopolymers, the average molar mass has no effect on the rate of transformation. However, even at very small concentration, the presence of ethylene units highly enhances the rate of the process, to the extent that structural interconversion at room temperature requires only few hours in a copolymer with 5.5 wt % of counits, while more than 10 days is needed to complete the transformation in the homopolymer. By coupling the information obtained from different techniques, it has been found that, together with the usual development of stable hexagonal (form I) crystals with melting temperatures higher than that of the parent metastable tetragonal form (form II), a fraction of low-melting form I crystals are readily generated in the early stages of transformation. Thermal curves recorded at various aging times exhibit multiple endotherms, which also include transient peaks or shoulders. This complex thermal behavior can be tentatively explained by assuming that, before being converted into the hexagonal modification, the highly mobile as-crystallized form II undergoes an isostructural transformation through migration and redistribution of the defects initially trapped in the crystal lattice. The resulting tetragonal crystals, being characterized by widely different defect content, exhibit different transformation rates.

Introduction

Isotactic poly(1-butene) (*it* PBu) crystallizes into several crystal modifications differing in their helical conformation and chain packing.[1−8] One of the most important aspects of the polymorphic behavior of this polymer is the slow spontaneous transformation, from the tetragonal form II to the twinned hexagonal form I, that characterizes melt-crystallized samples and has a very strong impact on materials properties. Form II, in which chains in a 11_3 helix conformation are packed in the low-density tetragonal unit cell, is the kinetically favored modification commonly obtained by melt crystallization in quiescent conditions at atmospheric pressure. At room temperature, this metastable modification slowly transforms into the most stable modification, form I, which is characterized by a 3_1 helix conformation.[2,3,9] The II−I transformation is accompanied by a considerable structural change which results in an extension of the chain conformation in crystalline strands of around 14% and a decrease in the cross section of around 10%. Form I exhibits higher density, melting temperature, melting enthalpy, and stiffness than form II.[3,9−12]

It is well established that the transition from the tetragonal to the hexagonal phase is irreversible and that the initial crystal modification II can only be obtained by remelting the sample (monotropic polymorphism). The polymorphic transformation occurs over a wide temperature range, from T_g (−25 °C) up to 100 °C,[4,9] with a maximum rate at around 20 °C;[5,9,13] at this temperature, completion of the transformation requires several days.[4,5,11,14,15]

Despite the rewarding physical and mechanical properties of *it* poly(1-butene), the slow transformation kinetics is the main reason that has so far restricted its commercial development. This has stimulated many researchers to find suitable strategies to accelerate the II → I transition. It has widely been reported that the application of hydrostatic pressures,[5,16] shear or tensile stresses,[17−20] and addition of suitable substances[18,21,22] can remarkably increase the rate of transformation. Recent results obtained by thermal analysis and microindentation hardness measurements suggested that the morphology of the as-crystallized form II also plays a role in the kinetics of transformation, and a faster conversion to form I was observed in samples crystallized at higher temperatures.[11,15]

It was claimed that molecular characteristics, such as molecular weight,[4,23,24] degree of isotacticity,[4,24] and content of comonomer units,[4,25,26] also influence the rate of the solid−solid transformation. Foglia[4] and Chau and Geil[23] reported that the transformation rate increases with decreasing chain length. However, in the results obtained by Schaffhauser[24] no clear trend in the rate of transformation as a function of the molar mass was observed, probably because experiments were performed on samples also differing in isotacticity. More recent results obtained by thermal analysis demonstrated that the transformation rate is barely affected by chain length when homopolymers with similar microstructure are compared.[15]

On the other hand, the effect of comonomeric units randomly distributed along the chain has been less studied. To our knowledge, the only available information on *it* 1-butene copolymers was reported by Foglia,[4] Gianotti and Capizzi,[25] and Turner-Jones[26] in their

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Table 1. Molecular Characteristics of Poly(1-butene) Homopolymer and Random Ethylene Copolymers

sample code	M_w, 10^{-3} g/mol	Et units (wt %)	fraction of isotactic pentads (%)
PBu 0200	398	0	87.5
PBu 8240	383	0.75	88.8
PBu 8340	293	0.75	87.0
PBu 8640	470	0.75	87.6
PBu 8220	400	2.2	85.7
PBu 8310	305	5.5	82.0

investigation of copolymers of 1-butene with various α-olefins. They observed that copolymerization of isotactic poly(1-butene) with α-olefins with less than 5 carbon atoms increase the transformation rate while long linear α-olefins (with C > 5) or branched counits speed up the rate of the process.[26] Turner-Jones explained these results by considering that the insertion of counits having a small cross-sectional area favors the 3_1 helical conformation and therefore increases the transformation rate. On the contrary, long linear counits, with more than 5 carbons, or branched comonomers, stabilize the 11_3 helix due to steric factors and hinder the II → I transformation. It is important to remark that Turner-Jones investigated samples containing a large amount of comonomer units and that no information on microstructural characteristics of the copolymers was provided. Therefore, because of possible interference from other molecular features, it is impossible to draw firm conclusions on the specific effect of comonomeric units from the above data.

Several experimental techniques were used in the past for the quantitative investigation of the progress of polymorphic transformation. The widely employed differential scanning calorimetry has recently been shown to provide reliable data even in the case of partially superimposed melting endotherms.[15] Wide-angle X-ray diffraction[14,27] and infrared[14,24,28,29] and Raman[30,31] spectroscopies have often been adopted to quantify the development of form I in the homopolymers.

As a part of a broad project, we are currently investigating the polymorphic transformation of a series of 1-butene/ethylene copolymers by thermal analysis, small- and wide-angle X-ray diffraction, and vibrational spectroscopy. The complex melting behavior of these copolymers was recently investigated by simultaneous SAXS/WAXS synchrotron experiments.[32] In this paper, we discuss the effect of molecular weight, ethylene content, and aging temperature on the rate of II → I transformation in samples that were rapidly cooled from the melt to room temperature. The thermal and structural behavior of the copolymers is analyzed and compared with that of the homopolymers crystallized in the same conditions. The influence of crystallization temperature on the transformation kinetics of these copolymers will be presented in a subsequent paper.

Experimental Section

Materials and Techniques. The investigated commercial samples were produced using Ziegler−Natta catalysts and were kindly supplied by Dr. J. de Clippeleir (Basell Polyolefins, Louvain la Neuve, Belgium). Their molecular characteristics are shown in Table 1. The degree of isotacticity was determined by ^{13}C NMR at 90 °C in a 20% (w/v) 1,2-dichlorobenzene-d_4 solution. The ethylene content was determined by solution ^{13}C NMR and FTIR; close correspondence was found between the molecular weights obtained by GPC and melt flow index measurements.

Films, about 250 μm thick, were prepared from as-received pellets by compression-molding at 180 °C in a Carver press and subsequent quenching in cold water.

Differential scanning calorimetry (DSC) measurements were performed using a Perkin-Elmer DSC 7/7700 calorimeter. An automatic calibration with high-purity indium (T_m 156.6 °C, ΔH_m 28.45 J/g) and zinc (T_m 419.47 °C, ΔH_m 108.37 J/g) was carried out. DSC traces were obtained under a blanket of dry nitrogen at a heating rate of 20 °C/min. It should be remarked that adoption of different heating rates causes minor shifts in the peak temperatures and that the extent of overlapping of the endotherms is reduced when low heating rates are used. However, the relative ratio of the actual melting enthalpies of the two crystal populations is substantially unaltered by this experimental variable.

Samples for DSC measurements were flat disks, weighing 8 ± 0.2 mg, punched out from the compression-molded films and placed into aluminum DSC pans. Each specimen was first held at 180 °C for 5 min in order to erase the previous thermomechanical history and to obtain a completely relaxed melt; afterward, the DSC pans were quickly transferred into test tubes immersed into a thermostatic bath at 20 °C. Under these conditions, as demonstrated by the signal obtained from a microthermocouple placed into a polymer film submitted to the same thermal history, most of the crystallization takes place during cooling, around 50 and 20 °C for the homopolymers and the copolymer with the highest ethylene content, respectively. After 5 min at 20 °C, during which primary crystallization completes, the test tubes were transferred into another thermostatic bath at the selected aging temperature, T_a, and held there for suitable times, t_a, until the DSC measurements were made.

Wide-angle X-ray diffractograms were recorded at room temperature using a Philips Geiger counter X-ray diffractometer, at a scanning rate of 2°/min over a 2θ range between 5° and 35°, using Ni-filtered Cu Kα radiation. The X-ray samples were 500 μm films prepared by compression-molding at 180 °C and quenching between water-cooled plates at 15 °C. Strips of the films were submitted to exactly the same thermal history used in the DSC experiments before recording the WAXD curves.

Analysis of Data. For the homopolymers, the extent of polymorphic transformation, $\epsilon(t)$, was evaluated directly from the total melting enthalpy corresponding to the bimodal endotherm appearing when both crystal structures are simultaneously present in the sample. Under the assumption that the overall degree of crystallinity remains constant during the polymorphic transformation, it has been shown that, even if the endotherms corresponding to melting of the two crystal populations are partially superposed, the progress of transformation can be evaluated from the relationship[15]

$$\epsilon_{DSC}(t) = \frac{x_I(t)}{x_{TOT}(t)} = \frac{\dfrac{\Delta H_{TOT}(t)}{\Delta H_{t=0}} - 1}{R - 1} \qquad (1)$$

In eq 1, $x_I(t)$ is the time-dependent weight fraction of crystals in the hexagonal modification and $x_{TOT}(t)$ is the overall degree of crystallinity, assumed constant throughout the whole process of structural interconversion, $\Delta H_{TOT}(t)$ is the enthalpy of the overall endotherm, including the melting of both form II and form I types of crystals, $\Delta H_{t=0}$ is the melting enthalpy measured at zero aging time, when only form II crystals are present, and R is the ratio between the melting enthalpy of ideal crystals of form I, ΔH_I^0, and that of form II, ΔH_{II}^0.

There are large uncertainties on the values of both ΔH_I^0 and ΔH_{II}^0. In the literature, values of ΔH_{II}^0 between 60 and 115 J/g have been reported;[3,13,33] similarly, ΔH_I^0 was estimated to be in the range between 110 and 150 J/g.[3,13,34] By coupling measurements of density and melting enthalpy of samples containing only crystals of either modification, it was previously shown[15] that $\Delta H_{II}^0 = 62 \pm 3$ J/g and $\Delta H_I^0 = 141 \pm 10$ J/g are reliable values since they lead to crystallinity indices from thermal analysis that very closely correspond to those

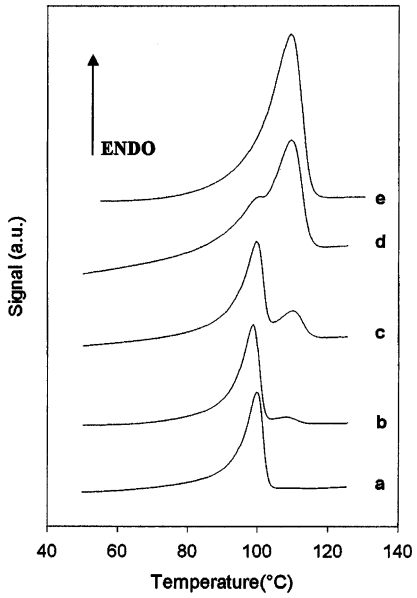

Figure 1. DSC curves of *it* 1-butene/ethylene copolymer with the 0.75% ethylene content after crystallization and aging at 20 °C for the indicated time (in hours): (a) 1.5, (b) 6, (c) 20, (d) 54, (d) 110.

obtained from density measurements. Furthermore, a value of the ratio between ΔH_I^0 and ΔH_{II}^0 of 2.27 corresponds well with that obtained in Rubin's original investigation.[13]

The same criterion of data analysis was adopted to extract information on the progress of transformation for the copolymers with the lowest ethylene content (0.75 wt %) under the assumptions that the melting enthalpies of both types of crystalline structures are not affected by a small fraction of counits and that, also in this case, the limiting level of crystallinity is attained well before the onset of the II → I transformation.

Unfortunately, this approach could not be applied to copolymers with larger ethylene content due to the presence of several endotherms in the DSC traces and because it is evident that a substantial amount of crystallinity slowly develops at 20 °C, in parallel with the polymorphic transformation of the tetragonal crystals generated during cooling.

The development of form I was also quantitatively evaluated from the WAXD patterns using the relation[20,35]

$$\epsilon_{WAXD}(t) = \frac{I_I(t)}{I_I + I_{II}} \qquad (2)$$

where I_I and I_{II} are the integrated areas under the (110) reflection of form I and of the (200) reflection of form II, appearing at $2\theta = 9.9°$ and 11.9°, respectively. The integrated area values were obtained by deconvolution of the crystalline and amorphous diffraction peaks using Peak Fit V.4.0 software.

Results and Discussion

Dependence of Transformation Rate on Weight-Average Molar Mass. First, the influence of the molar mass on the rate of the polymorphic transformation of the series of copolymers with 0.75 wt % of ethylene will be considered. Figure 1 shows a series of DSC heating curves of the copolymer with the largest weight-average molar mass. These curves were obtained on samples that were quenched and aged at room temperature for different amounts of time. As confirmed by the X-ray experiments, described later, the low-temperature peak at 97 °C is associated with melting of crystals in form II, while the endotherm at 106 °C is clearly due to melting of form I crystals. For this copolymer, the peak temperatures of the endotherms assigned to the tetragonal and the hexagonal modifications are remarkably lower than those observed in a homopolymer with similar average chain length and crystallized under the same conditions, which are around 110 and 120 °C, respectively.[15] The strong melting point depression due to the small amount of ethylene counits suggest that ethylene is largely included in the loose crystal lattice of the tetragonal structure.[36]

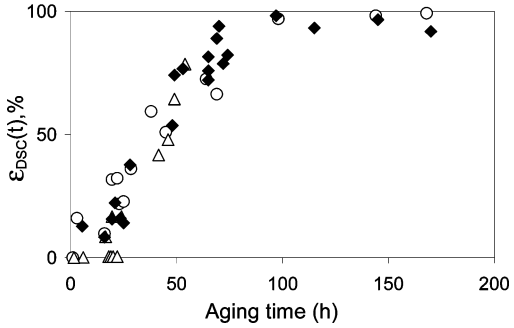

Figure 2. Degree of transformation, $\epsilon_{DSC}(t)$, as a function of aging time at 20 °C for copolymers with 0.75 wt % ethylene and different weight-average molar mass: (○) 383 000, (△) 293 000, and (◆) 470 000 g/mol.

Table 2. Half-Transformation Times Obtained from WAXD Experiments as a Function of Ethylene Content for Samples Crystallized and Aged at 20 °C

sample code	Et units (wt %)	$\tau_{1/2}$ (h)
PBu 200	0	170
PBu 8240	0.75	96
PBu 8220	2.2	25
PBu 8310	5.5	3.5

On inspection of the whole series of DSC traces, it is evident that a small amount of form I is already detectable after 16 h of aging and that the apparent completion of crystal transformation, as indicated by the presence of only the high-temperature endotherm, requires about 100 h. The independence of transformation kinetics on the weight-average molar mass is illustrated in Figure 2, where the degree of transformation, $\epsilon_{DSC}(t)$ calculated from eq 1, is plotted as a function of aging time at room temperature for the three copolymers with 0.75 wt % ethylene. Although some scattering can be observed in the data, a single sigmoidal curve can be traced through the whole set of points. Independent of chain length, the II−I polymorphic transformation is completed in a time that is appreciably less than that required for a homopolymer with similar molecular weight.[15] At least in the range from medium to high molar masses the value of the half-transformation time, $\tau_{1/2}$, defined as the time corresponding to 50% of transformation, is independent of chain length as it was observed in homopolymers[15] (see Table 2). The remarkable role of randomly distributed constitutional defects on transformation kinetics can be appreciated: less than 1 wt % of ethylene counits is sufficient to halve the room temperature half-transformation time. This evidence is clearly in agreement with the results of Schaffhauser[24] and suggests that other claims were based on data pertaining to a very low molecular weight range or were obtained using series of samples in which both chain length and tacticity were simultaneously varied.

Dependence of Transformation Rate on Ethylene Content. A collection of DSC heating curves

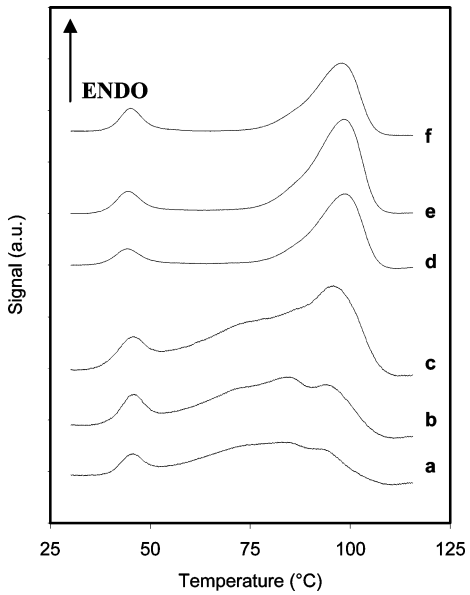

Figure 3. DSC heating curves of the copolymer with the 5.5 wt % ethylene crystallized and aged at 20 °C for the indicating times (in hours): (a) 0.5, (b) 1.5, (c) 4.5, (d) 20.5, (e) 28, (f) 118. The signal of curves a, b, and c have been multiplied by 4 to better disclose weak thermal effects.

recorded after various aging times at room temperature for the copolymer with 5.5 wt % of ethylene counits are shown in Figure 3. The DSC traces are more complex than those obtained for the copolymer with the lowest ethylene content. At short aging times a very broad endotherm spans from around 50 to 110 °C, with a barely appreciable shoulder at ca. 95 °C; a rather sharp low-temperature endotherm, whose origin cannot be assigned a priori to either modification, is also detected at around 50 °C. On aging, the overall endothermic effect increases, and at least two broad maxima, at around 84 and 96 °C, acquire better definition. The overall melting enthalpy levels off, and the high-temperature peak becomes prominent at relatively long aging times. From the evolution of the thermal curve with aging time, the above two maxima can safely be associated with melting of form II and form I crystals, respectively. Indeed, the intensity of the peak at 96 °C progressively increases with aging time at the expense of the broad peak at lower temperatures. This behavior suggests that the very broad and ill-defined endotherm appearing in the early stages of aging is due to melting of form II crystals that, on cooling from the melt, originated over a wide temperature range and, therefore, had a variety of different morphologies and stabilities. The presence of a small amount of form I crystals already at short aging times implies that melt crystallization of this copolymer leads to formation of form II crystals that readily undergo polymorphic transformation.

As deduced from the changes in the shape of the whole melting curve, during the first hours of aging an increase of the overall degree of crystallinity accompanies the structural modification. This indicates that the constitutional defects represent a strong hindrance to crystallization both at a kinetic level and in reducing the extent of order eventually attained.

The whole landscape of melting behavior is consistent with the hypothesis of Marand and collaborators[37] that the slow secondary crystallization at low temperatures leads to crystals with very poor stability that are formed

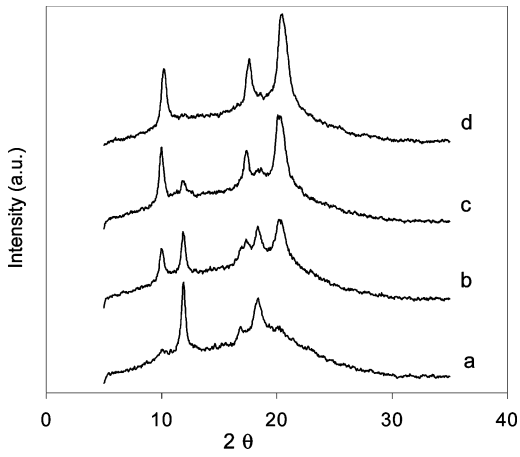

Figure 4. WAXS profiles recorded at room temperature for the copolymer with 5.5 wt % ethylene crystallized and aged at 20 °C for the indicated times (in hours): (a) 0.5, (b) 3, (c) 9, (d) 23.

by the shorter regular sequences under conditions of high topological constraints. From a different point of view, the crystallization behavior of random copolymers undergoes two types of fractionation: The first is thermodynamic in nature and takes place at high crystallization temperature or upon slow cooling from the melt. This process leads to formation of lamellar crystals and involves only those sequences of regular units that are sufficiently long to form ordered domains with the thickness dictated by the actual undercooling. The other is of a kinetic nature and takes place at relatively low temperatures and involves successive clustering of residual regular sequences. To find a convenient register is not easy under these conditions, and segmental mobility plays a key role in the formation of crystals under strong geometrical and topological constraints. In the early stages of this slow process, metastable domains with an intermediate level of order are formed in which a fraction of defective units might be included into the loose lattice.

A wide distribution in the length of isotactic sequences should be expected in polyolefins obtained by Ziegler−Natta catalysis, and shorter sequences only crystallize in the highly constrained state, resulting from the architecture generated by the firstly consumed parts of the macromolecules. The endotherm near 50 °C can be attributed to melting of thin and defective crystals slowly formed by the short isotactic sequences at the aging temperature. Indeed, the intensity of this peak continues to slowly increase up to very long times.

The complex multiple endotherms in the melting curves of the copolymers rich in ethylene units, and the simultaneously occurring transformation and crystallization, do not allow one to use data from thermal analysis to quantify the extent of the II−I transformation. To clarify the origin of the low-temperature endotherm and to monitor the progress of the structural interconversion, wide-angle X-ray diffraction experiments were performed. Figure 4 shows a series of diffractograms acquired after various aging times on the copolymer with 5.5 wt % ethylene crystallized and aged at 20 °C. Initially (Figure 4 a), the reflections at $2\theta =$ 11.9°, 16.9°, and 18.4°, associated with the (200), (220), and (301) planes of the tetragonal modification, exhibit high intensity; however, the presence of weak reflections at $2\theta =$ 9.9°, 17.3°, 20.2°, and 20.5°, assigned to the (110), (300), (220), and (211) planes of the hexagonal

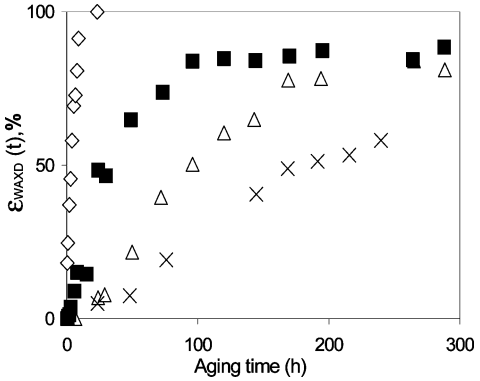

Figure 5. Degree of transformation, $\epsilon_{WAXD}(t)$, as a function of aging time at room temperature for samples with the same weight-average molar mass: (×) homopolymer (PBu 0200), (△) copolymer with 0.75 wt % ethylene content (PBu 8240); (■) copolymer with 2.2 wt % ethylene, (◇) copolymer with 5.5 wt % ethylene.

modification, indicates that some amount of form I is already present at very short aging times. On aging, the peaks associated with form II decrease in intensity, while those characteristic of form I increase. No reflection, in addition to those associated with the presence of the two most common polymorphs, is detected in the diffractograms at any aging time. Therefore, the low-temperature endotherm observed in the DSC traces of the copolymers is not due to the presence of a different crystalline modification, and its origin must be explained on other grounds. To further investigate this issue, simultaneous time-resolved SAXS /WAXS experiments using synchrotron radiation were carried out, and the results were presented elsewhere.[32] These experiments provided evidence for the origin of the low-temperature endotherm. The evolution of the maximum and width of the SAXS peaks during the heating of aged samples, coupled with the changes observed by WAXS, demonstrated that the low-temperature DSC peaks correspond to melting of small and very defective crystals of form I generated during the aging process. If one rules out the possibility of direct production of the hexagonal modification by melt crystallization, the presence of low melting form I crystals in the very early stages of aging can be explained by admitting that the poor form II crystals developing at the aging temperature transform at a much faster rate into the stable modification than those grown at higher temperatures.

The overall progress of the polymorphic transformation in the copolymers has been quantified by X-ray diffraction. Figure 5 shows the degree of transformation, ϵ_{WAXD} (t), calculated according to eq 2 for samples with different ethylene content and similar molecular weight, upon aging at room temperature. The higher the amount of ethylene counits, the faster the transformation. It is also evident that the copolymer with 5.5 wt % ethylene completes the transformation in 25 h, about 10 times faster than the homopolymer. The values of the half-transformation times obtained from Figure 5 are collected in Table 2. These results are in line with those obtained by Gianotti and Capizzi[25] on 1-butene/propylene copolymers, in which an increase on the transformation rate with increasing propylene content was reported.

Dependence of Transformation Rate on Aging Temperature. The kinetics of the II−I transformation has also been studied at various temperatures. In this investigation samples were initially quenched from the melt to room temperature and then aged, until completion of transformation, at four different temperatures: 0, 20, 40, and 60 °C.

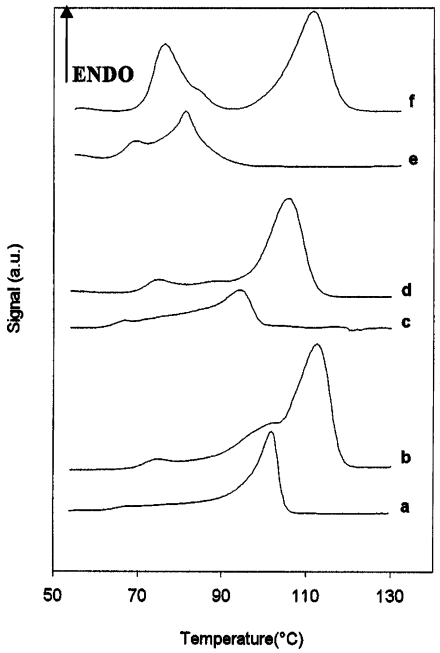

Figure 6. DSC heating curves of 1-butene/ethylene copolymers with different ethylene content crystallized at 20 °C and aged at 60 °C. Curves a, c, and e correspond to the beginning of the transformation (no aging); curves b, d, and f have been obtained at the end of the transformation. Curves a and b: 0.75 wt % ethylene (PB8240); curves c and d: 2.2 wt % ethylene; curves e and f: 5.5 wt % ethylene.

When the aging process is performed at a temperature that is higher than the crystallization temperature, the thermal behavior observed in the copolymers is very complex. Figure 6 compares the DSC heating curves recorded at the initial and final stages of the transformation from copolymers with various ethylene contents aged at 60 °C. At the very beginning, i.e., for samples that were just heated to 60 °C and immediately cooled back to room temperature (curves a, c, and e), the main peak is clearly related to melting of form II crystals. As expected for random copolymers,[36,38] irrespective of inclusion or segregation of the constitutional defects from the lattice, the temperature of the peak maximum decreases with increasing ethylene content. Upon aging, this endotherm transforms into a higher melting peak, associated with the melting of the more stable form I. Besides these two main peaks, other endothermic effects are also detected, even at the very start of the aging process, and are also seen to evolve with time. At very long aging times, traces of form II are still present in the samples, as indicated by the shoulder at around 82 °C in the DSC trace (curve h) of Figure 7 and by the surviving reflections at $2\theta = 11.9°$ (curve e of Figure 8).

The intensity and the position in the temperature scale of the multiple endotherms, as well as their evolution during aging, depend on ethylene content. A peculiar behavior, exhibited by all samples, is the presence of transient peaks or shoulders. This is exemplified in Figure 7, which refers to the copolymer with 5.5 wt % ethylene. Besides the main melting peak of form II crystals, at around 82 °C, and the low-temperature melting endotherm of the very defective form I, at around 71 °C, a shoulder at ca. 87 °C appears in the

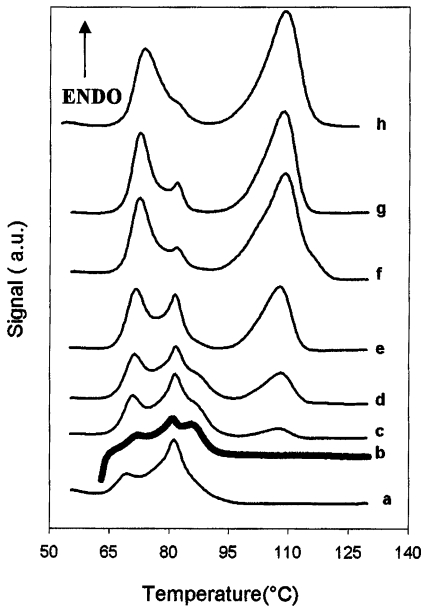

Figure 7. DSC curves of the copolymer with 5.5 wt % ethylene after crystallization at 20 °C and aging at 60 °C for the indicated times (in hours): (a) 1, (b) 2, (c) 5, (d) 8, (e) 13, (f) 46, (g) 92, (h) 189. Curve b has been acquired after 2 h of aging at 60 °C by directly heating from the aging temperature without room temperature cooling.

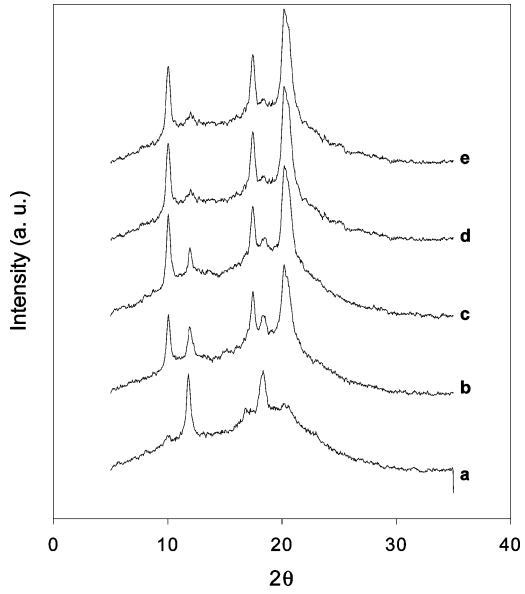

Figure 8. WAXS profiles recorded at room temperature for the copolymer with 5.5 wt % ethylene content crystallized at 20 °C and aged at 60 °C for the indicated times (in hours): (a) 5, (b) 24, (c) 48, (e) 70, (e) 165.

curves labeled c and d, which correspond to 5 and 8 h of aging, respectively. This shoulder is barely appreciable in the sample aged 13 h (curve e) and completely disappears after 46 h of aging (curve f). It should be noted that this thermal effect is not related to the adopted protocol of thermal analysis; in fact, the thick curve (curve b), also showing a clear shoulder at ca. 87 °C, was obtained by performing the whole experiment in the DSC, and the reported curve was acquired on heating directly from the aging temperature.

The origin of this unexpected thermal effect is not straightforward. It cannot be associated with melting of a population of form I crystals because the hexagonal modification is the most stable polymorph, and there would be no reason for its disappearance during isothermal aging. Being transient, it must be associated with crystals in the metastable modification. One possibility is that, when the system is brought to this high aging temperature, the residual amorphous fraction undergoes further crystallization, leading to a population of form II crystals whose rate of transformation is faster than that of the thinner crystals originated at lower temperatures during cooling. This would be consistent with the results obtained by some of us from microhardness measurements[11] and results previously reported by Danusso and Gianotti[9] and Vidotto and Kovacs,[39] indicating that the rate of transformation increases with increasing temperature at which the crystals are produced. An alternative way of explaining the observed thermal behavior is to consider an internal reorganization inside the as grown form II. We anticipate here that experimental evidences obtained from crystallization in isothermal conditions[40] demonstrate that a highly disordered form II, incorporating a large amount of constitutional defects, is the initial result of melt crystallization. Because of the high chain mobility in the loose tetragonal lattice,[41] this initial structure undergoes an isostructural transformation, producing two populations of form II crystals that are characterized by very different rates of polymorphic interconversion.

An insight into the complex thermal behavior can be obtained by coupling DSC and X-ray diffraction experiments performed under the same conditions. From the WAXS reported in Figure 8, it is evident that (110) reflections characteristic of form I are already detectable at very short aging times and that their intensity progressively increases with time at the expense of those identified with form II. Using time-resolved SAXS/WAXS experiments, we have recently demonstrated that this small amount of form I is constituted of highly defective crystallites resulting from a fast polymorphic transformation involving a fraction of very defective form II crystals.[32] The increase of intensity of the DSC endotherm at ca. 72 °C, and its slight shift to higher temperature with increasing aging time, can be associated with secondary crystallization and annealing occurring during aging at 60 °C. Irrespective of their higher structural stability, these form I crystals are the first to disappear on heating due to the large free energy penalty associated with their small size and high content in defects.

Because of the complexity of the thermal curves, the progress of transformation has been studied by WAXS, where no distinction is made between the different morphologies of the same crystalline modification. The degree of transformation as a function of aging time at some temperatures for the sample with the lowest ethylene content (PBu 8240, 0.75 wt %) is shown in Figure 9. Similar to the homopolymers,[4,9] the rate of the tetragonal−hexagonal transformation is found to exhibit a maximum close to room temperature; at high temperature the transformation is so slow that only 40% of form I is attained in samples aged at 60 °C for about 1 month. Similar trends have also been detected for the other copolymers. As shown in Figure 10, also at the highest aging temperature, the rate of transformation is strongly dependent on the content of ethylene counits. It can be appreciated that while the copolymer with the

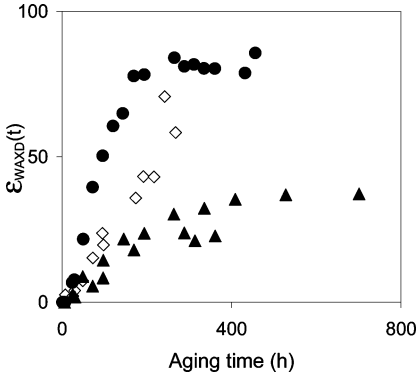

Figure 9. Degree of transformation, $\epsilon_{WAXD}(t)$, as a function of aging times for the copolymer with 0.75 wt % ethylene (PBu 8240) crystallized at 20 °C and aged at different temperatures: (◇) 0, (●) 20, and (▲) 60 °C.

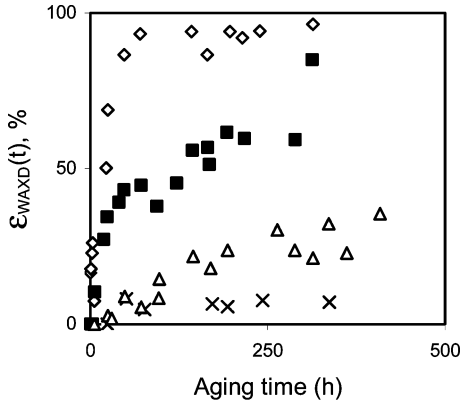

Figure 10. Degree of transformation, $\epsilon_{WAXD}(t)$, as a function of aging times for samples crystallized at 20 °C and aged at 60 °C: (×) homopolymer (PBu 0200); (△) copolymer with 0.75 wt % ethylene (PBu 8240); (■) copolymer with 2.2 wt % ethylene; (◇) copolymer with 5.5 wt % ethylene content.

highest ethylene content completes transformation in about 70 h, under the same crystallization and aging conditions only about 10% of form I develops in the homopolymers aged for 300 h.

The combined effect of aging temperature and copolymer composition on the kinetics of the polymorphic transformation is illustrated in Figure 11, where the half-transformation times, $\tau_{1/2}$, for the three copolymers and the homopolymer are plotted on a logarithmic scale as a function of temperature. In agreement with the behavior of 1-butene/propylene copolymers,[4,25] the minimum is always found at around room temperature, independent of composition. This is probably the temperature range in which the best compromise between segmental mobility and driving force for the transformation is established. At low temperatures, just above the glass transition, mobility in the form II lattice is analogous to that of the amorphous phase[42,43] and is the rate-determining factor for the transformation; at high temperatures the rate control is transferred to the actual free energy difference between the small crystalline domains of the two modifications that, due to different size and defect content, can be expected to decrease with increasing temperature.

Conclusions

The investigation into the polymorphic transformation from the kinetically favored tetragonal modification

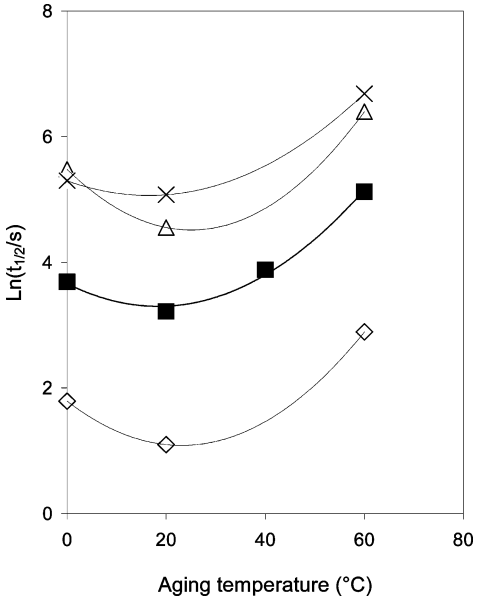

Figure 11. Half-transformation time as a function of aging temperature for samples crystallized at 20 °C: (×) homopolymer (PBu 0200), (△) copolymer with 0.75 wt % ethylene (PBu 8240), (■) copolymer with 2.2 wt % ethylene, (◇) copolymer with 5.5 wt % ethylene.

(form II) to the stable hexagonal structure (form I) in a series of isotactic poly(1-butene) copolymers containing randomly distributed ethylene units has demonstrated that, similar to the homopolymers, the rate of the process does not depend on the average length of constituent chains. On the other hand, a small amount of this type of counit is sufficient to strongly accelerate the transformation to the extent that, at room temperature, only a few hours is sufficient to complete the process, while in the case of the homopolymers complete transformation takes several days. Over the range of compositions studied, the rate of transformation is seen to increase with increasing content of counits at any aging temperature. It has also been shown for the copolymers that the rate of transformation is faster at room temperature and is severely reduced at high temperature. When the aging process is carried out above the crystallization temperature, the aging temperature also plays a very important role in the characteristics of the crystal populations, as revealed by the complex DSC traces recorded at various stages of transformation, in which several endotherms are simultaneously detected.

Coupling of thermal analysis to WAXS has enabled us to assign the various endotherms to crystals of form I and form II with different morphological features and content of defects and to ascertain that a low melting population of small and defective form I crystals is already generated in the early stages of the process. Formation of transient crystalline domains has also been found upon high-temperature aging of ethylene-rich copolymers, and some suggestions to explain their origin have been put forward.

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