Dependence of phase transitions on composition in isotactic poly(propylene-co-1-pentene-co-1-hexene) terpolymers

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Different crystalline lattices are found to be developed in isotactic poly(propylene-co-1-pentene-co-1-hexene) terpolymers (synthesized by using a metallocene catalytic system) depending on: (a) overall content in comonomers, (b) 1-pentene/1-hexene ratio, and (c) crystallization and recrystallization conditions. The various polymorphs (monoclinic, orthorhombic, mesomorphic and trigonal crystallites) can be either the unique crystalline form present in the resulting terpolymer specimen or can coexist with other crystalline lattices. The knowledge of the experimental conditions for obtaining a certain modification or for its transformation into another ordered phase is of a significant relevance because of the importance for tuning final structures, seeking particular properties. The evaluation of these fundamental variables is carried out here by differential scanning calorimetry using broad ranges of cooling rates and subsequent heating. A clear assignment of the crystalline polymorphs is performed by X-ray diffraction using either conventional or synchrotron radiation.

Introduction

The discovery of metallocene catalysts opened an interesting opportunity for the synthesis of propylene based copolymers owing to the control of microstructural features.1,2 Also, these catalysts allowed attaining more homogeneous propylene copolymers,3 and lead to levels of solubles (even at high count incorporation)4 lower than those when normal Ziegler-Natta catalysts were used.

These new copolymers offer additional and interesting properties, such as improved transparency and enhanced impact strength in relation to isotactic polypropylene5–8 as well as low density and easy processability. It is well known that their versatility can be ascribed to the polymorphic behavior and their microstructure. Propylene copolymers with ethylene are the most commercialized. Nevertheless, some industrial applications use 1-butene and other olefins as comonomers. Comonomers like 1-pentene or 1-hexene are not usual in the synthesis of commercial copolymers but could generate attractive materials if the appropriate balance of characteristics is achieved. Moreover, an additional crystalline lattice has been reported to be developed9–28 in these copolymers with relatively high amounts in 1-hexene and/or 1-pentene. This polymorph was labeled as trigonal {\textdeg} form and it was exclusively obtained at contents above around 14 mol\%, while variable proportions of {\textdeg} crystals with the monoclinic {\textalpha} modification were found in the comonomer range from around 10 to 13 mol\%. Afterward, it was reported that this trigonal form appeared also in competition with the mesomorphic phase in addition to that with the monoclinic polymorph, depending on the composition and the applied thermal treatment.28

Years later metallocene terpolymers23 were prepared based on propylene with 1-pentene and 1-hexene as comonomeric units at a global comonomers composition of around 25 mol\%. Those authors described that, at the unique composition explored, only the trigonal form of iPP was developed by cooling from the melt and subsequent ageing at room temperature. Its dimensions were dependent on the overall content of comonomers and on the 1-pentene/1-hexene molar ratio because the counts were included in the trigonal unit cell. In addition, it was found that the rate of crystallization decreased on increasing the amount of 1-hexene counts and the {\textdeg} form was stable until fracture upon drawing at room temperature. Other terpolymers of propylene with 1-pentene and 1-hexene were simultaneously reported22 by our group but those now being synthesized in a broad range of overall compositions (up to around 14 mol\%), and, also, at different 1-pentene/1-hexene ratios for a given total content. The specimens at the highest comonomers content used were able to develop the trigonal form even under adverse crystallization conditions, i.e., a fast cooling from the melt. A comprehensive evaluation of their microstructural features22 allowed concluding from the reactivity ratios obtained that the synthetic protocol used leads to random propylene copolymers and terpolymers.

There is not in literature a complete evaluation of phase transitions for either those propylene based copolymers with 1-pentene or 1-hexene or their terpolymers, although several
analyses at room temperature of crystal morphology, stretched fibers and mechanical properties as well as melting and crystallization behavior at a specific scanning rate have been performed. Accordingly, due to their fundamental academic interest and their empirical importance, this work is now focused on learning about the dependence of phase transitions that take place in these terpolymers as function of global comonomers content, comonomers ratios, and crystallization and recrystallization conditions as well. The eventual competition between polymorphs will be established and compared with that existing in the corresponding poly(propylene-co-1-pentene) and poly(propylene-co-1-hexene) copolymers. Exact knowledge of the specific conditions for generating one or another pure crystal lattice or different proportions of several polymorphs is a primary key to tune the whole spectrum of properties of these relatively new polypropylene based architectures. Thus, DSC and X-ray diffraction studies (by using both conventional and synchrotron radiation) are performed, mainly analyzing the effects of composition and thermal history applied.

**Experimental part**

**Materials**

Random metallocene isotactic terpolymers based on propylene with 1-pentene and 1-hexene were synthesized in a broad range of compositions. Polymerizations were carried out in a stainless steel autoclave at −5 °C with rac-dimethylsilylbis(1-indenyl) zirconium dichloride/MAO as activated catalyst system. The details of the synthesis processes and microstructural features (including the stereoregularity of the samples) have been described in previous works. Four different series of terpolymers have been synthesized, each one with three different 1-pentene/1-hexene ratios in the feed: namely 75Pe : 25He, 50Pe : 50He and 25Pe : 75He. The corresponding homopolymer, iPP, has been also synthesized under the same conditions.

**13C nuclear magnetic resonance analysis**

Composition in comonomers, tacticities and propylene average lengths were determined by carbon nuclear magnetic resonance (13C NMR). The samples with the smallest global molar content (around 4 mol%), T4) were analyzed from 1,2,4-trichlorobenzene solutions in a Bruker Avance DPX-300 (75 MHz) at 100 °C, using deuterated o-dichlorobenzene as an internal reference. Terpolymers with higher overall compositions in comonomers (about 7, 10 and 14 mol%, T7, T10 and T14, respectively) were studied from polymeric solutions in 1,1,2,2-tetrachloroethane-(about 7, 10 and 14 mol%, T7, T10 and T14, respectively) were studied from polymeric solutions in a Bruker Avance DPX-300 (75 MHz) at 100 MHz). A minimum of 8000 scans were recorded in all cases with broad band proton decoupling and using an acquisition time of 1 s, a relaxation delay of 4 s and a pulse angle of 45°. Molar composition in every comonomer for the different terpolymers was estimated from the relative intensities of the methyl signals.

The main microstructural results for the four series of terpolymers are summarized in Table 1. These terpolymers are referred as T followed by the closest integer related to the total mol% content in comonomers, and the corresponding 1-pentene and 1-hexene proportion used in the feed is indicated next. Thus, for instance, T7-25Pe-75He stands for a terpolymer that yields a total composition in comonomers around 7 mol% and with a 1-pentene/1-hexene molar ratio of 25 : 75. It can be observed that the actual comonomer content ratios in the terpolymers are very close to those in the feed. Moreover, the tacticity results display a decrease in the content of mmmm propylene units as comonomer composition is increased. Also, average propylene length values ($n_p$) decrease with the comunit content.

**DSC analysis**

A conventional DSC calorimeter (PerkinElmer DSC-7) was used for analyzing the thermal transitions of the homopolymer and terpolymers. Sample weights were around 2 mg for all the specimens. The calorimeter, connected to a cooling system, was calibrated with different standards. The heat flows (both on cooling and on heating) have been normalized to sample weight (as usual) and also to the scanning rate. The maximum cooling rate that can be reached by the calorimeter shows an evident dependence on the temperature range of interest. For instance, when the cooling rates used are 10 and 80 °C min⁻¹ the equipment is able to control down to −40 and 60 °C, respectively. As will be shown, the transition temperatures on cooling are decreasing rather appreciably with the comonomer content, so that the cooling rates accessible by the calorimeter change accordingly.

**X-ray diffraction with conventional and synchrotron radiation**

Conventional wide-angle X-ray diffraction (WAXD) patterns were recorded in the reflection mode by using a Bruker D8 Advance diffractometer provided with a PSD Vantec detector (from Bruker, Madison, Wisconsin). Cu Kα radiation (λ = 0.15418 nm) was used, operating at 40 kV and 40 mA. The parallel beam optics was adjusted by a parabolic Göbel mirror.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Comonomer content (mol%)</th>
<th>Total</th>
<th>Pe</th>
<th>He</th>
<th>$[\text{mmm}]$</th>
<th>$n_p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>T4-75Pe-25He</td>
<td></td>
<td>4.3</td>
<td>3.2</td>
<td>1.1</td>
<td>86.6</td>
<td>24</td>
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<td>T4-50Pe-50He</td>
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<td>2.1</td>
<td>1.8</td>
<td>87.4</td>
<td>24</td>
</tr>
<tr>
<td>T4-25Pe-75He</td>
<td></td>
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<td>0.8</td>
<td>2.9</td>
<td>90.2</td>
<td>25</td>
</tr>
<tr>
<td>T7-75Pe-25He</td>
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<td>7.1</td>
<td>5.3</td>
<td>1.7</td>
<td>90.8</td>
<td>14</td>
</tr>
<tr>
<td>T7-50Pe-50He</td>
<td></td>
<td>6.6</td>
<td>3.5</td>
<td>3.1</td>
<td>90.0</td>
<td>14</td>
</tr>
<tr>
<td>T7-25Pe-75He</td>
<td></td>
<td>6.6</td>
<td>1.9</td>
<td>4.7</td>
<td>91.5</td>
<td>14</td>
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<td>T10-75Pe-25He</td>
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<td>10.3</td>
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<td>4.8</td>
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<td>9.6</td>
<td>2.9</td>
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<td>88.1</td>
<td>11</td>
</tr>
<tr>
<td>T14-75Pe-25He</td>
<td></td>
<td>13.7</td>
<td>10.3</td>
<td>3.4</td>
<td>83.8</td>
<td>8</td>
</tr>
<tr>
<td>T14-50Pe-50He</td>
<td></td>
<td>14.4</td>
<td>7.3</td>
<td>7.1</td>
<td>82.6</td>
<td>7</td>
</tr>
<tr>
<td>T14-25Pe-75He</td>
<td></td>
<td>13.5</td>
<td>3.4</td>
<td>10.1</td>
<td>82.2</td>
<td>8</td>
</tr>
</tbody>
</table>
with horizontal grazing incidence Soller slit of 0.12° and LiF monochromator. The equipment was calibrated with different standards. A step scanning mode was employed for the detector. The diffraction scans were collected with a 2θ step of 0.024° and 0.2 s per step.

The phase behavior was also confirmed by real-time variable-temperature X-ray diffraction experiments with synchrotron radiation on beamline BL11-NCD at ALBA (Cerdanyola del Vallès, Barcelona, Spain) at a fixed wavelength of 0.1 nm. The WAXD profiles were acquired with a Rayonix LX255-HS detector, placed at about 19 cm from sample and a tilt angle of around 30 degrees. The calibration of spacings was obtained by means of silver behenate and Cr$_2$O$_3$ standards. The temperature control unit was a Linkam hot stage, connected to a cooling system working with liquid nitrogen. The diffraction profiles were acquired in time frames of 12 s. Since the heating rate used was 10 °C min$^{-1}$, the temperature difference between two consecutive frames on melting is 2 °C.

In all cases, the initial 2D X-ray pictures were converted into 1D diffractograms, as function of the inverse scattering vector, $s = 1/d = 2 \sin \theta/\lambda$.

Results and discussion

Conventional differential scanning calorimetry has been used to evaluate, at first approximation, the phase transitions that take place in these terpolymers. The distinct series were analyzed in broad ranges of cooling rates and subsequent heating, differing to what has been reported in literature$^{11,15,19,20}$ for the corresponding copolymers and terpolymers.$^{21}$ The results are gathered together at each series of terpolymers with distinct global comonomer composition.

Calorimetric experiments at variable cooling rate have been proved to allow observing the formation of the mesophase of iPP. It is well known that very high cooling rates (outside the range of conventional DSC) are needed to develop such mesomorphic entities, even though this terpolymer shows the highest total comonomer content in the series. It is also observed in Fig. 2 that lower cooling rates are needed to develop the mesophase-low temperature component for sample T7-25Pe-75He than in the case of T7-50Pe-50He. The importance of the branch chain-length, as reported in literature,$^{25}$ is, therefore, well evident.

change is now noticeable: the DSC cooling exotherms for T7-50Pe-50He and T7-25Pe-75He samples show already a low-temperature component, at around 10–20 °C (most probably arising from the mesophase) in competition with the usual monoclinic (high-temperature component). On the contrary, a single peak is still exhibited by T7-75Pe-25He sample, indicating that it requires higher cooling rates (outside the range attained by the calorimeter) to develop the mesomorphic entities. The subsequent melting experiments (not shown) indicate also a moderate dependence of the transition temperatures and enthalpies with both the previous cooling rates and ratio of comonomers (see below).

The behavior in the T7 terpolymer series is shown in Fig. 2. As before in the T4 series there is a slowdown of crystallization as the 1-hexene proportion increases. But a rather significant
The phase transitions exhibited by the T10 series are even more interesting, as deduced from the DSC cooling curves displayed in Fig. 3. Now, the three compositions show clearly the low-temperature component, most probably associated with the development of the mesomorphic phase. This assignment will be assessed by the diffraction experiments (see below), which, additionally, will demonstrate if the trigonal polymorph can be obtained under any of these conditions, considering that the total comonomer content may be high enough to develop a certain proportion of trigonal crystals.\textsuperscript{21,11,18,20,24} The effect of the ratio between 1-pentene and 1-hexene in this series is not so evident, probably owing to the fact that sample T10-50Pe-50He presents an overall comonomer content significantly inferior.

Additional experiments by means of X-ray diffraction have been also performed on these terpolymers, for establishing the nature of the different phases that are obtained and the transitions and competition between them. As a first approximation, conventional X-ray diffraction experiments have been performed on samples cooled from the melt at different rates. For instance, diffractograms for terpolymer T10-75Pe-25He are shown in Fig. 4. It can be observed that when cooling at 30 °C min\(^{-1}\) a typical profile of the mesophase is obtained. At decreasing cooling rates, higher amounts of monoclinic modification are increasingly seen. Additionally, a small content of trigonal modification is clearly observed (with its characteristic diffraction at around 11\(^{\circ}\)) for cooling rates below around 10 °C min\(^{-1}\). Finally, at very low cooling rates (0.5 °C min\(^{-1}\)) a higher amount of trigonal polymorph is attained, and, importantly, the orthorhombic \textgreek{g} modification (diffraction at around 20\(^{\circ}\)) appears to be in a proportion even higher than the one for the monoclinic \textgreek{a} phase.

Since the amorphous molten profile for sample T10-75Pe-25He is known (see below the real-time diffraction experiments), the X-ray degree of crystallinity can be determined from the diffractograms in Fig. 4, as well as the amount of the different polymorphs, following the procedures reported before.\textsuperscript{27,28} The corresponding results are shown in Table 2, where the aspects commented above can be clearly deduced.

The results from these diffraction experiments can be compared with the DSC findings (upper part of Fig. 3), having in mind that the X-ray specimens have remained at room temperature for a considerable time after their cooling from the melt at a certain rate. Anyway, the two kinds of experiments are very much in agreement and the assignment of the low-temperature component in the exotherms to the formation of the mesophase is correct. And, in principle, it is also accurate that the high-temperature component corresponds to the crystal formation, although it seems obvious that different polymorphs are competing.

As a final remark, it is also interesting to observe in Fig. 3 that for terpolymers T10-75Pe-25He and T10-25Pe-75He the enthalpy involved in the exotherms corresponding to high cooling rates is significantly diminished, indicating that the

![Fig. 3](image1)

**Fig. 3** Plot of DSC curves for the T10 series at the indicated cooling rates (\(\text{cx}, x \text{ in °C min}^{-1}\)) and after normalization to sample weight and cooling rate. For better clarity in the plots, a vertical shift was applied to these curves.

![Fig. 4](image2)

**Fig. 4** X-ray diagrams (acquired with conventional radiation at room temperature) for T10-75Pe-25He on cooling from the melt at the indicated rates (\(\text{cx}, x \text{ in °C min}^{-1}\)).

**Table 2** Degree of crystallinity (total and of the different polymorphs) deduced from the X-ray diffraction experiments for the indicated specimens of T10 and T14 terpolymers

<table>
<thead>
<tr>
<th>Sample\textsuperscript{a}</th>
<th>Total</th>
<th>Monoclinic</th>
<th>Orthorhombic</th>
<th>Trigonal</th>
<th>Meso</th>
</tr>
</thead>
<tbody>
<tr>
<td>T10a-c0.5</td>
<td>0.35</td>
<td>0.12</td>
<td>0.18</td>
<td>0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>T10a-c2</td>
<td>0.32</td>
<td>0.19</td>
<td>0.04</td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td>T10a-c5</td>
<td>0.31</td>
<td>0.16</td>
<td>0</td>
<td>0.01</td>
<td>0.15</td>
</tr>
<tr>
<td>T10a-c10</td>
<td>0.30</td>
<td>0.06</td>
<td>0</td>
<td>0.01</td>
<td>0.23</td>
</tr>
<tr>
<td>T10a-c15</td>
<td>0.28</td>
<td>0.02</td>
<td>0</td>
<td>0.00</td>
<td>0.26</td>
</tr>
<tr>
<td>T10a-c30</td>
<td>0.28</td>
<td>0</td>
<td>0</td>
<td>0.00</td>
<td>0.20</td>
</tr>
<tr>
<td>T14c-c0.2</td>
<td>0.33</td>
<td>0.06</td>
<td>0</td>
<td>0.27</td>
<td>0</td>
</tr>
<tr>
<td>T14b-c0.2</td>
<td>0.38</td>
<td>0.06</td>
<td>0</td>
<td>0.32</td>
<td>0</td>
</tr>
<tr>
<td>T14a-c0.2</td>
<td>0.40</td>
<td>0.07</td>
<td>0</td>
<td>0.33</td>
<td>0</td>
</tr>
<tr>
<td>T14a-c2</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>T14a-c7.5</td>
<td>0.34</td>
<td>0</td>
<td>0</td>
<td>0.16</td>
<td>0.18</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Compositions 75Pe-25He, 50Pe-50He and 25Pe-75He are abbreviated by a, b and c, respectively.
ordering processes on cooling are not completed. This aspect is clearly assessed in the subsequent melting experiments, shown in Fig. 5. Thus, the melting curves corresponding to terpolymers T10-75Pe-25He and T10-25Pe-75He after cooling at 40 °C min⁻¹ show a clear cold crystallization on melting. Moreover, a first melting peak appears at around 60 °C in the experiments performed at the highest cooling rates where the mesophase is supposed to have been formed. This process is tentatively assigned to the melting and recrystallization of the mesophase into crystals that finally melt at around 90 °C.

Finally, the DSC cooling curves for the T14 terpolymers series are shown in Fig. 6. Now the cooling rates for the different events are significantly reduced in relation to the T10 series, in such a way that completely amorphous samples are achieved at rather low cooling rates. Moreover, the effect of the 1-pentene/1-hexene ratio is even more pronounced, deduced from the rates needed to obtain those totally amorphous samples or when comparing the temperature location and enthalpy at a certain cooling rate. From all those features it is clearly deduced that the rates of the various ordering processes follow the sequence: T14-25Pe-75He ≪ T14-50Pe-50He ≪ T14-75Pe-25He.

Considering the overall comonomer content of this T14 series, the new trigonal polymorph is likely to be a competitor with the mesophase and/or the monoclinic crystals, as it has been ascertained from diffraction experiments. Thus, the diffractograms for terpolymer T14-75Pe-25He (abbreviated as T14a) after cooling from the melt at different rates are shown in the lower part of Fig. 7. Now, the profile when cooling at 7.5 °C min⁻¹ is typical for the trigonal modification, but with very broad peaks and with a relative area considerably high of the diffraction at around 21°. Since the mesophase main diffraction is expected to appear at this position (see Fig. 4), the tentative conclusion is that both the trigonal polymorph and the mesophase are coexisting when cooling takes place at such rate (7.5 °C min⁻¹). And this fact is in agreement with the two components observed in the upper part of Fig. 6. At lower cooling rates, the amount of trigonal modification is clearly enlarged (a single high-temperature component is observed in Fig. 6 below 2 °C min⁻¹), and a significant amount of monoclinic crystallites is also developed at the lowest cooling rate of 0.2 °C min⁻¹.

In fact, the amount of the different polymorphs (and the total degree of crystallinity) deduced from these diffraction profiles is shown in Table 2. As mentioned above, the X-ray specimens stayed at room temperature (around 25 °C) for a considerable time, and at this temperature the formation of the trigonal crystals appears to be favored in relation to the mesophase.

Fig. 7 also depicts the diffractograms for specimens of terpolymers T14-50Pe-50He (T14b) and T14-25Pe-75He (T14c)
after cooling at a rate of 0.2 °C min⁻¹. The profiles are very similar to the one observed for sample T14-75Pe-25He, with the exception of the slightly lower crystallinities attained in the former specimens (see Table 2). In the three cases, nevertheless, the trigonal and monoclinic modifications are coexisting. It is also interesting to notice that there is a small but noticeable displacement of the trigonal diffractions to lower angles (higher spacings) as the proportion of 1-hexene increases in the terpolymers. This feature implies that 1-hexene comonomer leads to an expansion of the trigonal unit cell higher than the one involved by 1-pentene, as expected and reported before,¹¹,¹³,²⁰ considering the sizes of the lateral branches in the counits.

T14 terpolymers exhibit evident cold crystallization on heating (Fig. 8), so that the formation rate of ordered entities in these samples is very low, since the crystallization is not completed on cooling at rates above only 2-5 °C min⁻¹ (depending on composition).

A quantification of all the different DSC experiments has been carefully carried out. The results deduced from the cooling curves are especially interesting. Thus, Fig. 9 shows the variation with cooling rate of the peak temperatures in the exotherms for the different terpolymers. As indicated above, only one component (the crystal) is obtained for the T4 terpolymer series. The same stands for T7-75Pe-25He. On the contrary, the mesophase component is also observed for terpolymer T7-50Pe-50He and T7-25Pe-75He and for all the other samples (T10 and T14).

It can be also deduced from Fig. 9 that the crystal component appears at around 10-15 °C above the mesomorphic one, similarly to the results found in other iPP copolymers.²⁴,²⁶,²⁹ This is clearly seen by the step observed in the solid thicker lines in Fig. 9, which represent the absolute minimum in the exotherm. That jump indicates the transition region where the mesophase or the crystal components are predominant (as seen above, the high-temperature component corresponds to the formation of different polymorphs, depending mainly on the composition).

Variation of the total exothermic enthalpy with the cooling rate for the terpolymer series T10 and T14 is represented in Fig. 10, and also the values corresponding to the two individual component peaks (mesophase and crystal) of the enthalpy in the exotherms: total enthalpy (open squares), mesophase (solid circles) and crystal (open triangles) components for the different T10 (above) and T14 (below) terpolymers.

Regarding the T10 series, it can be observed in the upper part of Fig. 10 that the total enthalpy is clearly decreasing with increasing cooling rate, in such a way that terpolymer T10-25Pe-75He shows a decrease of about 50%. The results for T14 samples are more interesting, since now, and at the three Pe/He ratios, zero enthalpy values are reached, meaning that the cooling rates attained by this conventional calorimeter are high enough to produce completely amorphous samples. Moreover,
the variations of the enthalpy corresponding to the low-temperature (mesophase) component in the exotherms show well defined maxima at intermediate cooling rates. The position and intensity of these maxima are clearly dependent on the ratio of comonomers: they are located at lower cooling rates and its intensity rises as the 1-hexene composition in the terpolymers increases. And the relative proportion of mesophase is even higher, considering that the total enthalpy decreases also with increasing 1-hexene content.

Obviously, the position of the maximum in the mesophase enthalpy is primarily dependent on the total comonomer content, so that it appears at considerably higher cooling rates for the T10 series, as observed in the upper part of Fig. 10. From these results, the cooling rates needed for detecting the mesophase formation (in the case of T7-50Pe-50He, T7-25Pe-75He and all the T10 and T14 series) and for obtaining totally amorphous specimens (only for the T14 series) have been determined. The corresponding values for these two rates are displayed in Fig. 11, comparing with the ones reported for the copolymers with 1-pentene, 1-heptene and 1-octene. This graph resembles the continuous cooling curve diagrams frequently employed for quenched steels in metallurgy.

It was shown previously that rate parameters are related to the copolymer contents expressed in weight%, since the key feature in such case is the size of the comonomeric units. And this is also the case for the present terpolymers, which display rather similar values than those found for the 1-pentene, 1-heptene and 1-octene copolymers, as observed in Fig. 11, for the two depicted limiting rates.

**Real-time synchrotron X-ray diffraction study**

Real-time variable-temperature X-ray diffraction experiments with synchrotron radiation have been also performed on selected samples. Fig. 12 shows one of these experiments, corresponding to the melting at 10 °C min⁻¹ of terpolymer T10-75Pe-25He after cooling at 80 °C min⁻¹. This rate is high enough to produce a completely amorphous sample, as seen in the initial upper diffractogram. On heating, the formation of the mesophase is observed to take place at around 0 °C, coinciding with the cold “crystallization” exotherm appearing in the DSC melting curve, shown at the right of Fig. 12. At increasing temperatures, the mesophase melts and recrystallizes (at about 55 °C) into monoclinic crystals, and these crystals melt finally at 100 °C. These transitions are in perfect agreement with the DSC results, and, evidently, the nature of the phases for the different transitions is unambiguously determined here: amorphous glass, mesophase, monoclinic and isotropic melt.

A similar recrystallization of the mesophase into monoclinic α crystals is also observed in iPP homopolymer, although, evidently, at a higher temperature: beginning at around 90 °C. Another distinctive feature is that the mesophase in the homopolymer has to be obtained by sufficiently quenching the molten polymer into ice water, while rather mild cooling rates are needed to generate the mesophase (and even the totally amorphous sample) in the case of T10-75Pe-25He.

The results for terpolymer T14-75Pe-25He are presented in Fig. 13, which shows the diffractograms on melting at 10 °C min⁻¹ of a sample after cooling at 40 °C min⁻¹, together with the corresponding DSC melting curve. As deduced from Fig. 6...
and 10, entirely amorphous specimens are expected when cooling at rates above around 20 °C min⁻¹. The initial X-ray profile in the experiment of Fig. 13 (upper diffractogram) clearly indicates that feature. Similarly to the case of terpolymer T10-75Pe-25He, the diffractograms on heating show the formation of the mesophase at around 0 °C, coinciding with the cold “crystallization” exotherm in the DSC melting curve. A close inspection, however, allows observing a rather wide and not very intense diffraction (see highlighted diffractogram) centered at around 1.2 nm⁻¹, characteristic of the trigonal polymorph. It is deduced, therefore, that a small amount of rather disordered trigonal crystals are formed simultaneously to the development of the mesophase.

On further heating, the mesophase melts and recrystallizes (at about 50 °C) into much more perfect trigonal crystals, judging from the width of the corresponding diffraction peaks. Subsequently, the trigonal modification melts at around 70 °C, but there is a subtle recrystallization into monoclinic crystals (highlighted diffractogram), which melt totally at 85 °C.

The DSC results are in perfect qualitative agreement, but the diffraction findings are much more revealing and crucial about the different polymeric transformations. The sequence of phases for this experiment is, therefore: amorphous quenched sample, mesophase plus imperfect trigonal modification, more perfect trigonal crystals, very small amount of monoclinic polymorph, and molten amorphous phase.

We are now analyzing the final properties of these materials as function of the phase (or phases) present in a particular specimen.

Conclusions

Cooling experiments performed within a broad range of scanning rates have pointed out that either a unique (ascribed to a crystalline or mesophase peak) or two exothermic processes (associated with crystalline and mesophase peaks) are observed in these isotactic poly(propylene-co-1-pentene-co-1-hexene) terpolymers under study, depending on overall composition and 1-pentene/1-hexene ratio. The simplest phase behavior is exhibited by the T4 terpolymer series where only the crystalline peak is observed at the rates analyzed. Different scenario is seen for the T7-50Pe-50He and T7-25Pe-75He samples where a low-temperature component, at around 10–20 °C, is in competition with the crystalline high-temperature component and depending on cooling rates. The T7-75Pe-25He specimen requires higher cooling rates (outside the range attained by this conventional calorimeter) to develop the low-temperature component.

Phase transitions exhibited by the T10 series are considerably more interesting. The three compositions clearly show that the low-temperature component is associated with the development of the mesomorphic phase. Moreover, results indicate that the ordering processes on cooling are not complete for some of the 1-pentene/1-hexene ratios and, then, an obvious cold crystallization is found on melting.

The results on the T14 terpolymers show that the cooling rates for the different events are significantly reduced in relation to the T10 series, in such a way that completely amorphous samples are achieved at rather low cooling rates. In addition, the effect of the 1-pentene/1-hexene ratio is more pronounced, deduced either from the rates needed to obtain those totally amorphous samples or when comparing the temperature location and enthalpy at a certain cooling rate. The variations of the last magnitude corresponding to the low-temperature (mesophase) component in the exotherms show well defined maxima at intermediate cooling rates. The position and intensity of these maxima are clearly dependent on the ratio of comonomers: they are located at lower cooling rates and its intensity rises as the 1-hexene composition in the terpolymers increases. And, the relative proportion of mesophase is even higher, considering that the total enthalpy decreases also with increasing 1-hexene content.

The corresponding study by means of X-ray diffraction has clearly established the nature of these different phases as well as the transitions and comparison between them, and the degrees of crystallinity (total and of the different polymorphs). First of all, the assignment of the low-temperature component in the exotherms to the formation of the mesophase is correct. And, in principle, it is also accurate that the high-temperature component corresponds to the crystal formation, although it seems obvious that different polymorphs are competing. The T10-75Pe-25He specimen after being cooled at 80 °C min⁻¹ leads to a completely amorphous sample that on heating is transformed on the mesophase at around 0 °C, melting and recrystallizing at higher temperatures (at about 55 °C) into monoclinic crystals, these crystals finally melting at 100 °C. These transitions are in perfect agreement with the DSC results.

The terpolymer T14-75Pe-25He is also obtained as an entirely amorphous specimen after its cooling at 40 °C min⁻¹. Its diffractograms on heating indicate the formation of the mesophase at around 0 °C, coinciding with the cold “crystallization” exotherm in the DSC melting curve, in addition to a small amount of rather disordered trigonal crystals. Again, the mesophase melts and recrystallizes (at about 50 °C) into much more perfect trigonal crystals, which melt at around 70 °C but generating a subtle recrystallization into monoclinic crystals, which melt totally at 85 °C. All these transitions are in perfect agreement with the DSC results and a rather complete picture of the complex phase transitions existing in these isotactic poly(propylene-co-1-pentene-co-1-hexene) terpolymers has been established as function of global composition, comonomers ratio, and crystallization and recrystallization conditions.

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