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CRYSTALLINE ORDER AND MELTING BEHAVIOUR OF ISOTACTIC POLYPROPYLENE (α-FORM)

III. Isothermally crystallized samples*

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The dependence of the order in the orientation of the chains in the crystalline structure on the crystallization temperature is described for the α-form of isotactic polypropylene.

From the present and previous results it is concluded that, for a fixed isotactic polypropylene sample, a biunivocal relation holds between a parameter selected as a measure to the degree of order and the melting endotherm position.

It is well established [1–3] that the crystalline structure of the α-form of isotactic polypropylene (i-PP) may show various degrees of disorder in the up and down positioning of the chains, while the unit cell and the ordered disposition in it of three-fold right- and left-handed helical chains remain substantially unchanged. It has been pointed out [1, 2, 4, 5] that transitions from more disordered modifications (nearer a limiting structure α_1) to more ordered ones (nearer a limiting structure α_2) are obtained during annealing procedures; the degree of ordering attained in the up and down positioning of the chains in the thermal treatment is dependent on the annealing temperature, and is preserved when the samples are cooled down to room temperature.

We have pointed out that no α_1 towards α_2 transition is possible without partial melting and successive recrystallization [4]; the temperature range for the transition is strictly related to the melting endotherm positions of the different samples [5].

For all the studied samples, after the annealing procedures, increases in the melting peak position (T_m) are observed concomitantly with increases in a parameter (R) selected as a measure of the up-down degree of order, independently of their starting values.

In particular, if the order parameter R is plotted *vs.* T_m, independently of the annealing procedure, all the data for a quenched i-PP sample are fitted by a single straight line [4, 5].

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* Papers I and II correspond to references 4 and 5.

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The melting behaviour of an isothermally crystallized i-PP sample has recently been reanalyzed by some of us. The occurrence of two crystallization temperature regions (T_c) which produce samples recrystallizing during the DSC melting scans has been pointed out [6, 7].

In this paper the characterization of the degree of order, in the up and down positioning of the chains, for isothermally crystallized samples, will be presented. The aim is to contribute to the definition of the factors which determine the degree of order in the up and down positioning of the chains in unannealed samples, and to clarify how general is the found correlation between such kind of order and the melting temperature.

Experimental

The polymeric samples were supplied by Montepolimeri S.p.A. The homopolymer is highly isotactic, being approximately 97.5% isoluble in *n*-heptane, and it has an intrinsic viscosity of 2.5 dl/g.

Isothermal crystallization from the melt was effected by employing the following procedure: samples were kept for 15 min at 200° in a N_2 atmosphere, and were then rapidly cooled down to the selected isothermal crystallization temperature.

The thermal treatments and the calorimetric measurements were carried out in a Perkin–Elmer differential scanning calorimeter (DSC–2) in a flowing N_2 atmosphere. To avoid as much as possible changes in the shapes and positions of the DSC peaks, the masses of material used in the different runs were always practically identical ($\cong 5$ mg). The DSC scans were performed at a heating rate of 10 deg/min; the reported peak temperature of the melting endotherms (T_m) was always evaluated under such conditions.

The X-ray diffraction patterns were obtained as reported in [4]. As described previously [1, 2], the two limiting modifications α_1 and α_2 have substantially similar X-ray spectra. However, while only reflections with $(h+k)$ even are allowed in the α_1 modification, reflections with $(h+k)$ uneven may also be present in the α_2 modification, though generally associated with a lower intensity. Due to the overlapping of reflections in the powder spectra, it is possible to demonstrate in a clear way the degree of disorder present in a sample only in some regions of the X-ray spectra. As previously [4, 5], the ratio R of the areas below the peaks located between 34.4–36.0° and 36.4–38.0° in 2 θ(Cu Kα), has been taken as an index of the degree of ordering.

Results and discussion

Isothermally crystallized i-PP samples were analyzed by WAXS and DSC. A series of X-ray diffraction patterns for different crystallization temperatures T_c are reported in Fig. 1 in the 2 θ interval 28–48° (Cu Kα). The choice of crystallization temperature influences the X-ray diffraction pattern in this interval significantly; the change is further evidenced in Fig. 2 where the ratio R (index of up and down ordering of the chains) is plotted against T_c; only T_c values for which the crystallization was complete in a fixed crystallization time (14 h) were considered.

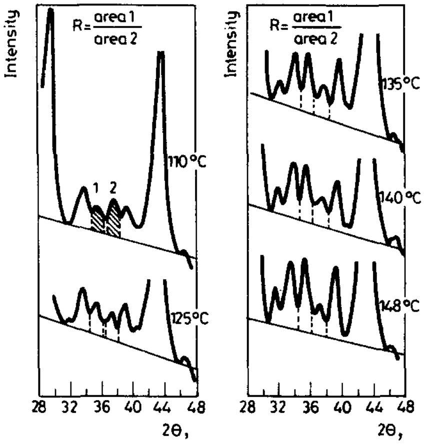

Fig. 1 X-ray diffraction patterns in the 2 θ interval 28° to 48° (Cu Kα) of isothermally crystallized samples at the indicated temperatures. The definition of the order parameter R, previously reported [4], is illustrated in the upper pattern

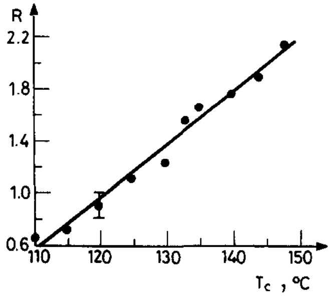

Fig. 2 The index R of the up and down ordering of the chains, measured from patterns of the kind of Fig. 1, is reported against the crystallization temperature (T_c). The order of magnitude of the error in the index R is indicated by a vertical bar at one point only

Figure 2 shows a nearly linear dependence of the order parameter on the crystallization temperature, with R ranging in an interval which includes the lowest and highest values so far observed [4, 5].

A DSC analysis of the same samples was effected at a heating rate of 10 deg/min, which is sufficiently high to avoid double peak melting endotherms for $T_c < 135°$ [7].

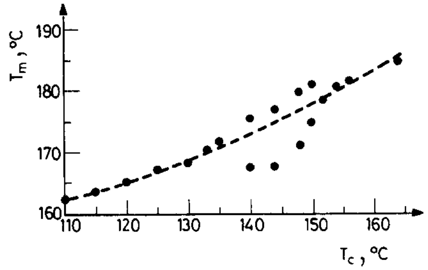

Fig. 3 The peak positions of the melting endotherms (T_m), are reported *vs.* T_c, for the heating rate 10 deg/min. A tentative interpolating curve for the "original samples" melting temperatures is also drawn (see text)

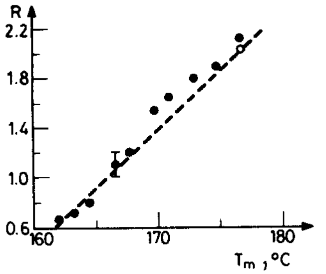

Fig. 4 The up-down order parameter (R) is reported *vs.* the melting endotherm peak temperature (T_m) for all the studied samples (●). The open circle (○) refer to a sample crystallized at T_c = 144°C and then annealed at 165°C for 14 h. The dashed line, taken from Fig. 6 of ref. [5], interpolates the data for i-PP samples rapidly cooled from the melt

The peak positions of the melting endotherms (T_m) analogous to Fig. 4 in [7] are reported *vs.* T_c in Fig. 3. For the T_c values for which double peak shape melting endotherms (due to recrystallization phenomena [6]) are present, both peak temperatures are indicated.

In order to obtain the melting peaks of the "original samples" (T_m), a tentative interpolating curve for the T_c region for which double peak shapes are observed in the DSC scans is also drawn in Fig. 3.

The degree of order R is reported *vs.* the T_m values for all the examined samples in Fig. 4. The line which fits the R *vs.* T_m data for i-PP samples rapidly cooled from the melt and subsequently submitted to different annealing procedures is also reported in Fig. 4; such a line fits nearly the data for the unannealed isothermally crystallized samples.

As expected, suitable annealing procedures on the isothermally crystallized samples can produce increases in R and T_m, as already shown for i-PP samples with different thermomechanical histories [5]. Again, such annealed samples are characterized by R and T_m values which are well represented by the same line; as an example, the R and T_m values for a sample isothermally crystallized at 144° and then annealed at 165° are reported in Fig. 4.

From these results and the previous ones [4, 5], we conclude that for a fixed i-PP sample, when a monomodal distribution of melting species is present in the "original samples", a biunivocal relation between the degree of order and the melting endotherm position seems to be valid.

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References

1 M. Ikosaka and T. Seto, Polymer J., 5 (1972) 111.

2 P. Corradini, G. Giunchi, V. Petraccone, B. Pirozzi and H. M. Vidal, Gazz. Chim. Ital., 110 (1980) 413.

3 P. Corradini, V. Petraccone and B. Pirozzi, Eur. Polym. J., 19 (1983) 299.

4 G. Guerra, V. Petraccone, P. Corradini, C. De Rosa, R. Napolitano, B. Pirozzi and G. Giunchi, J. Polym. Sci., Polym. Phys. Ed. 22 (1984) 1029.

5 C. De Rosa, G. Guerra, R. Napolitano, V. Petraccone and B. Pirozzi, Eur. Polym. J., 20 (1984) 937.

6 V. Petraccone, C. De Rosa, G. Guerra and A. Tuzi, Makromol. Chem. Rapid. Commun., 5 (1984) 631.

7 V. Petraccone, G. Guerra, C. De Rosa and A. Tuzi, Macromolecules, 18 (1985) 813.

Zusammenfassung — Die Abhängigkeit der Orientierungsordnung von Ketten in kristallinen Strukturen von der Kristallisationstemperatur wird für die α-Form von isotaktischem Polypropylen beschrieben. Aus den jetzt und früher erhaltenen Ergebnissen wird geschlossen, daß für eine fixierte isotaktische Polypropylenprobe eine Beziehung zwischen einem als Maß für den Ordnungsgrad gewählten Parameter und der Lage der endothermen Schmelzpeaks besteht.

Резюме — Описана зависимость степени ориентации цепей в кристаллической структуре α-формы изотактического полипропилена на температуру его кристаллизации. На основании результатов настоящей работы и ранее полученных, установлен двухзначный характер связи между параметром, взятым в качестве меры упорядоченности твердого образца изотактического полипропилена, и положением эндотермы его плавления.