

UNUSUAL RECRYSTALLIZATION AND MELTING BEHAVIOUR IN DSC SCANS OF ISOTACTIC POLYPROPYLENE SAMPLES

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The unusual dependence of the melting peak temperature of the species recrystallized during DSC scans on the isothermal crystallization temperature (T_c) is discussed for isotactic polypropylene samples.

It is pointed out that such a phenomenon is not due to superheating effects; it is believed to be accounted for by assuming that the rates of the recrystallization phenomena at the same temperature are higher for samples obtained at higher T_c values.

In several studies on the extrapolation of experimental melting temperatures to the equilibrium melting temperature (T_m^0) of crystals of linear macromolecules according to the method suggested by Lauritzen and Hoffman [1], recrystallization phenomena during the measurements have been pointed out for samples isothermally crystallized from the melt.

The recrystallization phenomena usually give rise to melting endotherms having typical double peak shapes. Such double peak melting endotherms are generally already present for the lowest crystallization temperatures (T_c) and disappear for sufficiently high values of T_c , depending on the measurement heating rate.

Moreover, it is generally observed that the melting peak positions of species generated by recrystallization during the measurement scans are largely independent of the original crystallization temperature and reach different constant values only on change of the heating rates in DSC scans. This is the observed behaviour, for instance, for polystyrene [2], poly-p-fluorostyrene [3], polypropylene oxide [4], nylon 6 [5] and nylon 66 [6].

In recent papers [7, 8] we have pointed out the occurrence of recrystallization phenomena during DSC scans, for isotactic polypropylene (i-PP) samples isothermally crystallized in two distinct T_c regions.

In the lowest T_c region the usual, previously described, behaviour is observed. However, for samples crystallized in a higher T_c region the double peak shape endotherms reappear and an unusual dependence on the crystallization temper-

ature of the melting temperatures of the species recrystallized during the scans is observed [8]. Such results allowed us to contribute to the elucidation of the conflicting literature results on extrapolation to the equilibrium melting temperature of i-PP [8].

In this paper the results of our investigations on this unusual behaviour of the melting peaks of the species recrystallized during the DSC scans of isothermally crystallized i-PP samples are reported.

Experimental

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

The isothermal crystallization from the melt was effected by employing the following procedure: samples were kept for 15 min at 200° in a N₂ atmosphere, and were then rapidly cooled down to the selected isothermal crystallization temperature.

The calorimetric measurements were carried out on a Mettler differential scanning calorimeter (DSC 30) in a flowing N₂ 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 (~5 mg).

Results and discussion

The peak positions of the melting endotherms of isothermally crystallized i-PP samples, taken from [8], are reported *vs.* T_c in Fig. 1, for a heating rate of 2.5 deg/min. For the T_c values for which double peak shape endotherms are obtained, both the lower and higher peak temperatures, hereafter referred to as T'_m and T''_m , are indicated.

According to our previous results [7], all the T''_m peaks correspond to the melting of species recrystallized during the measurements.

However, the recrystallization phenomena present different characteristics, depending on the crystallization temperature region.

The recrystallization rates observed in samples for which $T_c < 125^\circ$ are low compared with those observed for samples crystallized in the T_c range 140–150°; indeed the first recrystallization disappears at heating rates higher than 10 deg/min [8] (as happens for quenched samples [9–11]), while the second ones are also present

for high heating rates at least up to 40 deg/min [7]. Hence, in contrast with the higher recrystallization temperatures (which generally imply lower rates), higher recrystallization rates are observed for the more perfect samples isothermally crystallized in the higher temperature region.

Moreover, as previously mentioned, for T_c in or near the range 140–150°, the T_m'' values plotted vs. T_c show unusual behaviour: the points are fitted by a straight line

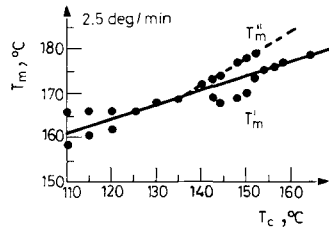


Fig. 1 The peak positions of the melting endotherms (T_m) of isothermally crystallized i-PP samples are reported vs. the crystallization temperature (T_c). The full line represents the extrapolation to the equilibrium melting temperature [8]. The dashed line fits the T_m'' values for $T_c > 135^\circ\text{C}$

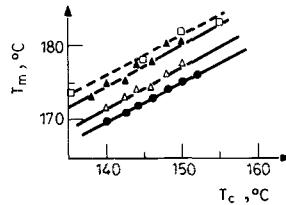


Fig. 2 Peak positions T_m'' (see Fig. 1), obtained at different heating rates, reported vs. T_c : (▲) 10 deg/min; (△) 2.5 deg/min; (●) 0.5 deg/min; (□) 0.5 deg/day (Fatou's data [12])

having a positive slope higher than the slope which characterizes the extrapolation line to the T_m^0 value (Fig. 1).

The peak positions T_m'' obtained at heating rates varying from 0.5 deg/min to 10 deg/min, are shown vs. T_c in Fig. 2. The slopes of the lines fitting the experimental data are nearly independent of the heating rate; moreover, the slope is similar to that obtained by Fatou [12] from dilatometric melting measurements at a heating rate of 0.5 deg per day for i-PP samples crystallized in such a T_c region. These results lead us to the conclusion that superheating is not the cause of the higher slope.

When T_c is increased from 135°, the T_m'' values increase (as described in Fig. 1), and correspondingly the areas of the second peaks decrease, as shown in Fig. 3 for a heating rate of 2.5 deg/min. Above 152°, only single melting endotherms are obtained, whose width also decreases with increasing T_c .

The shape of the melting curves in Fig. 3 suggests that the recrystallization phenomena revealed by the double melting endotherms for T_c higher than 135° could already be present for lower T_c values and the single melting endotherms could be produced by the high rate of the phenomenon.

The presence of superheating being excluded in such a hypothesis, the T_m values for $T_c < 135^\circ$ should be aligned to the T_m' values in the plots T_m vs. T_c . The different

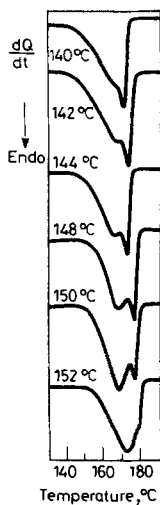


Fig. 3 DSC scans for isotactic polypropylene samples isothermally crystallized at the indicated temperatures. The heating rate is 2.5 deg/min

slopes for the T_m and T_m' data support instead the hypothesis that a new crystallization phenomenon appears for samples crystallized at T_c higher than 135 – 140° .

Further evidence favouring such a hypothesis is that the T_m values for higher T_c , for which the double peak shape disappears, are aligned with the T_m values observed for T_c below 135° .

In spite of the dependence of T_m' on T_c , recrystallization at a fixed temperature for a sufficiently long time produce, as expected, T_m values essentially dependent on T_r and nearly independent of T_c .

We have to conclude that higher T_m' values correspond to the accessibility of higher T_r values during the scan. In other words, we assume that the recrystallization phenomena (which appear in samples for which T_c is at least 135 – 140°) at the same temperature are faster for samples obtained at higher T_c values.

On the other hand, with increasing T_c , the melting temperature regions, and hence the minimum temperatures at which the recrystallization phenomena may be observed [13], are shifted toward higher values; in turn, for each sample, higher recrystallization temperatures correspond to lower recrystallization rates. This fact would account for the disappearing of the second melting peak on further increase of T_c .

The reappearance of recrystallization phenomena and the accessibility of higher T_r values with the increase of T_c could be connected with the higher morphological perfection of the samples crystallized at higher temperature, which could increase the rates of rearrangement of the chains after partial melting. We can only guess that such unusual behaviour may be related in some way with the unusual nature of the recrystallization of i-PP, which is always accompanied by transitions toward more ordered crystalline modifications, as reported in our previous papers [11, 12].

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Zusammenfassung — Die ungewöhnliche Abhängigkeit der Temperatur des Schmelzpeaks der während des DSC-Versuchs rekristallisierten Species von der isothermen Kristallisationstemperatur (T_c) wird diskutiert. Es wird gezeigt, daß solch ein Phänomen nicht Überhitzungseffekten zuzuschreiben ist; unser Meinung nach kann es durch die Annahme erklärt werden, daß die Geschwindigkeiten der Rekristallisationsphänomene für bei höheren T_c -Werten erhaltene Proben bei gleicher Temperatur größer sind.

Резюме — Для образцов изотактического полипропилена обсуждена необычная зависимость температурного пика плавления частиц, рекристаллизующихся в течении ДСК измерений на температуру изотермической кристаллизации T_c . Отмечено, что это явление не может быть обусловлено эффектами перегрева и объясняется тем, что при той же самой температуре скорость рекристаллизации выше для образцов, полученных при более высоких значениях T_c .