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Crystallinity of isotactic polypropylene films annealed from the quenched state

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Quenched isotactic polypropylene films were annealed at 130, 140 and 155 °C for 24 h. The structural organization, after annealing, was analysed by wide-angle X-ray diffractograms (WAXD), differential scanning calorimetry (DSC), density and sorption of dichloromethane vapour at low activity. The comparison of the different methods used to obtain the crystallinity shows that, even at the highest annealing temperature, the transformation of the smectic phase into the monoclinic phase, is not complete. WAXD and DSC give the amount of monoclinic phase, whereas the amorphous fraction was derived from sorption of dichloromethane vapour at low activity. From the density, it was possible to derive the residual smectic fraction in the different samples. The results indicate that, at temperatures higher than 150 °C, there is an accelerated decrease of smectic phase and an accelerated increase in the crystal dimensions and perfection.

1. Introduction

Structural organization in polymers has a determinant influence on the physical properties, particularly those correlated with mechanical behaviour [1–4].

Since structural organization is mainly influenced by thermal treatments, it is important therefore to understand the correlations between structural and processing variables. Isotactic polypropylene (iPP) can be quenched from the melt to a mesomorphic state, variously described as smectic [5], paracrystalline [6], or condis crystal [7], in the literature. Here we call it "smectic", the most common name historically.

The smectic phase is stable at room temperature for long periods of time, but transforms into the monoclinic α form, when heated above 60 °C. The crystallization phenomenon has been studied by many authors [8–12], and an invariance has been observed of the initial morphology upon annealing up to high temperature [10, 11]. Furthermore, a series of states of intermediate order, depending on the annealing temperature, was suggested [9]. This would imply that the smectic phase does not transform completely; in this case we have a three-phase system: amorphous–smectic–monoclinic, with composition dependent on the annealing temperature, T_A, the higher the monoclinic fraction, the higher the annealing temperature, T_A.

We already found that, for relatively low annealing temperatures ($T_A < 120$ °C), the system is three phasic, and the composition was determined through measurements of vapour sorption and density [12–14]. In this paper we analyse the phase composition of smectic iPP samples annealed at high temperatures for long times in order to determine the temperature for which we observe the complete transformation of the original smectic phase. Furthermore the data of crystallinity obtained with different techniques, on cold crystallized smectic iPP samples, also allows the comparison of values obtained in different experiments.

2. Experimental procedure

The isotactic polypropylene of $M_w = 307\,000$ and $M_n = 15\,600$ was a product of RAPRA (UK). The smectic films were obtained by melting iPP pellets under pressure at 200 °C in a film shape, 0.02 cm thick, and quickly cooling in a dry-ice acetone bath at -70 °C. The films obtained were biphasic smectic–amorphous systems with a density of 0.8845 g cm^{-3}, which gives a smectic fraction, $\alpha_{sm} = 49\%$ [14]. Annealing was performed on small pieces of the quenched film at three temperatures, i.e. 130, 145 and 155 °C for 24 h, under nitrogen. The quenched film is denoted as SM; the annealed samples with the letter A followed by the annealing temperatures, i.e. A130, A145, and A155.

The density was measured by floating the sample in a mixture of 1,2 diethoxy-ethane and 2 ethoxy ethanol.

The wide angle X-ray diffractograms (WAXD) were obtained by using a PW 1050 Philips powder diffractometer (CuK_α, Ni filtered radiation). The scan rate used was 1° θ per min.

The sorption of dichloromethane vapour was measured by a microgravimetric method, using a quartz spring balance having an extension of 15 mm mg^{-1}, as a function of vapour activity $a = p/p_T$, where p is the actual pressure to which the sample was exposed and p_T is the saturation pressure at the temperature of the experiment, 25 °C. The samples were tested 1 week after the annealing procedure.

Differential scanning calorimetry (DSC) was carried out over the temperature range − 70 to 250 °C using a Mettler TA 3000 DSC purged with nitrogen and chilled with liquid nitrogen. Runs were conducted at a heating rate of 10 °C min^{-1}.

3. Results and discussion

3.1. Wide-angle X-ray scattering

In Fig. 1 we show the wide-angle X-ray diffractograms of: (a) A130; (b) A145, and (c) A155, annealed from the smectic iPP sample 24 h at the respective temperatures. The patterns correspond to the monoclinic α form of iPP, crystallized from the smectic form. From the diffractograms it is possible to derive the crystallinity of the samples, by comparing the area of the crystalline peaks, obtained by subtracting the amorphous area, with the total area of the pattern (Fig. 1). The derived crystallinities are reported in Table I, showing that on increasing the annealing temperature we obtain higher and higher levels of crystallinity.

Furthermore, the reciprocal of the half-height broadening of the peak at $2\theta = 14°$, $1/A$, is an index for the degree of order developed during the crystallization; as a matter of fact this parameter represents a qualitative measure of the ordered domain's dimensions; it is reported in Table I for all the samples. Also this parameter increases on increasing the annealing temperature, showing that at each temperature a different saturation level of crystallization is attained, both as a fraction of crystalline phase and as dimensions of the ordered domains.

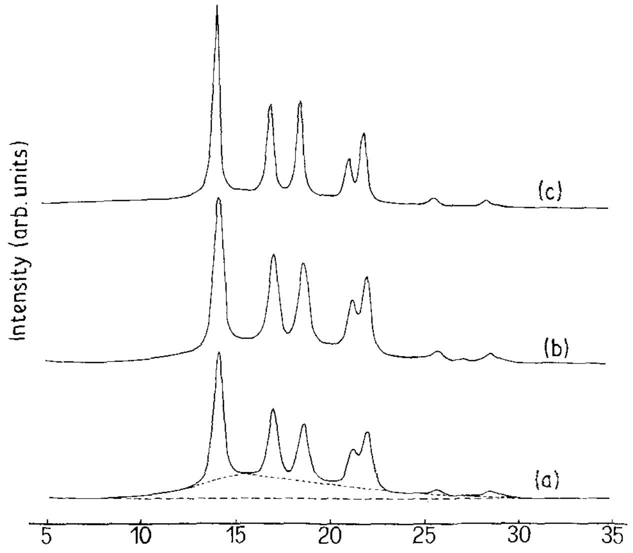

Figure 1 Wide angle X-ray diffractograms (WAXD) of: (a) A130; (b) A145, and (c) A155.

TABLE I The crystallinity derived from X-rays, α_c, the inverse of the half-height broadening of the peak at $2\theta = 14°$, $1/A$ (deg^{-1}), the crystallinity derived from DSC, α'_c, and $\Delta T = T_m - T_0$ for the analysed samples

Sample	α_c	$1/A$	α'_c	ΔT
A130	0.57	1.54	0.58	17.5
A145	0.62	1.67	0.63	14.0
A155	0.69	2.2	0.68	8.0
A80[a]	0.40			23.0
A100[a]	0.47			21.0

[a] From [12].

In Fig. 2 the crystallinity derived from X-rays and the $1/A$ parameter are reported as a function of the annealing temperature, T_A. The experimental points for the lower temperatures 80, and 100 °C are taken from a previous paper [12]. Either the X-ray crystallinity or the $1/A$ parameter, for samples annealed 24 h at each temperature, are linearly dependent on T_A up to 145 °C. At higher temperatures we observe a more than linear increase of both crystallinity and order parameter, indicating that at high temperature different effects are operative.

3.2. Differential scanning calorimetry (DSC)

In Fig. 3 we report the DSC curves for the annealed: (a) A130; (b) A145, and (c) A155 samples.

The A130 sample shows a broad melting range, with a double melting peak character. The appearance of a small melting peak at a temperature which is about 20° higher than the annealing temperature has already been observed in samples crystallized from the smectic iPP [9–12]. In this case, since the low melting peak is very close to the main peak, it appears as a shoulder in the thermogram. The analysis of the double peak character for the annealed samples will be the subject of a forthcoming paper.

The sample annealed at high temperature, A155, shows a very narrow melting range and an increased melting temperature. A careful inspection of the baseline shows that in all the samples the deflection of the baseline, due to the melting, starts at about 90 °C, as already observed by Grebowicz *et al.* [7]. This temperature was therefore used as a starting point for the determination of the melting enthalpy, as shown in the figure. The values of crystallinity, obtained by dividing the melting enthalphy by the thermodynamic melting enthalpy $\Delta H_0 = 6943\ \text{J mol}^{-1}$ [7], are reported in Table I. They are coincident with the X-ray crystallinities.

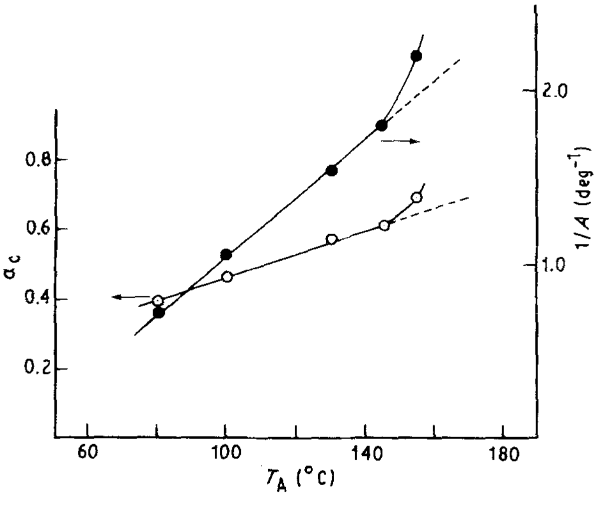

Figure 2 The crystallinity, α_c, derived from (○) X-rays, and (●) the 1/A parameter (deg^{-1}), are reported as a function of the annealing temperature, T_A.

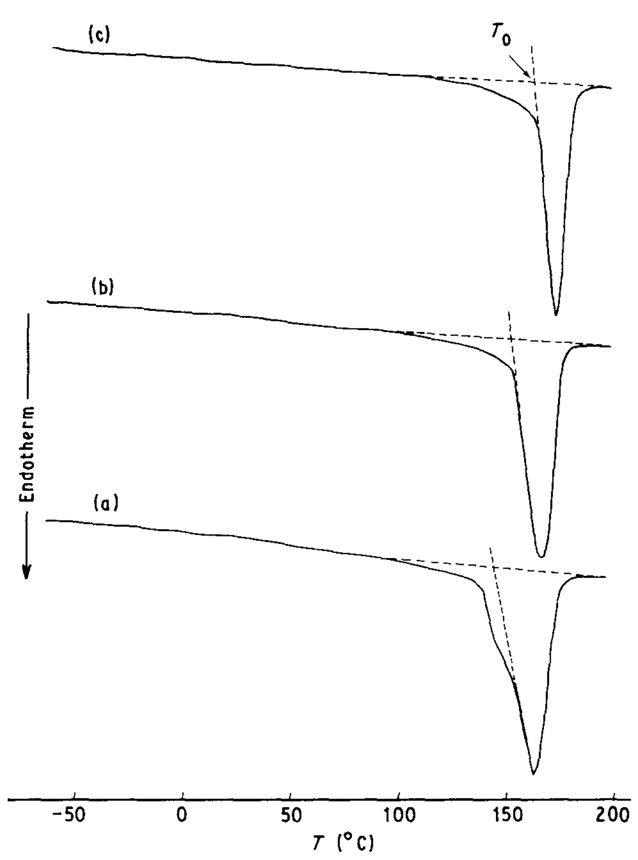

Figure 3 DSC thermograms for sample: (a) A130; (b) A145, and (c) A155.

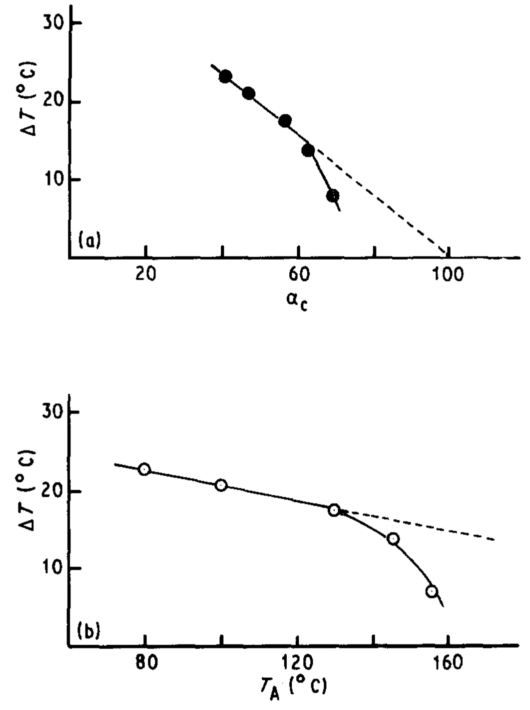

Figure 4 The dispersity of crystal thickness $\Delta T = T_m - T_o$, is reported as a function of: (a) crystallinity α_c, and (b) annealing temperature, T_A.

Although the crystallization from the smectic form was performed in isothermal conditions, a broad distribution of crystal thicknesses is present, particularly at the lower temperature. The dispersity of crystal thickness in each sample can be represented by $\Delta T = T_m - T_o$, where T_m is the peak melting temperature, and T_o the onset temperature, corresponding to the melting of crystallites with smaller dimensions. The onset temperature was determined from the intersection of the slope on the left of the melting endotherm and the baseline (Fig. 3). The values of ΔT are reported in Table I and in Fig. 4 as a function of: (a) the annealing temperature T_A and (b) the crystallinity. Also in the figure samples of a previous work are reported. We observe a linear correlation between ΔT, representing the dispersion of the crystal dimensions, and the crystallinity of the samples, up to the annealing temperature of about 150 °C, corresponding to a crystallinity of 65%. For higher values of T_A, and therefore of crystallinity, a steeper decrease of dispersity is observed. As already observed from the X-ray results, the annealing temperature, 150 °C, seems a transition temperature, above which an increased perfection of the crystalline phase is obtained.

3.3. Density

Table II reports the density values of the samples. It is normal practice to derive the crystallinity of a sample from its density assuming a two phase crystalline amorphous model. Knowing the ideal density of the crystals and of the amorphous component, the derived mass crystallinity is

$$\alpha_c = \frac{d_c\,(d - d_a)}{d\,(d_c - d_a)} \qquad (1)$$

In the case of iPP, $d_c = 0.936\ \mathrm{g\,cm^{-3}}$ and $d_a = 0.856\ \mathrm{g\,cm^{-3}}$. In Table II the crystallinities obtained from Equation 1 are compared with the X-ray crystallinities. The comparison shows that the values obtained from density are higher, in all cases, than the X-rays crystallinities, and the difference is too high to be disregarded.

We already showed that annealing smectic iPP up to 120 °C gives a three phase system, in which the smectic phase has not been completely transformed into the monoclinic phase [12]. The not negligible difference in the values of crystallinity obtained from X-rays and density means that, also at higher temperatures we do not observe the complete transformation of the smectic phase. When we obtain three phase systems, the crystallinity derived from Equation 1 is fictitious and it is necessary to employ another technique in order to derive the exact distribution of the three components.

TABLE II The density ($\mathrm{g\,cm^{-3}}$), the crystallinity, derived from Equation 1, α_c'', the crystallinity derived from X-rays, α_c, the amorphous fraction, derived from sorption, α_a, and the smectic, α_{sm}, and the monoclinic, α_{mon}, fractions derived from density and Equations 2 and 3, for the crystallized samples

Sample	d ($\mathrm{g\,cm^{-3}}$)	α_c''	α_c	α_a	α_{sm}	α_{mon}
A130	0.9088	0.68	0.57	0.29	0.13	0.58
A145	0.9122	0.73	0.62	0.25	0.12	0.62
A155	0.9165	0.78	0.69	0.20	0.09	0.71
A80[a]	0.8985	0.54	0.40	0.38	0.24	0.38

[a] [12].

If the mass fractions of the crystalline, smectic and amorphous components are α_c, α_{sm} and α_a, respectively, the density of the system has to be expressed as

$$\frac{1}{d} = \frac{\alpha_a}{d_a} + \frac{\alpha_{sm}}{d_{sm}} + \frac{\alpha_c}{d_c} \qquad (2)$$

The three fractions α_c, α_{sm} and α_a, are linked by the expression

$$\alpha_a + \alpha_{sm} + \alpha_c = 1 \qquad (3)$$

We can derive α_a from sorption measurements, as already shown [13, 14], and therefore the crystalline and smectic fractions from Equations 2 and 3.

3.4. Sorption

The procedure to obtain the amorphous fraction in a three phase amorphous–smectic–monoclinic system consists of determining the sorption of dichloromethane vapour in the analysed sample, as a function of vapour activity. It has been already shown that at low penetrant activity, neither the smectic nor the monoclinic phase diffuse and sorb the vapour [13, 14]. Therefore it is assumed that different equilibrium concentrations of vapour in different samples are due to different amorphous fractions, being the specific sorption, i.e. the equilibrium sorption normalized by the amorphous fraction, coincident in all the samples, that is

$$C_{sp} = C_{eq}(X)/\alpha_a(X) \qquad (4)$$

where (X) represents a crystallized sample and C_{sp} is the equilibrium concentration of vapour in atactic polypropylene [15]. At each vapour activity (provided low activities are explored), the ratio between the sorption of the crystallized sample and that of the atactic sample gives the amorphous fraction, α_a.

In Fig. 5 the equilibrium concentration of vapour is reported as a function of vapour activity for samples A130, A145, and A150. The curve of atactic polypropylene [15] is reported up to activity $a = 0.35$, for the calculation of the amorphous fractions. They are calculated from the reduction of sorption at each activity, up to $a = 0.35$. The obtained mean values of α_a are reported in Table II for the three samples.

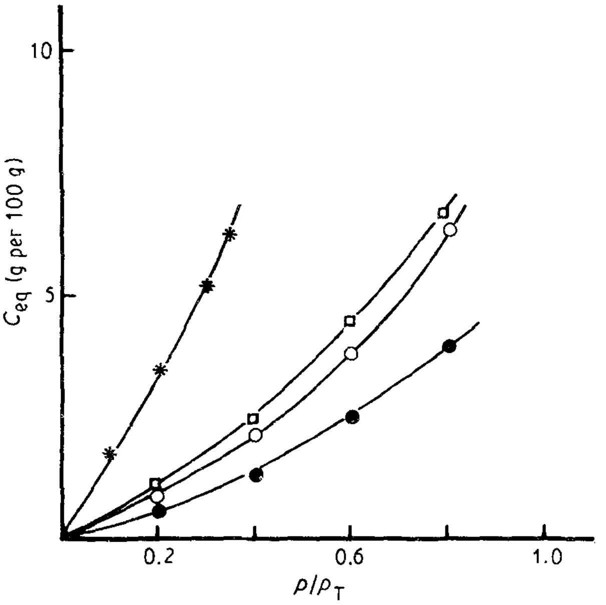

Figure 5 The equilibrium concentration of dichloromethane vapour is reported as a function of activity $a = p/p_T$, for (✱) atactic polypropylene; (☐) sample A130; (○) sample A145, and (●) sample A155.

Each value of α_a allows us to obtain the composition in terms of α_{sm} and α_c, from the density of the sample, using Equations 2 and 3. In Table II we report the calculated values for the three samples.

It is worth noting that the values of α_c coincide with the X-ray and DSC crystallinities, confirming the reliability of the sorption method to determine the phase composition. Therefore, even at high temperature the starting smectic phase does not transform completely into the monoclinic phase, but three phase systems are obtained, although at the highest temperature the fraction of smectic phase tends to zero.

We report in Fig. 6 the: (a) amorphous and (b) smectic fractions as a function of the annealing temperature, T_A. Also in the figure the values of α_a and α_{sm} of a sample annealed 24 h at 80 °C of a previous paper [12] are reported. We observe a linear decrease of the two fractions up to about 150 °C, and a more than linear decrease after this temperature. After 150 °C, the smectic fraction tends to zero and we observe a more than linear increase of crystallinity and crystal perfection.

4. Conclusions

The thermal crystallization of smectic isotactic polypropylene leads to the obtainment of three phase systems amorphous–smectic–monoclinic. In these systems, the determination of crystallinity, through the use of X-ray diffractograms or differential scanning calorimetry gives the exact amount of monoclinic phase, but does not give a reliable value of the amorphous fraction. On the contrary the density method for the determination of crystallinity gives an overestimated crystalline fraction, since there is a fraction of smectic phase influencing the density value, that is not taken into account. The sorption of dichloromethane vapour at low activity allows the determination of the amorphous fraction in the system and, therefore, through the density, of the complete composition in terms of α_c, and α_{sm}.

The dependence of the three fractions on the annealing temperatures shows that after 150 °C there is

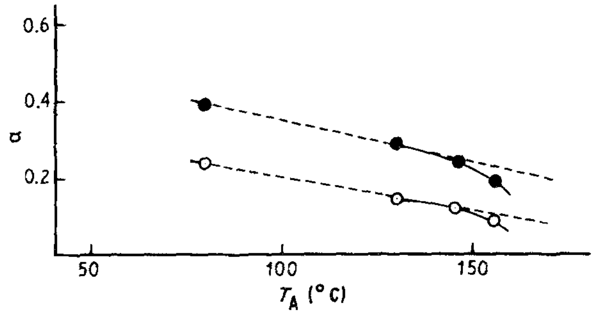

Figure 6 The fraction of: (●) amorphous phase α_a, and (○) smectic phase, α_{sm}, are reported as a function of T_A.

an accelerated decrease both of the amorphous and of the smectic phase. Corresponding to this decrease there is the obvious accelerated increase of the monoclinic fraction, but also, more interesting, an accelerated increase in the crystal dimensions and perfection, shown either by the $1/A$ parameter or by the $\Delta T = T_m - T_0$ parameter. We can suggest that, when the smectic phase tends to zero, then an accelerated process, leading to large crystalline dimensions and higher perfection, becomes operative.

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References

1. R. J. SAMUELS, in "Structured Polymer Properties" (John Wiley, New York, 1974) Ch. 1.
2. A. PETERLIN, *Colloid and Polym. Sci.* **265** (1987) 357.
3. I. M. WARD, in "Structure and Properties of Oriented Polymers" (Applied Science Publishers Ltd, London, 1975) Ch.1.
4. F. de CANDIA, G. ROMANO, R. RUSSO and V. VITTORIA, *Colloid and Polym. Sci.* **265** (1987) 696.
5. G. NATTA, M. PERALDO and P. CORRADINI, *Rend. Acc. Naz. Lincei* **26** (1959) 14.
6. R. L. MILLER, *Polymer* **1** (1960) 135.
7. J. GREBOWICZ, I. F. LAU and B. WUNDERLICH, *J. Polym. Sci. Polym. Symp.* **71** (1984) 19.
8. R. ZANNETTI, G. CELOTTI, A. FICHERA and R. FRANCESCONI, *Makromol. Chem.* **128** (1969) 137.
9. A. FICHERA and R. ZANNETTI, *ibid.* **176** (1975) 1885.
10. C. C. HSU, P. H. GEIL, H. MIYAJI and K. ASAI, *J. Polym. Sci. Phys. Ed.* **24** (1986) 2379.
11. D. T. GRUBB and D. Y. YOON, *Polym. Commun.* **27** (1986) 84.
12. V. VITTORIA, *J. Macromol. Sci. Phys.* **B28** (1989) 489.
13. *Idem, J. Polym. Sci. Phys. Ed.* **24** (1986) 451.
14. V. VITTORIA and A. PERULLO, *J. Macromol. Sci. Phys.* **B25** (1986) 267.
15. R. RUSSO, R. NATALE and V. VITTORIA, manuscript in preparation.

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