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Low T_c growth transitions in isotactic polypropylene: β to α and α to smectic phases

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SUMMARY

Two growth transitions are observed by optical microscopy in the low T_c range (105-80°C) of isotactic polypropylene (iPP) : β to α and α to (probably) smectic phases. These transitions (notably β to α) may be the cause of the complicated annealing and recrystallization behaviour of β iPP, which is known to depend on the initial crystallization and post-crystallization thermal history.

INTRODUCTION

The crystallization and melting behaviours of isotactic polypropylene are complicated (1,2) as two crystalline phases are usually produced and coexist in the samples : the stable, monoclinic α and metastable hexagonal β phases (3). Two other phases of iPP are however known : a smectic phase produced at low T_c (4) and a highly unusual γ phase (5). Although metastable, the β phase has a faster growth rate than the α phase in the "conventional" range, i.e. for T < 140°C (6,7). Above 140°C, α growth is faster and a β to α growth transition takes place (8).

While investigating the natural and induced nucleations of iPP (9), we have observed further growth transitions in the low T_c range of iPP. These so far unsuspected transitions may help understand the curious and complicated recrystallization behaviour of the β phase after annealing and partial melting reported by Varga and Tòth (10).

EXPERIMENTAL

The growth transitions are revealed as follows :

An iPP sample of high tacticity is deposited as a thin film (< 1 μm) on a single glass cover slide i.e. not sandwiched, in order to reduce thermal inerty and seeded with crystals of γ-chinacridone, a nucleating agent of the β phase (11). The film is melted at ≈ 180°C on a hot stage, allowed to cool and crystallize partly in air for 5 to 10 seconds, and quenched by deposition on a surface held at room temperature.

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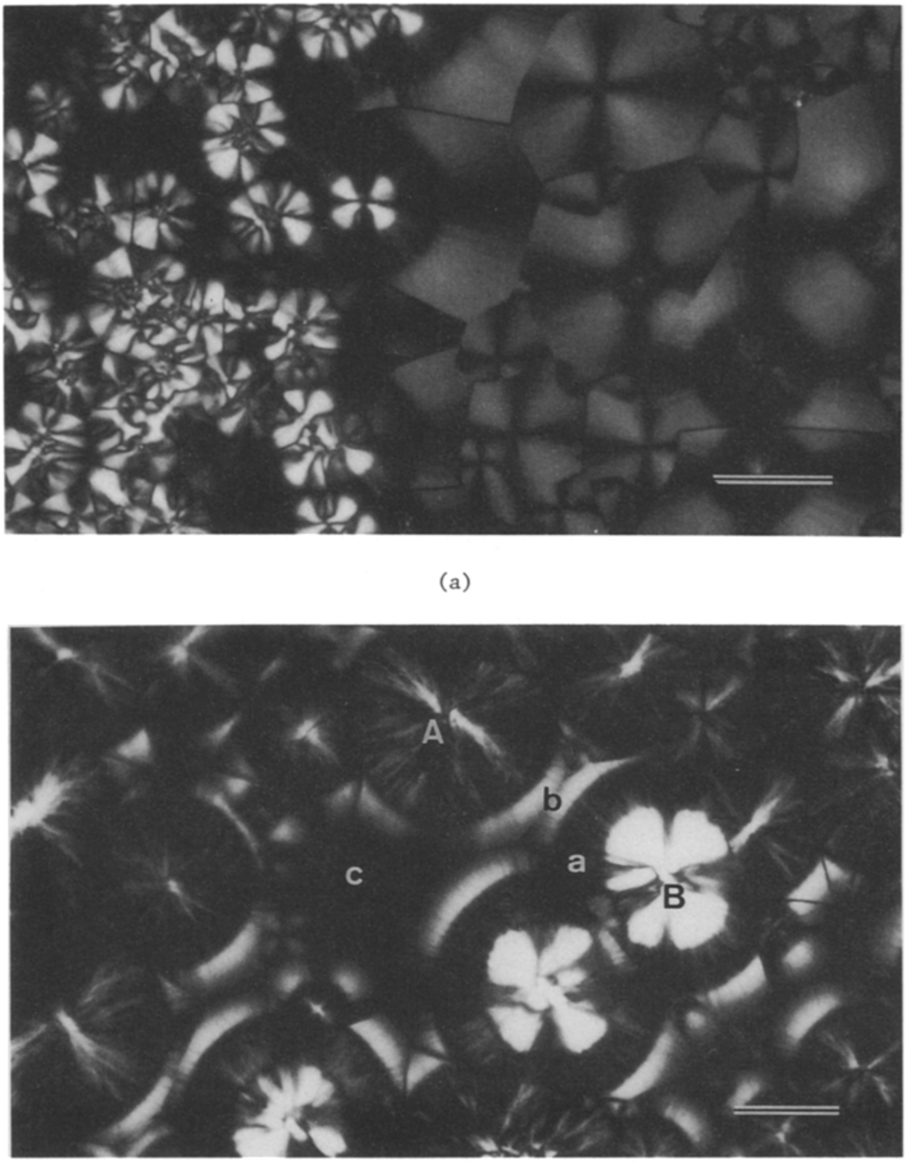

(a)

(b)

Figure 1. Complex spherulitic morphology obtained on fast quenching a thin iPP film seeded with γ-chinacridone in relatively (a) slow and (b) fast quench. Areas marked correspond to (B) high T_c β spherulites nucleated on γ-chinacridone crystals (A) high T_c α spherulites (a) α phase growth at $T < 105°C$ (positive birefringence) (b) "smectic" phase (c) homogeneous nucleation. Note development of new spherulites at every stage of the cooling process. Optical micrographs, crossed polars. Scale bars : 20 μm.

RESULTS AND DISCUSSION

Spherulite morphologies and structures

In the fast cooling process, spherulites nucleated at high T_c experience decreasing crystallization temperatures as they grow. Growth transition at any given T_c thus results in an isochronous circular boundary within the spherulite. Efficient quenching may even stop spherulitic growth, due to the onset of homogeneous nucleation (12).

The spherulitic morphologies obtained for two slightly different thermal histories are represented in Fig.1a and b. Spherulites of weak and positive birefringence (as assessed with the use of a gypsum plate) have formed as a result of conventional, heterogeneous nucleation. These spherulites are of the α phase (marked A) ; their low birefringence is a consequence of a characteristic lamellar branching (13-15). Bright, negatively birefringent spherulites have nucleated on the γ chinacridone particles. They are of the β phase (3,6). The bright β interior is surrounded by two rings : a weakly birefringent annular zone (marked a) and a more birefringent zone, distinctly different however from the inner, high T_c β one. If the quench is fast enough (Fig.1b), the bright zones are themselves limited by isotopic domains (marked c) which are not observed for milder quenches (Fig.1a).

The rings marked (a) are of the α phase, as revealed by their positive birefringence, and their overall similarity with high T_c α phase growth : indeed, this first growth transition does not show up in α spherulites. The stage of development of α phase spherulites at the time (or temperature) of the transition can nevertheless be "traced back" since the successive growth countours are equal.

The crystal phase of the bright outer zone is more ambiguous. It is tentatively assumed to be the smectic phase which is known to grow at low T_c, on quenching bulk samples (4,16). Its negative birefringence would also be compatible with α growth with reduced frequency of lamellar branching.

The outer, isotropic domains result from the onset of homogeneous nucleation : the absence of birefringence is due to the small size and random orientation of the structural units formed on quenching. Note however that nucleation takes place over the whole cooling cycle and may in particular create "pure" spherulites of the smectic phase (Fig.1a).

The actual T_c range of these growth transitions can be inferred. As already indicated, the onset of homogeneous crystallization in iPP is $\simeq$ 80°C, which fixes the T_c at the exterior of the outer bright growth ring. The initial β to α transition occurs most probably at 105°C, as can be inferred from an analysis of the work of Varga and Tòth (10) to be discussed now.

Crystal growth transitions and thermal behaviour of β spherulites

While investigating the melting and crystallization of β iPP, Varga and Tòth noted a very unusual thermal behaviour, highly dependent on the crystallization and post-crystallization thermal history. If in the course or after crystallization of iPP in the β phase, the sample is taken to a temperature $T < 105°C$ $(= T^*)$ and then annealed and recrystallized, the recrystallization yields the α phase (βα recrystallization). If the β phase is never taken to $T < 105^\circ$C, it yields only the β phase after the same annealing and recrystallization process (ββ recrystallization). Surprisingly, the same ββ recrystallization is also observed, even after quenching to $T < 105^\circ$C, provided the initial β phase is carefully stabilized by appropriate thermal treatments. These findings have not, so far, received any satisfactory explanation.

The low temperature βα growth transition may well provide a logical clue for the above rather confusing observations. It is suggested that the observed behaviour depends on the fate of the uncrystallized material within the β spherulites, i.e. on the secondary crystallization process. If in the initial crystallization history, uncrystallized material still exists when the sample is taken below 105°C it crystallizes in the α phase (low temperature βα growth transition). The resulting α phase units are highly dispersed in the spherulite as they develop on all existing β lamellar edges. These units are prone to thermal annealing and stabilization familiar in differential scanning calorimetry (17), and, in view of their different crystal structure are more stable than the β phase. These units can therefore survive the annealing and melting of the β phase and constitute very active, highly dispersed nuclei for α growth on further cooling (βα recrystallization). In effect, the process amounts to an efficient self-seeding (14). Conversely, if T remains above 105°C, or if careful annealing and stabilization above 105°C has depleted all crystallizable material, no α phase can develop at low temperature : the sample then behaves as an "homogeneous" β phase on remelting and recrystallization (ββ recrystallization).

CONCLUSION

Two low T_c growth transitions of isotactic polypropylene have been revealed by rapid quenching of a thin film with low thermal inerty. Optical microscopy reveals a β to α growth transition probably located at 105°C and an α to (probably) smectic phase growth transition before the onset of homogeneous nucleation at $T_c \approx 80^\circ$C.

Further details of the growth transitions and resultant different spherulite structures and morphologies are being assessed by permanganic etching (19) and electron diffraction.

The present results indicate that the β phase of iPP is kinetically favoured over the α phase only in a temperature interval ranging from ≈ 105° to 140°C. They also provide experimental conditions to be fulfilled in order to investigate possible low T_c growth transitions of other polymers.

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