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CRYSTALLIZATION, MELTING AND SPHERULITIC STRUCTURE OF β-NUCLEATED RANDOM PROPYLENE COPOLYMERS

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Abstract

The characteristics of crystallization, melting and spherulitic growth of a random propylene copolymer (PRC) containing small amount of ethylene were studied in the presence of a selective β-nucleating agent (calcium pimelate). It was established that the products of isothermal and non-isothermal crystallization are very rich in β-modification but have mixed polymorphic composition. The formation of α-modification may be attributed to βα-transition on the surface of growing β-spherulites resulting in αβ-twin-spherulites. During melting of PRC of β-modification, the characteristics observed with β-nucleated propylene homopolymers, namely, a βα-recrystallization of recooled samples and separated melting of non-recooled samples (i.e. the melting memory effect), as well as a ββ-recrystallization leading to a perfection of the structure within the β-modification, are also demonstrated. The disturbance of regularity of the polymer chain highly reduces the tendency to β-crystallization. In contrast to the observations with propylene homopolymers, the growth rate of α-modification (G_α) is higher than that of β-modification (G_β) and no critical crossover temperature can be found ($T(\beta\alpha)=413$ K) below which $G_\alpha < G_\beta$. The experimental results show that a partial disturbance of chain regularity by incorporation of comonomer units considerably reduces the tendency to β-crystallization.

Keywords: characterization, crystallization, propylene copolymers

Introduction

Our previous results on the preparation and characterization of crystallization, melting and supermolecular structure of β-modification of isotactic polypropylene (β-IPP) are summarized in a recent monograph [1]. The research was also extended to the random copolymers of propylene (PRC) with low comonomer content which were prone to crystallization. The partial disturbance of the chain regularity by the randomly incorporated comonomer units resulted in a reduced tendency to crystallization of PRC [2–7]. For this reason, it seemed to be promising to study how the disturbance of the chain regularity influenced the tendency to crystallization in the β-modification. According to the previous observations, the commercial grades of PRC crystallize in α-modification and,

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in contrast to IPP, the concomitant β-phase is generally not present even in a trace amount [2, 3]. However, by means of selective β-nucleating agents, PRC products rich in β-modification can be prepared [1]. The most important conclusions on the tendency to β-crystallization were also included in the aforementioned monograph [1]. The paper on this topic by Zhang and Shy [8] was published nearly at the same time.

In the present paper, the relative tendency to β-crystallization, the complexity of melting of the β-phase, and the specific features of the formation of the spherulitic structure of PRC are studied in the presence of an additive, developed in our laboratory [1], proved to be a selective β-nucleating agent for IPP. Our observations are then compared to the results of Zhang and Shy [8] and the contradictions in the interpretation of their experimental results are pointed out.

Experimental

Random propylene copolymer Tipplen R351 of Tisza Chemical Works (TVK, Tiszaújváros, Hungary) containing lubricant and antiblocking agent (M_n=61000, M_w=182300, MFI=10 g/10 min, comonomer content: 1.8% *w/w* of ethylene) was used throughout the experiments. Crystal water free calcium salt of pimelic acid (*cpm*) was used as selective β-nucleating agent [1]. This one-component β-nucleating agent is more efficient than the binary additives of similar chemical composition applied by Zhang and Shy [8] since the former one may lead even to pure β-modification of polypropylene under appropriate thermal conditions [1]. 0.01 to 0.1 per cent *w/w* of β-nucleating agent was incorporated into the basic polymer by means of a Brabender plastograph at 200°C. Crystallization and melting curves of 5 mg samples were recorded by a Perkin-Elmer DSC-2 in nitrogen atmosphere. In order to eliminate the thermal and mechanical memory of the samples, they were previously thermally treated at T_F=473 K for 5 min. During the non-isothermal crystallization, different cooling rates (V_c=2.5 to 20 K min^{-1}) and a fixed heating rate (V_h=10 K min^{-1}) were used for crystallization and melting, respectively. In order to study the tendency to recrystallization, samples crystallized at a consistent cooling rate (V_c=10 K min^{-1}) were melted at different heating rates (V_h=2.5 to 20 K min^{-1}). The temperature of recooling (T_R) during the crystallization of the β-nucleated systems was T_R=383 K, except for some control tests, in order to avoid a possible βα-recrystallization due to recooling below T_R^* [9]. The samples free of nucleating agent were recooled to the room temperature (T_{RT}). The initial, peak and final temperatures of crystallization (T_{co}, T_{cp} and T_{cf}, respectively) were determined on the crystallization curves while the peak temperature of melting (T_p) and the melting point (T_m) were read from the melting curves. For the isothermal measurements, samples were cooled from the final temperature of heating (T_F=473 K) to the temperature of crystallization (T_c) at a rate of V_c=

40 K min^{-1}. Crystallized samples were melted at heating rates of V_h=10 or 2.5 K min^{-1} starting from T_c.

Structural characteristics and kinetics of growth of spherulites were investigated by a Dialux 20 (Leitz) microscope equipped with a Mettler F82-type temperature-programmed hot stage.

Results and discussion

Non-isothermal and isothermal crystallization

In the first stage of this research, crystallization and melting of the random copolymers of propylene were studied. These investigations revealed, in accord with previous observations [2–7], that these random copolymers of propylene (PRC) could be supercooled at a higher extent, showed lower melting point and had lower degree of crystallinity than isotactic polypropylene (IPP) (Figs 1 and 2). Due to their more irregular chain structure, the characteristic temperatures of non-isothermal crystallization and melting of a certain PRC are lower by about 10 K than those of isotactic polypropylene (IPP) and of propylene block copolymers (PBC). In addition, due to their higher capability of supercooling, PRCs crystallize farther from the equilibrium conditions, consequently their structure is more unstable, being considerably different from the equilibrium structure. Because of this structural instability, the tendency to recrystallization of a PRC is high and during the recording of melting curves (heating) an exothermic recrystallization may superimpose to the endothermic melting process.

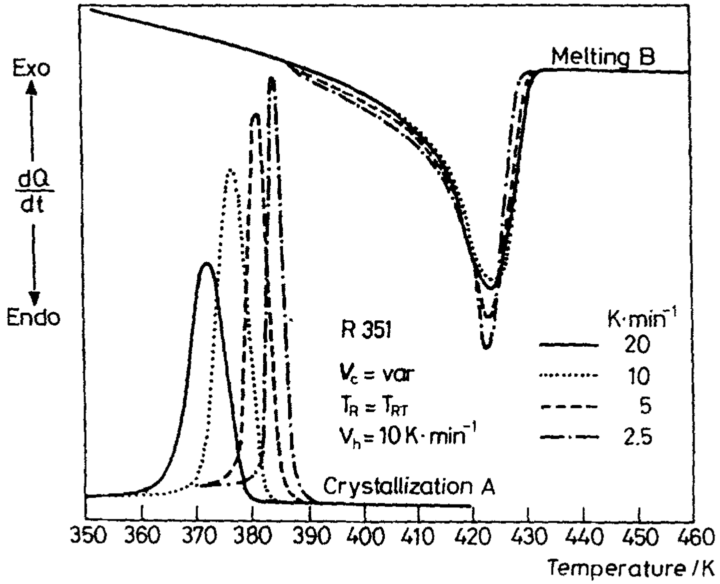

Fig. 1 Non-isothermal crystallization and melting curves of PRC (V_c=var, V_h=10 K min^{-1})

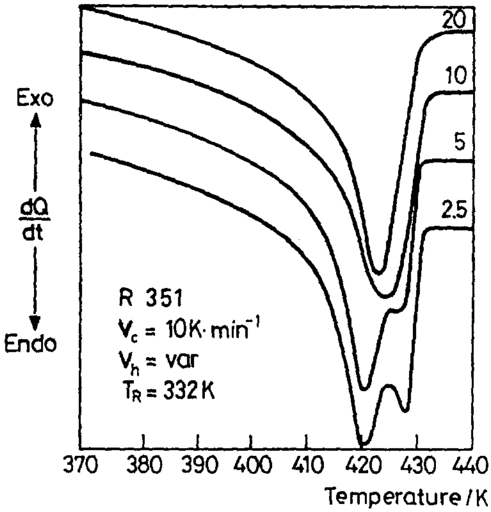

Fig. 2 Melting curves of PRC crystallized at fixed cooling rate as a function of heating rate (V_c =10 K min^{-1}, V_h=var)

Samples cooled at a constant rate result in an unimodal crystallization peak shifted toward lower temperatures and broadening with increasing V_c (Fig. 1). Melting curves of samples cooled at different rates show a single peak with identical T_p value again at a given heating rate. When cooled at higher rates, however, the melting curves will broaden due to recrystallization superimposed to melting. As another consequence of recrystallization, the calorimetric melting point is higher in spite of the more unstable structure of samples cooled more rapidly since the fraction of the material recrystallized has an improved strukture and thus will melt at higher temperature. That is the reason why T_m values are shifted toward higher temperatures with increasing V_c. Since recrystallization is time-dependent, the conditions of recrystallization during the melting are the more favourable the lower the heating rates appearing as a more and more distinct duplication of the recorded melting peaks (Fig. 2). The final temperature of melting as recorded calorimetrically (T_m) is shifted toward higher temperatures with decreasing V_h due again to the higher extent of recrystallization (Fig. 2).

The experimental results from non-isothermal crystallizations of β-nucleated PRC samples are shown in Figs 3 through 6. Figure 3 exhibits non-isothermal crystallization and melting curves of a sample containing 0.1 per cent of β-nucleating agent. It can be established from the crystallization curves that the range of crystallization has shifted toward higher temperatures by the influence of the β-nucleating agent at an increasing extent with enhancing V_c (about 5 K and about 8 K at V_c=2.5 and 20 K min^{-1}, respectively) and the temperature range of crystallization is narrower than that in the absence of β-nucleating agent (cf. Fig. 1).

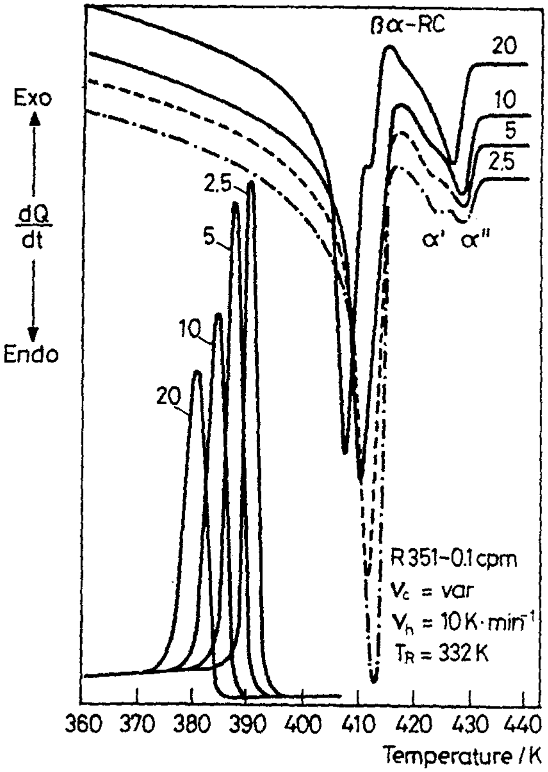

Fig. 3 Crystallization and melting curves of β-nucleated PRC samples crystallized at different cooling rates and cooled below T_R^* (V_c=var, $T_R=T_{RT}$, V_h=10 K min^{-1}, *cpm*=0,1 %)

Melting curves of β-nucleated samples are complex after non-isothermal crystallization. The lower-temperature peak of high intensity refers to melting of the β-modification while the higher-temperature doubled peak is attributed to the α-modification (Fig. 3). For the interpretation of these complex melting curves, the unique feature of melting of β-IPP should be considered as pointed out in our previous works [1, 2, 9–11]. Melting behaviour of β-IPP depends on the thermal history of the crystalline sample revealing a definite *melting memory effect*. β-IPP cooled below a critical recooling temperature (T_R^*=373 K) recrystallizes into α-modification (βα-recrystallization) during a partial melting while, if recooling is avoided, it melts distinctly, without recrystallization. In samples cooled below T_R^* the peak of α-melting always appears and the peak of β-melting becomes distorted due to βα-recrystallization. As a consequence of the βα-recrystallization superimposed to melting, an exothermic trace appears (the recorder pen moves above the baseline, especially for samples cooled rapidly or crystallized at low T_c and therfore having a more unstable structure). These characteristics are clearly perceptible in the records of Fig. 3. The melting memory effect can also be observed for β-nucleated PRC samples as unequivocal when Figs 3 and 4 are compared. With limited recooling ($T_R=383$ K $>T_R^*=373$ K), the course of the melting curve is much more simple (Fig. 4) as the exothermic peak referring to the βα-recrystallization is missing and the size of the α-peak is considerably smaller. However, besides the high-intensity peak of melting of the β-modification ($T_p=412$ K), melting curves of non-recooled samples always show a difiuse melting peak referring to the presence of the α-modification. On the other hand, in similar experiments with IPP samples, no α-modification was produced [9, 10]. Therefore, it can be concluded that a mixed polymorphic structure, though mainly β-modification, is formed in PRC in spite of the presence of a selective β-nucleating agent. The reason and interpretation of the formation of the α-modification will be dealt with in the discussion of polarizing optical microscopic results.

The real polymorphic composition can be determined on the basis of Fig. 4 when the disturbing effect of βα-recrystallization is eliminated. The heats of fusion ($\Delta H=58$–60 J g^{-1}), as determined from areas under β-peaks, increase slightly with increasing V_c and the tendency to recrystallization within the β-modification (ββ-recrystallization) is enhanced as indicated by the duplication of β-peaks. The proportion of the α-modification is slightly increased by reducing V_c but is estimated to be not higher than 5 per cent.

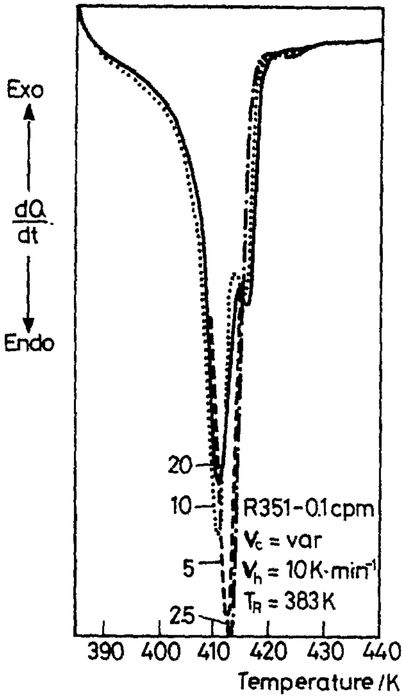

Fig. 4 Melting curves of β-nucleated PRC samples crystallized at different cooling rates with limited recooling (V_c=var, $T_R=383$ K, $V_h=10$ K min^{-1}, $cpm=0.1$ %)

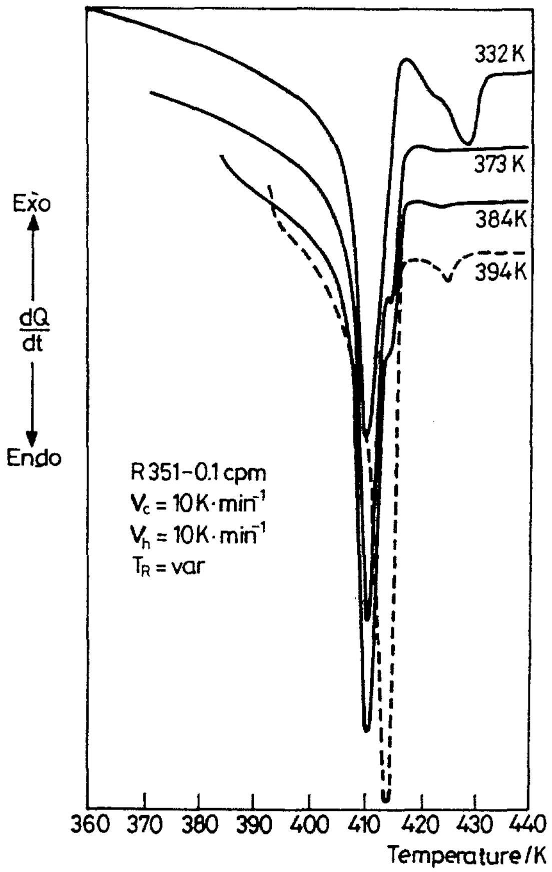

Fig. 5 The effect of temperature of recooling (T_R) on the feature of the melting curve of β-PRC ($V_c=V_h=10$ K min^{-1}, *cpm*=0.1 %)

It can also be established by the comparison of Figs 3 and 4 that the lower-temperature component (α′) of the doubled α peak on the melting curves of recooled samples represents melting of the fraction formed during the non-isothermal crystallization while the higher-temperature one (α″) refers to the part of the α-phase resulted from the βα-recrystallization. The higher the cooling rate used for the crystallization (leading to a higher structural instability of the crystallized sample), the greater is the role played by the βα-recrystallization during heating as indicated by the enhanced intensity of the peaks of the exothermic recrystallization and that of α″ melting (Fig. 3). With the increasing structural instability (increasing V_c), the βα-recrystallization takes place in progressively earlier stage of the partial melting of the β-phase whilst the calorimetrically recorded size of β-peaks decreases considerably in spite of the fact that the majority of the sample is β-modification and this proportion varies slightly as a function of V_c as shown in Fig. 4. Consequently, the intensity of β-peak does not refer to the real proportion of the β-modification and polymorphic composition in recooled samples because of βα-recrystallization. In this case the β-peak can not be assignated to an actual melting process since it is a result of two superimposed processes with opposite thermal effects and with different rates. The β-peak indicates the temperature at which the rate of heat flow (acceleration) of these two processes (i.e. exothermic βα-recrystallization and endothermic melting) are identical. As the rate of βα-recrystallization is influenced by several factors (conditions of crystallization, thermal history of the crystallized sample, heating rate), the effect of these on the β-peaks is also complex as discussed later. Therefore, the conclusions of Zhang and Shy [2] may be viewed with reservations because they disregarded the possible consequences from the melting memory effect [9] and interpreted the melting characteristics and polymorphic composition of β-PRC only on the basis of the melting curves of PRC samples cooled below T_R^*. This causes the remarkable discrepancy between the X-ray diffractometric and calorimetric results.

The tendency to βα-recrystallization of β-IPP cooled below T_R^* was attributed to formation of finely dispersed α-crystallites within the β-modification, as a consequence of a secondary crystallization below T_R^*. This α-phase acts as a nucleating agent during the partial melting of the β-phase [1, 9]. By lowering the temperature of recooling (T_R) the amount of α-nuclei increases, leading to

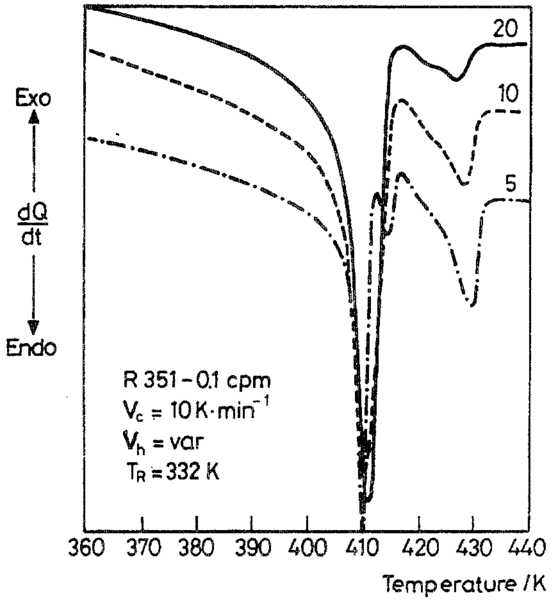

Fig. 6 Non-isothermal melting curves of β-nucleated PRC samples crystallized at fixed cooling rate and cooled below T_R as a function of heating rate (V_c=10 K min^{-1}, T_R=T_{RT}, V_h=var, *cpm*=0.1 %)

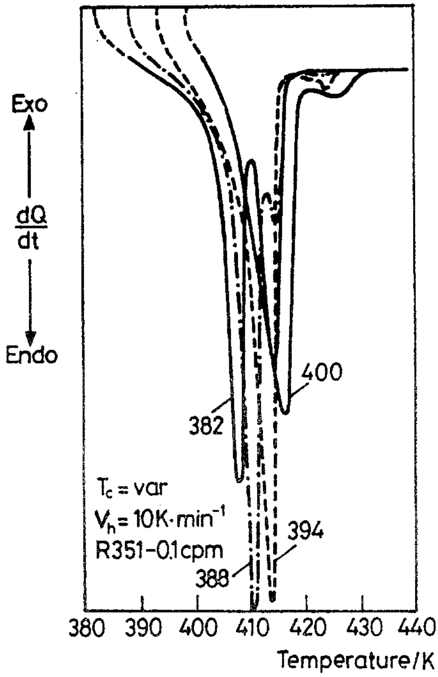

Fig. 7 The effect of temperature of crystallization on the melting curves of β-nucleated PRC samples (T_c=var, T_R=T_c, V_h=10 K min^{-1}, *cpm*=0.1 %)

an enhanced rate of βα-recrystallization (Fig. 5). The exact determination of T_R^* for PRC is rather difficult since during the direct crystallization α-modification is always formed. The interpretation of Fig. 5 makes it probable that T_R^* is below 373 K because at T_R ≥373 K, no α″-peak (the higher-temperature α-peak which refers to the βα-recrystallization) appears on the melting curves (Fig. 5).

Since βα-recrystallization is time-dependent, reducing the heating rate during the melting of recooled samples results in more and more definite recrystallization as indicated by the enhancing exothermic trace and α″-peak of melting (Fig. 6). It should be noted that reducing V_h promotes not only the βα-recrystallization but also a structural perfection within the β-modification (ββ-recrystallization). However, in the majority of cases, βα-recrystallization takes place in a lower temperature range than ββ-recrystallization. For this reason, the latter process cannot proceed. In some exceptional cases, both recrystallizations can be observed as shown by the doubled β-peak referring to ββ-recrystallization on the melting curve at a heating rate of 5 K min^{-1} in Fig. 6 and that of the sample crystallized at a cooling rate of 20 K min^{-1} in Fig. 3.

In the presence of the nucleating agent, even the isothermal crystallization leads to a mixed polymorphic product, though rich in β-modification. This is proved by the high-intensity (occasionally double) β-peak in the temperature range of 405 to 415 K and a low-intensity α-peak in the range of 415 to 425 K on the melting curve in Fig. 7. The high concentration of the β-phase is confirmed unambiguous by the X-ray diffractogram of a sample moulded at 488 K where the *k* value is 0.90 [1].

The characteristics of melting curves after isothermal crystallization depend on T_c. At low T_c double β-peaks appear in the temperature range of 405 to 415 K due to a recrystallization within the β-modification (ββ-recrystallization) because of the unstable structure as was observed for β-nucleated IPP as well [1, 9]. Since the higher-temperature peak of the dublet refers to the phase arrived at perfection by the preceding recrystallization (and not to the proportion formed at T_c), it is independent of T_c. Elevating of T_c makes the structure more and more stable and recrystallization is repressed at a given heating rate resulting in a single melting peak (melting curves to T_c=400 and 394 K in Fig. 7). The heats of fusion of β-phase increase with decreasing T_c in the temperature

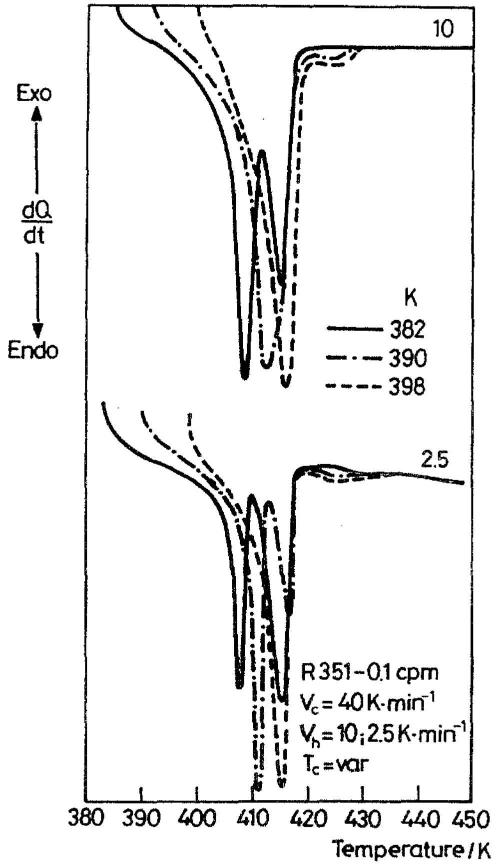

Fig. 8 The efifect of heating rate on the course of the melting curves of β-nucleated PRC samples after isothermal crystallization (V_c=40 K min^{-1}, T_c=var, V_h=2.5 or 10 K min^{-1}, *cpm*=0.1 %)

range 383–400 K ($\Delta H(\beta)=62$–56 J g^{-1}). It can also be established from Fig. 7 that the amount of α-phase is increasing with elevating of T_c. It should be emphasized once more that the samples were heated starting directly from T_c when melting curves of isothermally crystallized samples were recorded, i.e. βα-recrystallization did not occur.

The temperature-dependence of melting characteristics of isothermally crystallized β-nucleated PRC was evaluated by the extrapolation method of Hoffman and Weeks [12]. Based on the dependence of peak temperatures of single melting curves on T_c, the thermodynamic equilibrium melting point was $T_m^o(\beta)$ = 461 K. However, T_m values involved in the extrapolation lay in a very narrow temperature range thus, the realiability of this result is not high enough. This T_m^o value is not far from $T_m^o(\beta)=457\pm4$ K as measured earlier for β-IPP [11]. The proximity of $T_m^o(\beta)$ values of β-IPP and β-PRC makes it probable that the irregular chain segments that contain comonomer units are completely excluded from the β-lattice during the crystallization. A similar conclusion was drawn by Monasse and Haudin [3] for the α-modification of PRC. The temperature-dependence of the melting point of the accompanying low amount of β-phase formed in β-nucleated samples was not evaluated with the above technique because of its low-intensity diffuse peaks.

A reduced heating rate for melting is favourable to the ββ-recrystallization processes within the β-phase. The lower the T_c and V_h selected, the more expressed is the ββ-recrystallization, i.e. β-peak duplication takes place (Fig. 8).

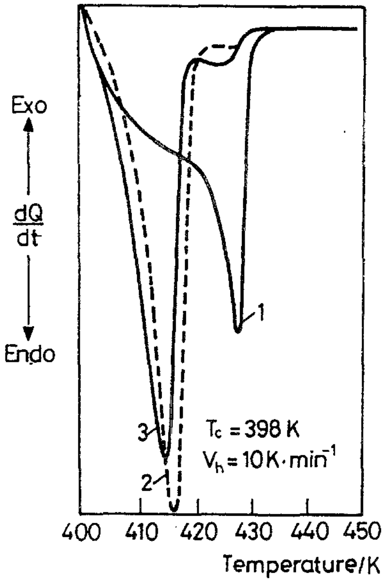

Fig. 9 The effect of concentration of the β-nucleating agent on the course of melting curves (1–0; 2–0.1 and 3–0.01% *w/w* of nucleating agent)

In our opinion, during the ββ-recrystallization, the structure is brought to perfection and the thickness of lamellae increases without any change in the geometry and orderedness of the elementary cells. It is rendered probable by the effects of the crystallization and melting conditions on the relative intensity of β-peaks. In contrast, Zhang and Shy [8] claimed the formation of a more ordered β_2-phase due to the recrystallization.

The effect of the amount of β-nucleating agent is illustrated by Fig. 9 where the melting curve of isothermally crystallized basic polymer is also included. It can be established from Fig. 9 that at lower contents of the nucleating agent a higher amount of α-modification is formed and the tendency to recrystallization is slightly increased.

It should be mentioned that the crystallization isotherms of PRC containing β-nucleating agent cannot be linearized by processing through the Avrami's equation. It may be explained by the formation of a mixed polymorphic structure on one hand and, similarly to the observations with low-density polyethylene [13], by a fractional crystallization according to the chain regularity on the other hand.

Spherulitic crystallization and structure of PRC

Due to their high supercoolability, random copolymers crystallize into spherulitic structure, readily resolved on optical level, even at low temperatures. During the crystallization radial α-spherulites are formed with positive birefringence (Fig. 10). The optical character of the α-spherulites of a given PRC is not changed during the heating, they preserve the positive character when molten. Therefore, their behaviour is different from that of the positive-type homopolymers and block copolymers produced by low-temperature crystallization as the latter ones transform gradually first into mixed then into negative birefringent spherulites during heating [2]. The β-modification crystallizes into radial spherulites with negative birefringence. β-Spherulites melt separated, without βα-recrystallization, when heated from the temperature of crystallization on (Fig. 10.b) while they recrystallize into α-modification when recooled previously below T_R.

During the isothermal crystallization of β-nucleated PRC a β to α modification change (βα-transition) takes place on the growing front of β-spherulites resulting in characteristic βα-twin-spherulites as shown in Fig. 10 for the crystallization of a sample containing a trace amount of β-nucleating agent. On the surface of the central β-spherulite α-nuclei are formed during the growth from which α-spherulite segments developed. They are very clearly discernible after the separated melting of the β-phase (Fig. 10.b). A similar βα-transition takes place during the step-wise isothermal crystallization of propylene homopolymers if the temperature of the second step is raised above $T(\beta\alpha)=413$ K [2, 14, 15]. It can also be established on the record shown that the effect of the β-nucleating agents inducing the formation of β-nuclei on the course of crystal-

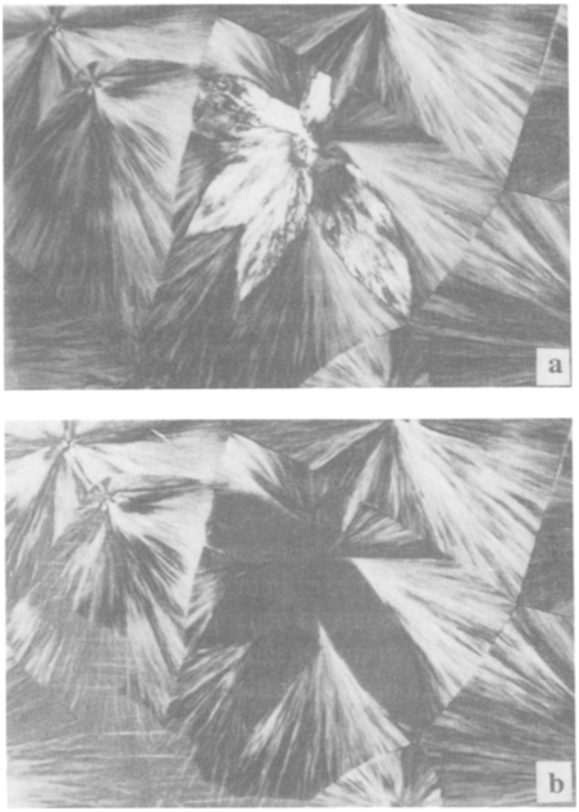

Fig. 10 A βα-twin-spherulite (a) formed due to βα-transition on the surface of the growing β-spherulite during an isothermal crystallization at 394 K and (b) the residual structure after the separated melting of the β-phase

lization ceased in a certain stage of growth. In other words, the phenomenon of an inverse epitaxy, i.e. an "antiepitaxy" exists in this case.

The kinetic precondition of the βα-transition on the growing crystal fronts is that the growth rate of the new phase (G_α) should be higher than that of the basic spherulite (G_β). Otherwise nuclei of the new phase would be overgrown by the original crystal front (the nuclei are "buried"). The fact of the βα-transition leads to the unexpected (different from the observations with propylene homopolymers) conclusion that at the above temperature of crystallization the growth rate of the α-phase (G_α) is higher than that of the β-phase (G_β). For this reason a comprehensive study on the kinetics of growth was conducted. Its results are shown in Fig. 11. In these experiments trace amount of β-nucleating agent was used in order to provide low nucleus density ensuring that β-spherulites grow high enough for obtaining more reliable data of growth. It is worth noting on the basis of the studies on kinetics of growth that the frequency of βα-transition on the surface of growing spherulites increases with raising T_c.

Since the segments of α-spherulites are covering the growing β-spherulite fronts, the growth rate cannot be determined reliably above T_c=402 K. It can be established from the results shown in Fig. 11 that in the temperature range studied $G_\alpha > G_\beta$. Consequently, the critical crossover temperature of β-IPP ($T(\beta\alpha)$=413 K [1, 2, 14, 15]) cannot be found for PRC below which $G_\alpha < G_\beta$. (It should be noted that Zhang and Shy [8] overlooked our earlier works on the relative growth rates of α- and β-modifications [14, 15, 16] in which the existence of the crossover temperature, $T(\beta\alpha)$, had been demonstrated.) Since the kinetic data of growth could be determined at an appropriate accuracy only above 388 K, it might not be excluded that PRC also had a $T(\beta\alpha)$ temperature well below 388 K. In view of our experimental results, the assumption of Zhang and Shy [8] that the formation of the β-phase is essentially provided by a kinetical factor, namely, the higher growth rate, seems to be erroneous. Based on the growth rates this kinetic condition is not valid for PRC still β-PRC can be prepared in nearly pure form. Consequently, the formation of the β-modification can be deduced, independently of the kinetic factors, to thermodynamical reasons, namely, to the favourable energetic conditions on the surface of β-nucleating agents for the formation of nuclei of the β-phase. This leads to the highly enhanced density of β-nuclei.

As a consequence of the βα-transition on the surface of growing spherulites, α-modification is also formed as an accompanying phase even in the presence

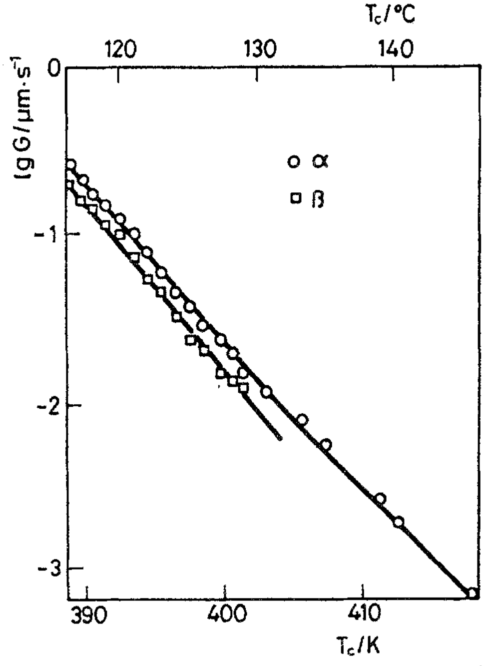

Fig. 11 Temperature-dependence of the linear growth rate of α- and β-spherulites in the random copolymer

of selective β-nucleating agents. For this reason, β-PRC cannot be prepared in pure form. The systematical appearance of α-peaks on the melting curves of non-recooled samples may also be deduced to the βα transition during the growth. Since βα-transition takes place in a definite stage of the growth of spherulites, the proportion of α-modification decreases as the average size of spherulites is smaller (i.e. at higher density of nuclei). This may explain the reduced proportion of α-phase when T_c is lower (Fig. 7) or the concentration of the β-nucleating agent is higher (Fig. 9) resulting in the enhanced average density of β-nuclei.

It has been proved by the spontaneous βα-transition during the isothermal crystallization of β-nucleated PRC and by the reduction in the growth rate of β-phase below that of the α-modification, in contrast to homopolymers, that a disturbance of the regularity of polymer chain decreases considerably the relative tendency to β-crystallization.

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