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MELTING MEMORY EFFECT OF THE β-MODIFICATION OF POLYPROPYLENE

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The pure β-modification of polypropylene has been prepared. It has been found that the nature of the melting of the β-modification strongly depends on the thermal history of the sample (melting memory effect). The melting of samples cooled to room temperature after crystallization is a complex process consisting of three partially overlapping processes (β-melting →recrystallization in the α-modification ($\beta\alpha$-recrystallization) →α-melting). If heating starts at the temperature of crystallization, the β-modification melts separately, without $\beta\alpha$-recrystallization. Under melting conditions free from the interference caused by $\beta\alpha$-recrystallization, the β-modification exhibits the melting characteristics of thermodynamically stable modifications. The thermodynamic equilibrium melting point of the β-modification has been determined to be $T_m^0(\beta) = 456$ K.

Several attempts have been made to prepare the thermodynamically unstable β-modification of polypropylene (PP) in pure form. Formation of the pure β-modification has not previously been described, although several methods are known for the preparation of samples rich in the β-modification (1–10]. Samples containing a high fraction of the β-modification were prepared by Turner–Jones et al. [1] by rapid cooling of a special PP type, and by Fujiwara [2] and Lovinger et al. [3] by crystallization using the temperature gradient method. Selective nucleating agents have also been used successfully to prepare nearly pure β-modification [4–10].

It has been found by structural [1, 9, 10] and calorimetric [2, 6, 8, 9] studies on samples with a high percentage of the β-modification that the melting of this modification is a complex process: melting is accompanied by partially overlapping crystallization processes, during which the $\beta \rightarrow \alpha$ modification change also takes place.

In our laboratory the pure β-modification has been prepared by the isothermal crystallization (crystallization temperature $T_c = 380$–403 K) of pigmented and

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stabilized special high molecular mass PP (MFI 190/5 = 0.6 g/10 min). By appropriate selection of the conditions of melting, we succeeded in eliminating the crystallization processes involving a modification change, which overlap the melting of the β-modification. This allowed the melting characteristics of the β-modification to be established and the thermal characteristics to be determined more accurately than before, using methods which are usually applied for the study of thermodynamically stable modifications. The recognition of the melting memory effect was of basic importance in the present work. The essence of the phenomenon is that the nature of the melting of the β-modification strongly depends on the thermal history of the sample. This is illustrated by the results of calorimetric measurements shown in Fig. 1. The melting of samples cooled to room temperature

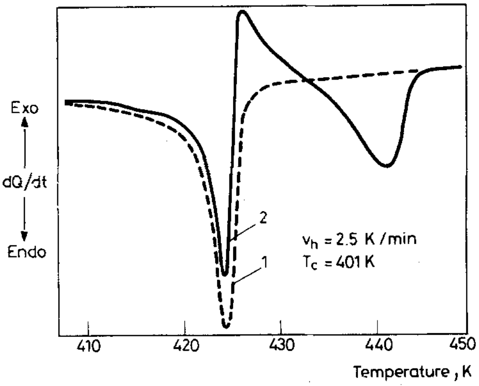

Fig. 1 Melting curve of a sample crystallized under isothermal conditions ($T_c = 401$ K; $V_h = 2.5$ K/min). 1. For melting starting at the crystallization temperature. 2. For melting of a sample previously cooled to room temperature from the crystallization temperature

from the temperature of isothermal crystallization is a complex process consisting of three partial processes: melting of the β-modification → recrystallization into the α-modification ($\beta\alpha$-recrystallization) → melting of the α-modification (Fig. 1, curve 2). When melting is started at the temperature of crystallization, however, the β-modification melts separately, without $\beta\alpha$-recrystallization. A single melting peak appears at around 430 K in the melting curve (Fig. 1, curve 1), indicating that the sample consists of the pure β-modification. The memory effect also occurs in the melting of samples containing both the α- and the β-modification prepared at T_c = 404–414 K (Fig. 2). A comparison of the melting curves obtained for samples containing a small amount of the α-modification reveals that the peak at lower temperature (α_1) is due to the melting of the α-modification originally present

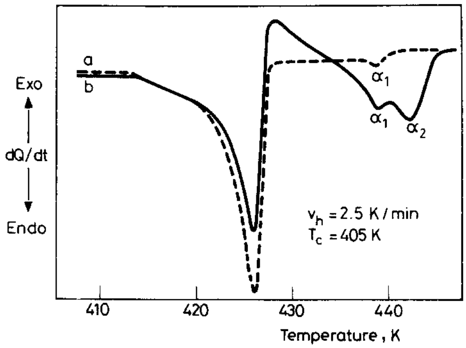

Fig. 2 Melting curve of a sample containing spherulites of both the α- and β-modifications crystallized under isothermal conditions (T_c = 405 K). a) melting starting at T_c; b) melting starting at room temperature

(formed at T_c), whereas the peak at higher temperature (α_2) is due to the melting of the α-modification formed during the βα-recrystallization. Hence, cooling has a basic role in the appearance of the tendency to βα-recrystallization; it is not influenced by the presence of the α-phase.

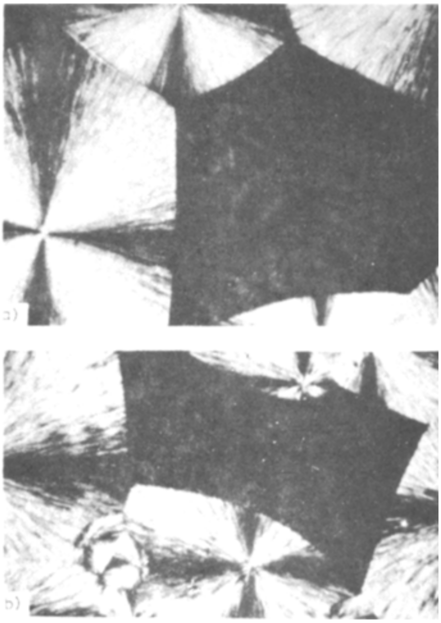

Fig. 3 Optical micrograph of a ring α-spherulite formed by βα-recrystallization *(a)* in a cooled sample and a separately melted β-spherulite heated from T_c *(b)*. Temperature: *a* 440 K; *b* 444 K

The optical micrographs in Fig. 3*a* show that an α-spherulite with ring structure is formed in place of the β-spherulite in the sample first cooled to room temperature and then heated. When heating starts at T_c, no βα-recrystallization can be observed in the optical micrographs after the melting of the β-spherulite (Fig. 3*b*).

It has been found that a critical cooling temperature (T_r^*) has to be reached for the βα-recrystallization tendency to appear. According to our measurements, $T_r^* \approx 378$ K*. In Fig. 4, the melting curves of samples crystallized at different temperatures are shown. If $T_c \leqslant 403$ K, there is only one peak in the curve, the position of the peak being shifted to lower temperatures as T_c decreases. On increase of $T_c (T_c > 403$ K), the peak indicating the melting of the α-modification appears and its size increases. The equilibrium melting point of the β-modification ($T_m^0(\beta)$) has been determined by the Hoffman–Weeks method [11], based on the dependence of the melting point (T_m) on the temperature of crystallization. According to Fig. 5, $T_m^0(\beta) = 456$ K.

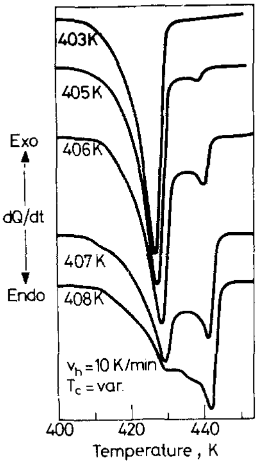

Fig. 4 Melting curves of samples crystallized under isothermal conditions for melting starting at $T_c / V_h = 10$ K/min

The βα-recrystallization tendency of the pure β-modification prepared by isothermal crystallization is very small when melting starts from T_c. For example, the βα-recrystallization was not observed even at very low rates of heating ($V_h = 1.25$ K/min) (Fig. 6). At low heating rates, however, a recrystallization can be observed within the β-modification (ββ-recrystallization), as indicated by the

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* This seems to be the lower temperature limit of formation of the β-modification.

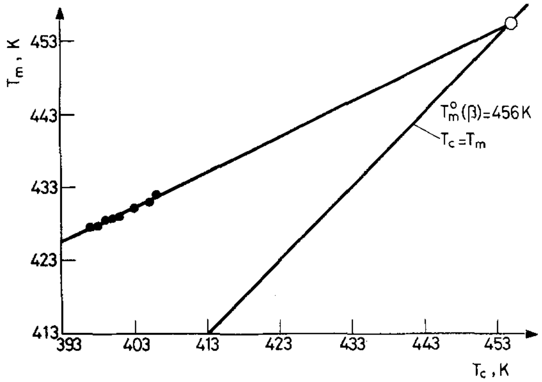

Fig. 5 Hoffman-Weeks [11] diagram of the *β*-modification of PP

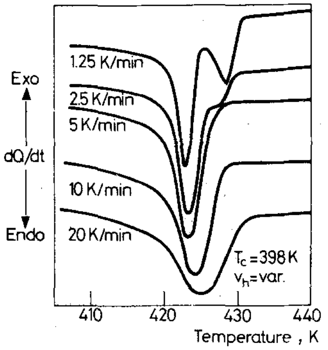

Fig. 6 Effect of heating rate (V_h) on the recrystallization of the *β*-modification crystallized under isothermal conditions

doubling of the peak corresponding to the melting of the *β*-modification. A reduction in the heating rate is favourable for the recrystallization, and consequently the higher temperature peak increases at the expense of the lower temperature one. It has been found that the tendency to *ββ*-recrystallization increases with decreasing T_c, as the structure of samples crystallized at lower temperatures (farther from the equilibrium conditions) is less regular and less stable. It can be seen from the data in Fig. 7 that the doubling of the melting peak of the *β*-modification appears and gradually becomes more pronounced as T_c decreases.

As concerns the experimental results presented, the difference between the *βα*-recrystallization and the *ββ*-recrystallization of the *β*-modification must be emphasized. Recrystallization into the α-modification is a two-phase (liquid-solid) transformation, as shown by optical and calorimetric studies. *ββ*-recrystallization

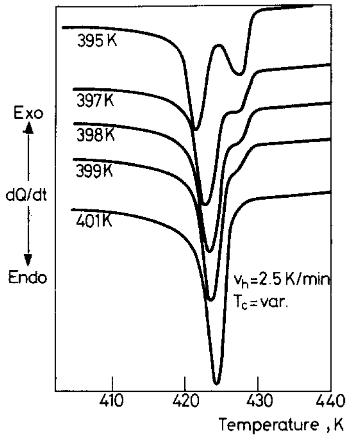

Fig. 7 Effect of crystallization temperature (T_c) on the recrystallization of the β-modification (V_h = 2.5 K/min)

can be considered a one-phase solid-solid transformation. The $\beta\beta$-recrystallization proceeds at a high temperature (above the critical temperature [$T(\beta\alpha)$] of the $\beta \rightarrow \alpha$ transformation [12]), and thus the appearance of a molten phase should lead to a $\beta \rightarrow \alpha$ modification change. In Figs 6 and 7, there is no peak corresponding to the melting of the α-phase which would indicate the $\beta\alpha$ transformation. This proves that the $\beta\beta$-recrystallization is a one-phase process.

The melting characteristics of the β-modification (C_β) crystallized under isothermal conditions are displayed in Fig. 8, together with melting memory effect. The marked difference in the melting characteristics and the appearance of the

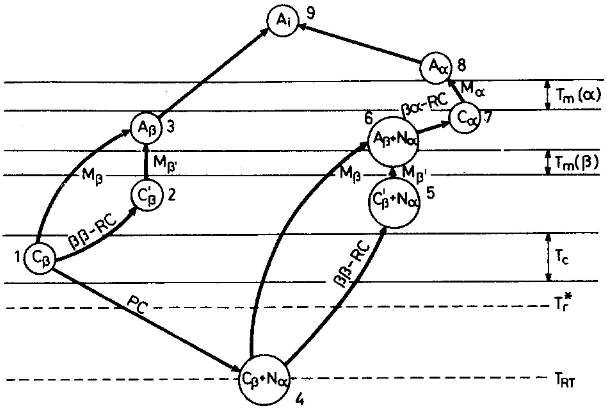

Fig. 8 Melting behaviour of the β-modification and the scheme of the melting memory effect (see text)

tendency to $\beta\alpha$-recrystallization ($\beta\alpha$-RC) on cooling to room temperature (RT) are presumably due to the fact that, as a result of the post-crystallization (PC) taking place during cooling ($T_r < T_r^*$), crystallization nuclei consisting of α-modification (N_α) are formed within the β-spherulites which induce the $\beta\alpha$-recrystallization ($\beta\alpha$-RC) of the molten β-spherulites in the α-modification. In Fig. 8, the $\beta\beta$-recrystallization process ($\beta\beta$-RC) leading to a more perfect β-structure (C'_β), and the melting of the α- and β-modifications (M_α, M_β, M'_β) in the $T_m(\alpha)$ and $T_m(\beta)$ melting ranges are also indicated. It seems advisable to distinguish between the isotropic melt (A_i) and the amorphous structure (A_α, A_β) formed after the melting of the α and β-spherulites, since in the latter a partial order reminiscent of the original structure is retained, in accordance with the observation illustrated by Fig. 3 (recrystallization of the molten β-ring spherulite into the α-ring spherulite).

Whether the β-modification melts directly [1–3 or 4–6] or through $\beta\beta$-recrystallization [1–2–3 or 4–5–6] depends on the crystallization temperature and rate of heating. On decrease of the crystallization temperature and rate of heating, the $\beta\beta$-recrystallization becomes predominant. The $\beta\alpha$-recrystallization [6–7] occurs only with cooled ($T_r < T_r^*$) samples.

In view of our experimental results, the literature statements concerning the $\beta \rightarrow \alpha$ modification change [1, 10, 13] and the tendency of the β-modification to $\beta\alpha$-recrystallization [2, 3, 7–9] can be considered as of only limited validity. They do not generally hold for the β-modification, but only for a form of it having a special thermal history (cooled below T_r^*).

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Zusammenfassung — Die β-Modifikation von Polypropylen wurde rein dargestellt. Es wurde festgestellt, daß die Natur des Schmelzens der β-Modifikation stark von der thermischen Vorgeschichte der Probe (Schmelzerinnerungseffekt) abhängt. Das Schmelzen von nach der Kristallisation auf Zimmertemperatur abgekühlter Proben ist ein komplexer, aus drei sich teilweise überlappenden Prozessen (β-Schmelzen →Rekristallisation in der α-Modifikation, die sog. $\beta\alpha$-Rekristallisation →α-Schmelzen) bestehender Vorgang. Wenn das Aufheizen bei der Kristallisationstemperatur beginnt, so schmilzt die β-Modifikation, ohne daß $\beta\alpha$-Rekristallisation eintritt. Unter Schmelzbedingungen frei von störenden Einflüssen der $\beta\alpha$-Rekristallisation zeigt die β-Modifikation die Schmelzcharakteristiken von thermodynamisch stabilen Modifikationen. Der thermodynamische Gleichgewichtsschmelzpunkt der β-Modifikation $T_m^0(\beta)$ liegt bei 456 K.

Резюме — Получена чистая β-модификация полипропилена. Было установлено, что природа плавления этой модификации сильно зависит от термической предистории образца (эффект памяти плавления). Плавление образцов, охлажденных после их кристаллизации до комнатной температуры, является сложным процессом, состоящим из трех частично перекрывающихся процессов: плавление β-образца →перекристаллизация его в α-модификацию, $\beta\alpha$-рекристаллизация →плавление α-модификации. Если нагревание начинается с температуры кристаллизации, то β-модификация плавится отдельно без $\beta\alpha$-рекристаллизации. В условиях плавления, свободных от мешающего влияния $\beta\alpha$-рекристаллизации, β-модификация показывает характеристики плавления термодинамически стабильных модификаций. Термодинамическая равновесная точка плавления β-модификации была равной $T_м^0(\beta)$ = 456 K.