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DOUBLE CRYSTALLIZATION OF BIAXIALLY ORIENTED POLYPROPYLENE

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The melting conditions of biaxially oriented polypropylene (BOPP) have a very strong effect on the courses of both non-isothermal and isothermal crystallization from the melt. It has been shown that the crystallization proceeds by two mechanisms. Depending on the melting conditions, both crystallization mechanisms can proceed individually or simultaneously (double crystallization). The high rate mechanism, occurring in non-isothermal crystallization at low undercooling and observed in isothermal crystallization, can be attributed to the ordered structure of the melt preserved after melting, presumably a mesomorphic state. The second component corresponds to crystallization from the isotropic melt.

Anomalous crystallization of BOPP samples can be eliminated by energetic heat treatment, by the destruction of ordered structures. As a result of this treatment, the characteristics of crystallization and its quantitative parameters will become similar to those of unoriented polypropylene.

The characteristics of the crystallization of isotactic polypropylene (PP) have been studied by several research groups [1–15]. It has been established on the basis of the dilatometric [1–4, 6–8], optical polarization [5, 10] and calorimetric [9, 10] investigations of isothermal crystallization that the crystallization isotherms can be described by the Avrami equation. Moreover, it has been observed that the rate of crystallization and its quantitative characteristics depend strongly on the thermal history of the samples [3, 4, 7, 15].

Our present work reports on the effect of the thermal history (melting conditions) of biaxially oriented polypropylene samples (BOPP) on the courses of isothermal and non-isothermal crystallization from the melt. A new type of crystallization memory effect, the phenomenon of "double crystallization", has been detected in these investigations.

Experimental

Samples cut out from biaxially oriented polypropylene flasks manufactured by two-step technology (Hercules Inc.) have been used for the investigations. The basic substances is PP of Pro-Fax 6723 type. According to X-ray analysis made with a Müller Micro 111 instrument, the α-modification of PP is present in the samples, and the orientation along the two axes is homogeneous. On the basis of our thermorelaxation investigations, the elongation during orientation is 300–400%.

A Perkin-Elmer Model DSC-2 instrument was used for thermoanalytical investigations. For calibration indium was used. In the recording of the non-isothermal crystallization and fusion curves, heating (H. R.) and cooling rates (C. R.) of 10°/min were applied. When the effect of the thermal history was studied, samples were heated at a rate of 10°/min to the final temperature of heating (T_F), the melting time (t_F) generally being 5 min. From T_F, samples were cooled at a nominal rate of 320°/min to the temperature of isothermal crystallization (T_0).

A microscope Model Polmi A, equipped with a thermostable stage, was used for the optical polarization investigation. The thickness of the slices was 5–10 μm.

Results and discussion

Melting curves of the original BOPP samples (Fig. 1, curve 1) is characteristic of oriented PP [15]. During non-isothermal crystallization from the melt at a constant cooling rate in most cases double-peak crystallization curves indicative of double crystallization were obtained (Fig. 1, curve 2). The character of the DSC curve of non-isothermal crystallization is considerably influenced by the preceding melting conditions of the BOPP samples. It was found that on increase of the number of melting-crystallization cycles (T_F = const., t_F = const.) the high temperature peak of the crystallization exotherm gradually disappears, passing into the lower-temperature peak (T_2) (Fig. 2). T_F also has a significant effect. At temperatures T_F close to the melting point (T_m) single-peak crystallization curves are obtained, and the position of the peak corresponds to T_1. On the increase of T_F, the crystallization exotherm is split because of the appear-

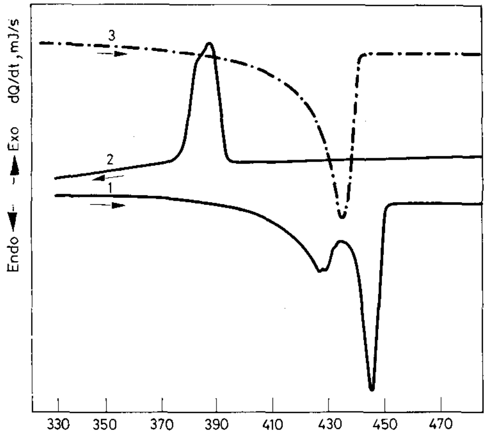

Fig. 1. Fusion and crystallization curves of biaxially oriented polypropylene (T_F = 493 K, heating rate H. R. = C. R. = 10°/min). (1) first melting, (2) crystallization; (3) second melting

Table 1

The effect of (T_F) on the characteristics of non-isothermal crystallization curves

T_F, K	Beginning of crystallization $T_{c,0}$ K	Number of peaks	Peak temperatures	
			T_1,	T_2,
			K	
463	401	1	393.5	
473	399	2	392.0	388.5
493	397	2	391.0	386.0
513	393	1		383.0

ance of the peak T_2. With the increase of T_F, the intensity of peak T_2 gradually increase at the expense of T_1. If T_F > 503 K, a single-peak crystallization curve is obtained again, but the peak is at the temperature T_2 (Table 1).

It can be established from these results that the double crystallization peak arises from two independent crystallization processes. The process starting at higher temperature (i.e. at lower undercooling), occurring alone only under very mild melting conditions, can be related to the partial order maintained in the polymer melt even above T_m. The crystallization process at lower temperature, which also occurs alone under vigorous melting conditions, can be assigned to crystallization from the normal isotropic melt. From the experimental results it can be seen that, simultaneously with the gradual disintegration of the ordered structure of the melt, this latter process becomes more and more dominant.

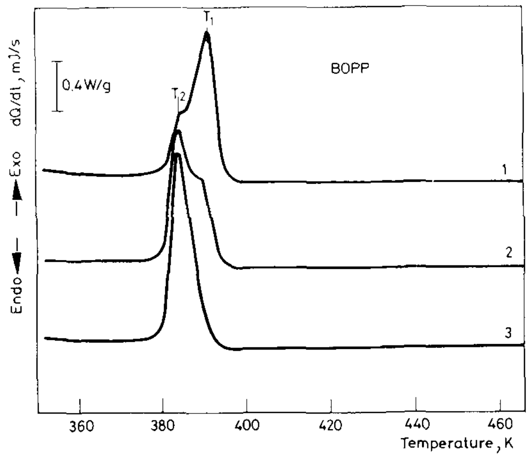

Fig. 2. Crystallization curves of three successive melting-crystallization cycles ($T_F = 453$ K, $t_F = 5$ min, H. R. = C. R. = 10°/min)

An important observation is that the structure formed by double crystallization gives a normal, single-peak fusion curve (Fig. 1, curve 3). This indicates that one kind of crystal modification is formed on double crystallization.

The phenomenon of double crystallization could also be observed during the isothermal crystallization of molten BOPP samples. This is illustrated by the curves shown in Fig. 3, which were recorded in numerous consecutive crystallization-melting cycles at T_F values close to T_m and at short melting times. In the first melting cycle rapid crystallization can be observed, and single-peak crystallization curves are obtained. With increasing number of cycles, a peak indicating crystallization at a lower rate also appears, the intensity of which gradually increases at the expense of the peak corresponding to rapid crystallization. After a large number of cycles the peak corresponding to rapid crystallization virtually disappears. Simultaneously with the above phenomenon, the overall crystallization rate gradually diminishes.

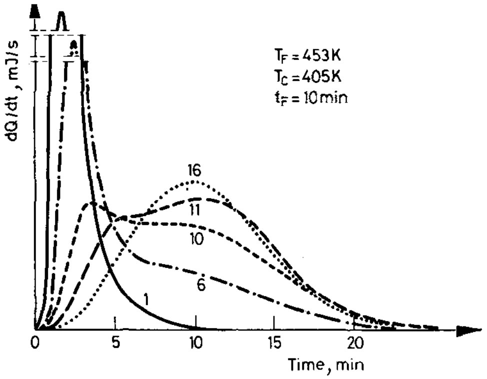

Fig. 3. Variation of crystallization isotherms with number of melting cycles. Numbers of cycles are indicated (T_F = 453 K, t_F = 10 min, T_c = 405 K)

The fusion curves recorded after the isothermal crystallizations shown in Fig. 3 can be seen in Fig. 4. They are similar to the fusion curves of PP crystallized isothermally in this temperature range [15]. The quantitative and qualitative differences observed during the crystallization process were not reflected in the fusion curves. The area below the melting curve is virtually independent on the number of melting cycles. With the increase of the cycle number, only the heights of the peaks increase to a small extent. In conformity with the findings during non-isothermal crystallization, these results indicate that an identical crystal modification is formed in rapid and slow crystallizations.

Isotherms recorded in the isothermal crystallization of different melting cycles were evaluated with the Avrami equation:

$$\ln \Theta = -K \cdot t^n \qquad (1)$$

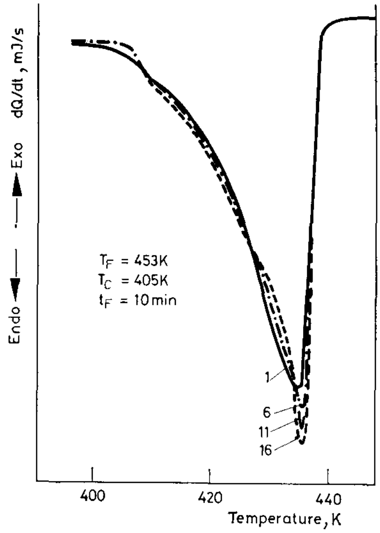

Fig. 4. Fusion curves of the samples isothermally crystallized in successive melting-crystallization cycles

where K is the rate constant of crystallization, n the Avrami exponent, and Θ the non-crystallized fraction of the substance. The latter was determined by calorimetric measurements, determining of the total heat of crystallization (ΔH_∞) and the heat of crystallization up to time $t(\Delta H_t)$, on the basis of the equation

$$\Theta = \frac{\Delta H_\infty - H_t}{\Delta H_\infty}. \tag{2}$$

It can be seen from the evaluation that crystallization isotherms can be linearized only after the disappearance of the rapid crystallization component (Fig. 5). With the increase of T_F, the number of cycles needed for the linearization of the curves gradually decreases. At high melting temperature ($T_F > 503$ K) the component corresponding to rapid crystallization disappears already after the first melting, and isotherms linearizable by the Avrami equation are obtained.

The high rate component of isothermal double crystallization, as well as the peak at higher temperature in non-isothermal crystallization, can be attributed to the residual order in the melt, and the low rate component to the crystallization from the isotropic melt.

Ordered structures preserved in the BOPP samples at T_F close to T_m can most likely be identified with the mesomorphic state probably formed by the mutual alignment of the helical chains, as presumed by several researchers [16–18]. However, in our opinion, the helical chain conformation is metastable above T_m and may be converted into a coiled chain conformation.

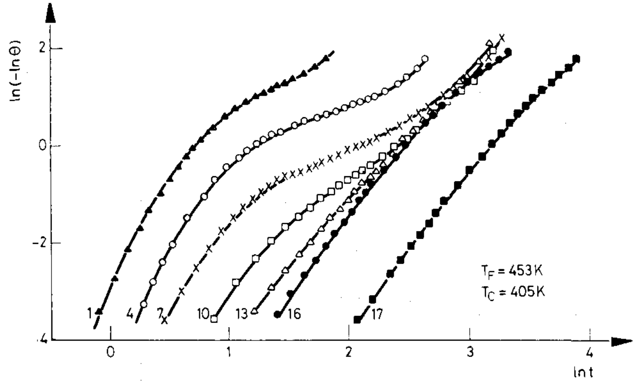

Fig. 5. Avrami plots for the crystallization of samples in successive melting-crystallization cycles. T_c=405 K. In runs 1—16 T_F=453 K, t_F=10 min; in run 17 T_F=493 K, t_F=10 min

We could not unambiguously detect the presence of the mesomorphic phase. At a T_F value close to T_m, the structure of the BOPP sample (Fig. 6a) reveals a characteristic optical pattern in polarized light (Fig. 6b), reminiscent of the mesomorphic state. A pattern indicative of some molecular order develops along the phase interfaces, surface disclinations and unevennesses. In the cooled samples, spherulitic crystallization is to be observed under isothermal conditions, the spherulites being located in ranges next to the original structure (Fig. 6c). The simultaneous formation of many spherulites can occasionally be observed at the phase interface, growing perpendicularly to the interface in practically one direction (Fig. 6c). On repeated melting at higher temperature, the characteristic picture of Fig. 6a disappears, and on subsequent cooling spherulitic crystallization can be observed at a considerably lower nucleation density.

In contrast to the investigations of Smit [17], thermal transitions indicative of the presence of the mesomorphic state could not be unambiguously detected by calorimetry in the range between T_m and 510 K.

It can be established on the basis of our observations that the melting conditions of oriented polymers, in contrast to unoriented PP [3, 4, 7, 15], influence both the quantitative characteristics and the qualitative picture (double crystallization) of the crystallization process. It should be mentioned in this connection that, similarly to the effect of orientation, certain nucleating additives may also induce non-isothermal double crystallization [11, 19].

The strong "crystallization memory effect" observed must also be taken into consideration in systematic investigations of the crystallization kinetics.

"Memory" introduced by mechanical history can be erased according to our investigations by conditioning the sample at higher T_F. This is illustrated by the results of the isothermal crystallization of BOPP samples melted at high temperature (Fig. 7). Crystallization isotherms have in this case a normal course and can be linearized by the Avrami equation. K and n values are listed in Table 2. The re-

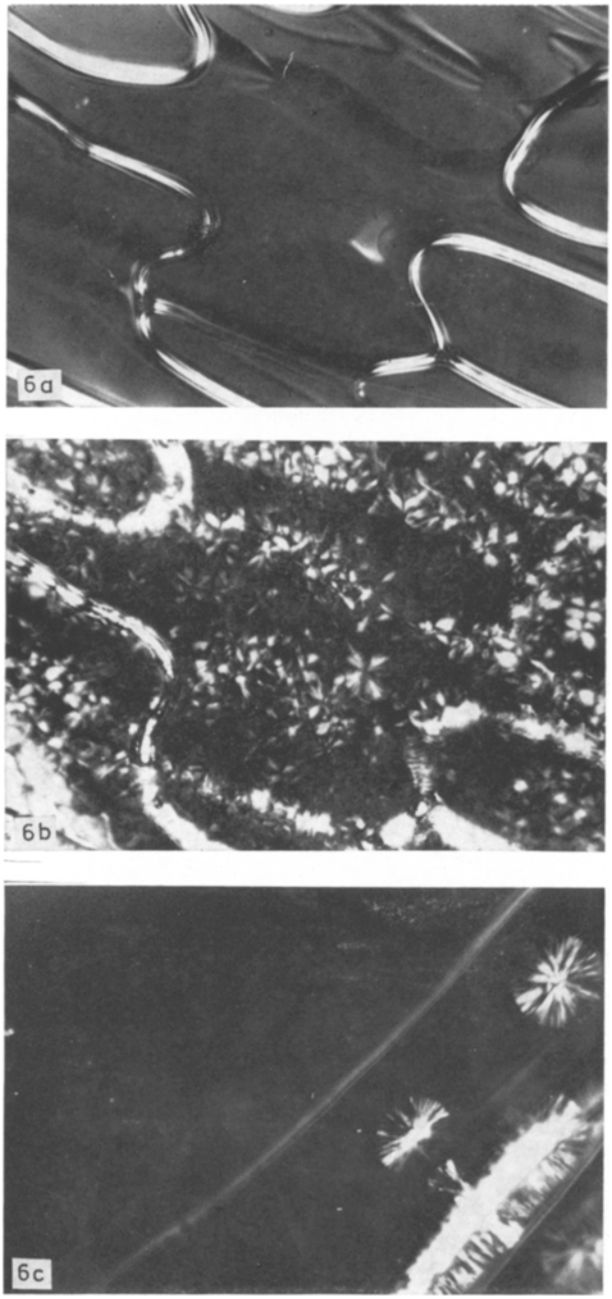

Fig. 6. Microphotographs between crossed nicols of BOPP samples. Magnification = 360×. (a) melted at 453 K; (b) crystallized at 403 K; (c) growth of spherulites at the phase interface

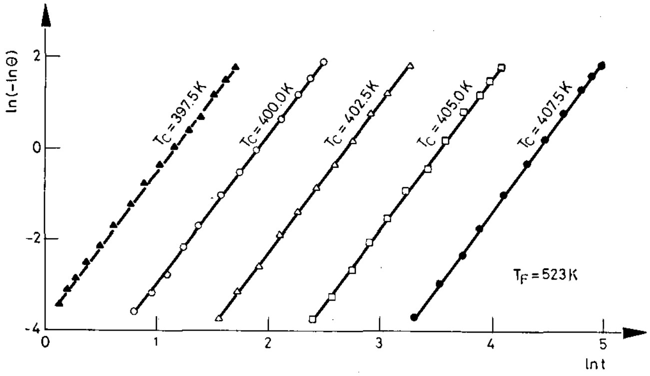

Fig. 7. Avrami plots of the crystallization isotherms after erasure of "memory". $T_F = 523$ K T_c are indicated

Table 2

Kinetic characteristics determined on the basis of isothermal crystallization performed after erasure of "memory" ($T_F = 523$ K, $t_F = 5$ min)

T_c	n	K
397.5	3.26	2.26×10^{-2}
400.0	3.30	1.90×10^{-4}
402.5	3.30	1.44×10^{-4}
405.0	3.35	7.89×10^{-6}
407.5	3.40	3.34×10^{-7}

sults obtained agree well with literature data for unoriented polymers [2–4, 10] and with data obtained for unoriented samples in our laboratory [20]. The dependence of the crystallization rate on temperature can also be satisfactorily described by the model proposed by Godowsky and Slonimsky [21], and results obtained are close to those found for unoriented PP [20, 21].

Further work is being undertaken for the quantitative description of double crystallization and for clarification of its structural causes.

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Résumé — Les conditions de la fusion du polypropylène à orientation biaxiale (BOPP) ont un effet très important sur le déroulement de la cristallisation isotherme ou non, à partir du produit fondu. On montre que la cristallisation s'effectue suivant deux mécanismes. Suivant les conditions de fusion, les deux mécanismes peuvent intervenir seuls ou simultanément (cristallisation double). Le mécanisme à grande vitesse observé lors de la cristallisation isotherme, et lors de la cristallisation non isotherme avec une faible surfusion, peut être attribué à la structure ordonnée, préservée dans le produit fondu après la fusion, probablement sous un état mésomorphe. Le second mécanisme correspond à la cristallisation à partir d'un produit fondu isotrope.

La cristallisation anormale des échantillons de BOPP peut être éliminée par un traitement thermique énergique, par destruction des structures ordonnées. Comme résultat de ce traitement, les paramètres quantitatifs et les caractéristiques de la cristallisation deviennent similaires à ceux du polypropylène non orienté.

Zusammenfassung — Die Schmelzbedingungen haben bei biaxial orientierten Polypropylenen (BOPP) eine sehr starke Wirkung auf den Verlauf der sowohl nichtisothermen als auch der isothermen Kristallisation aus der Schmelze. Es wurde gezeigt, daß die Kristallisation nach zwei Mechanismen verläuft. In Abhängigkeit von den Schmelzbedingungen können beide Kristallisationsmechamismen einzeln oder simultan verlaufen (doppelte Kristallisation). Der Hochgeschwindigkeitsmechanismus, der bei der nichtisothermen Kristallisation bei geringer Unterkühlung auftritt und bei der isothermen Kristallisation beobachtet wird, kann der geordneten Struktur der Schmelze zugeschrieben werden, welche nach dem Schmelzen bis zu einem mesomorphen Zustand erhalten bleibt. Die zweite Komponente entspricht der Kristallisation aus isotroper Schmelze.

Die anomale Kristallisation der BOPP-Proben kann durch energische Hitzebehandlung unter Zerstörung der geordneten Strukturen eliminiert werden. Als Ergebnis dieser Behandlung werden die Charakteristika der Kristallisation und ihre quantitativen Parameter denen von nicht-orientierten Polypropylenen ähnlich.

Резюме — Условия плавления двихосно-ориентированного полипропилена оказывают сильное влияние на течение как неизотермической, так и изотермической кристаллизации его из расплава. Показано, что кристаллизация протекает по двум механизмам. В зависимости от условий плавления, оба механизма кристаллизации могут протекать как раздельно, так и одновременно (двойная кристаллизация). Высоко скоростной механизм кристаллизации, наблюдаемый при неизотермической кристаллизации при низком охлаждении и при изотермической кристаллизации, может быть приписан упорядоченной структуре расплава, сохраняемой после плавления, вероятно, до мезоморфного состояния. Второй механизм соответствует кристаллизации из изотропной среды. Аномальная кристаллизация может быть устранена тепловой обработкой или деструкцией упорядоченных структур. Вследствие такой обработки, характеристики кристаллизации и ее количественные параметры становятся подобными тем, что для неориентированного полипропилена.