

## **$\beta$ -MODIFICATION OF POLYPROPYLENE AND ITS TWO-COMPONENT SYSTEMS**

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$\beta$ -modification and multi-component systems of  $\beta$ -polypropylene were prepared both under laboratory and processing conditions. Characteristic features of crystallization, melting, and annealing of  $\beta$ -PP are summarized. The very distinct memory effect in the melting and annealing of  $\beta$ -PP is also presented. The existence of a lower and an upper limit temperature of  $\beta$ -PP formation is demonstrated. The structural stability and the orientation-induced  $\beta\alpha$ -recrystallization of  $\beta$ -PP are analyzed. Preparation and properties of polymer blends and filled composites from  $\beta$ -PP are introduced, too.

Polypropylene is a polymorphic resin with several known crystal modifications ( $\alpha$ ,  $\beta$ ,  $\gamma$ ) [1–5]. Some experimental observations have suggested that the  $\alpha$ -modification is the thermodynamically stable one. For this reason, it has been supposed that the polymorphic polypropylene reveals monotropism in practice. Actually, commercial polypropylene grades have crystallized mostly in  $\alpha$ -modification under the usual industrial thermal conditions with only sporadic occurrence of  $\beta$ -modification formed at low crystallization temperature [5]. In the industrial practice, therefore,  $\beta$ - and  $\gamma$ -modifications have been considered as laboratory curiosities.

A systematic research work has been conducted at the Department of Plastics and Rubber, Technical University of Budapest leading to the first preparation of pure  $\beta$ -modification of polypropylene ( $\beta$ -PP) under laboratory and processing conditions, in the presence of specific  $\beta$ -nucleating agents, through an appropriate selection of the thermal conditions of crystallization. The principal physical and mechanical properties of the product have been determined as well.  $\beta$ -PP based polymer blends and filled composites were also developed [6–10].

*Susceptibility to  $\beta$ -crystallization of the polypropylene studied*

A specially pigmented and stabilized high-molecular-mass polypropylene was used that had a very pronounced susceptibility to  $\beta$ -crystallization. In comparison to the commercial grades of polypropylene and to our formulations containing widely known  $\beta$ -nucleating agents (such as quinacridone dyes or triphenodithiazine), the proportion of  $\beta$ -modification in the present polypropylene was extremely high or, when crystallized at a properly selected temperature, even 100 per cent. This was demonstrated inevitably by X-ray diffractometry and light microscopy. The latter technique revealed that a sample chilled rapidly below about 403 K crystallized in the form of radial  $\beta$ -spherulites having negative optical character. At higher temperatures, a mixed polymorphic structure or even pure  $\alpha$ -modification was formed. In the mixed phase, ring  $\beta$ -spherulites with negative optical character accompanied mixed radial  $\alpha$ -spherulites. These findings were confirmed by calorimetric investigations as discussed below. On this basis, the thermal preconditions of producing pure  $\beta$ -PP were revealed unequivocally.

*Melting memory effect of  $\beta$ -PP [6]*

The recognition of the phenomenon of melting memory was fundamental in the present study since it permitted a rapid and accurate determination of the polymorphic composition and its dependence on the thermal conditions of crystallization by means of a relatively simple calorimetric method.

An essential feature of the melting memory effect is the expressed dependence of the melting process of  $\beta$ -PP on its thermal history. It can be observed when the melting of  $\beta$ -PP is investigated that a sample formed in the temperature range  $T_c = 393$  to 412 K then cooled to room temperature, finally reheated recrystallizes into the  $\alpha$ -modification ( $\beta\alpha$ -recrystallization) through the partial melting of  $\beta$ -spherulites. The original ring  $\beta$ -spherulites with negative optical character are replaced by ring  $\alpha$ -spherulites with positive optical character that have higher melting temperature than  $\alpha$ -spherulites originally present in the sample. On the contrary, samples heated directly from the temperature of crystallization ( $T_c$ ) exhibit separated melting of  $\beta$ -spherulites without recrystallization into the  $\alpha$ -modification.

The melting memory effect can be indicated even more clearly by calorimetric measurements. Melting curves of pure  $\beta$ -PP crystallized isothermally then exposed to different thermal effects are shown in Fig. 1. When melting was started from  $T_c$ , only a single peak appeared along the melting curve referring to the melting of the  $\beta$ -modification. As the sample, crystallized under the same conditions, was cooled to room-temperature before melting, the DSC curve indicated three partially

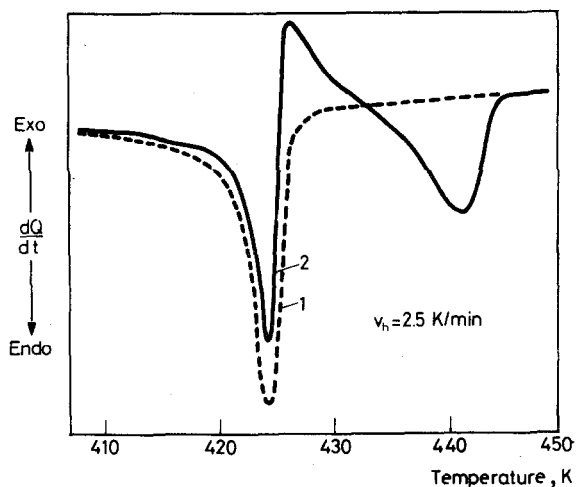
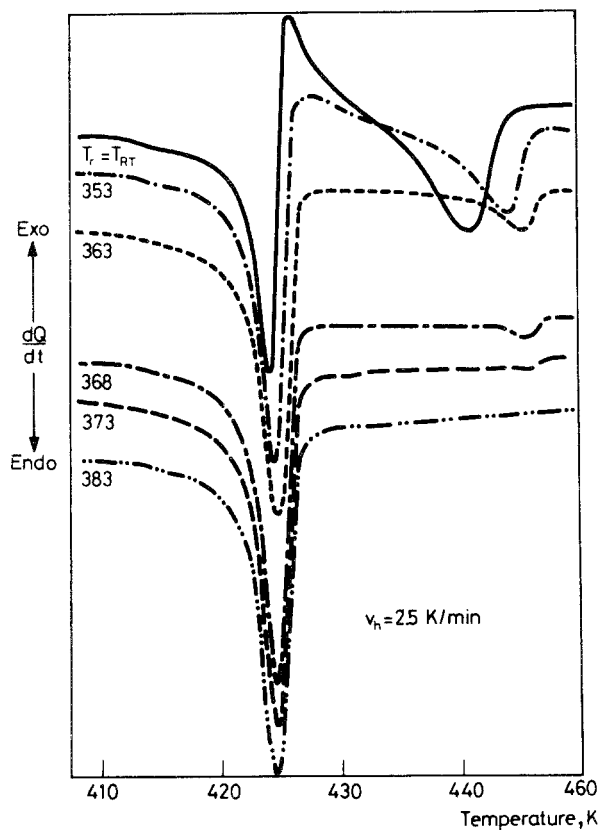


Fig. 1 Melting curves of PP crystallized isothermally ( $T_c = 401$  K). 1 – Started from the temperature of crystallization; 2 – Started from room temperature preceded by cooling after the crystallization

overlapping processes: a partial (endothermic) melting of the  $\beta$ -modification, a recrystallization into the  $\alpha$ -modification (exothermic), and melting of the  $\alpha$ -modification just formed (endothermic). By recooling, therefore, the  $\beta$ -modification became susceptible to  $\beta\alpha$ -recrystallization.

The next point of this study was to reveal the extent of cooling which is necessary for the emergence of the tendency to  $\beta\alpha$ -recrystallization. As shown in Fig. 2, the critical temperature below which the  $\beta\alpha$ -recrystallization tendency appears is between 373 and 383 K. This temperature was named critical temperature of recooling, designated by  $T_R^*$ . The onset of the tendency to  $\beta\alpha$ -recrystallization of samples recooled below  $T_R^*$  is supposed to be associated with a post-crystallization during recooling leading to the formation of a small amount of  $\alpha$ -modification inside the  $\beta$ -spherulites which acts as an  $\alpha$ -nucleating agent during the partial melting of the  $\beta$ -modification, inducing  $\beta\alpha$ -recrystallization. It was demonstrated that the presence of an  $\alpha$ -phase in mixed polymorphic samples (comprising both  $\alpha$ - and  $\beta$ -spherulites) did not influence the  $\beta\alpha$ -recrystallization tendency [6].

It can be stated in view of the melting memory effect that cooling the samples below  $T_R^*$  should be avoided before melting in order to eliminate the interference by a  $\beta\alpha$ -recrystallization when the preconditions to the formation of  $\beta$ -PP, the polymorphic composition, or melting and crystallization characteristics of  $\beta$ -PP are studied. Bearing this precaution in mind, the samples were melted starting just from  $T_c$  after the isothermal crystallization and, in non-isothermal crystallization (at constant cooling rate), the final temperature of cooling was not allowed to decrease below  $T_R^*$ .



**Fig. 2** The effect of temperature of recoiling ( $T_R$ ) after the isothermal crystallization ( $T_c = 401$  K) on the susceptibility of  $\beta$ -PP to  $\beta\alpha$ -recrystallization

*Melting and crystallization features and thermal characteristics of  $\beta$ -PP [8-12]*

The polymorphic composition of polypropylene having high susceptibility to  $\beta$ -crystallization depends on the circumstances of crystallization. Melting curves of samples crystallized at different temperatures are shown in Fig. 3. It can be established that pure  $\beta$ -modification can be formed if  $T_c$  is not higher than 403 K. Above this temperature, mixed polymorphic sample is produced wherein the proportion of  $\alpha$ -modification increases with temperature. Consequently, 403 K can be regarded as the *upper critical temperature limit of formation of pure  $\beta$ -PP*, designated by  $T_c^*$ .

The melting temperature ( $T_m$ ) and enthalpy ( $\Delta H_f$ ) are dependent on the temperature of isothermal crystallization. From the dependence of  $T_m$  on  $T_c$ , the

thermodynamical equilibrium melting point of  $\beta$ -PP ( $T_m^0(\beta)$ ) was determined by the method of Hoffman and Weeks [13] and was found to be  $457 \pm 4$  K [8]. The heat of fusion of fully crystalline  $\beta$ -PP obtained by the extrapolation procedure of Monasse and Haudin [14] was  $\Delta H_f(\beta) = 113 \pm 11$  J/g [8].

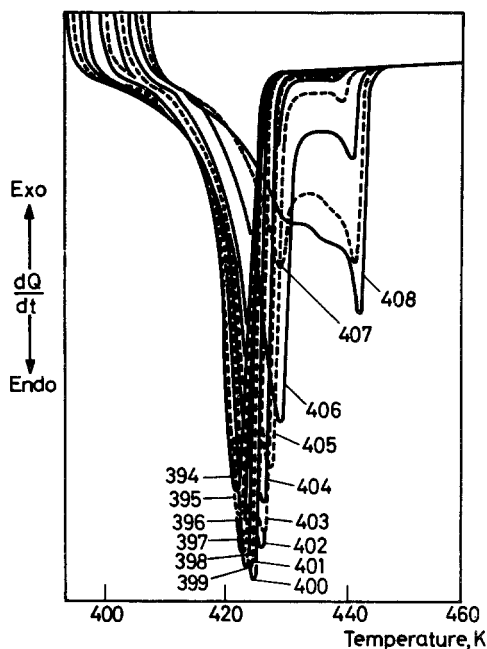


Fig. 3 Melting curves of samples crystallized at different temperatures without subsequent recooling (recorded on a common base-line)

The crystallization kinetics of  $\beta$ -PP was studied first in our laboratory [8]. Considering the above data, kinetic studies can be performed below  $T_c^*$ . The overall rate of crystallization was determined calorimetrically. Crystallization isotherms of  $\beta$ -PP can be linearized by the Avrami equation. Avrami's exponent ( $n$ ) is about 3, referring to athermal nucleation in view of the spherulitic (three-dimensional) crystallization of  $\beta$ -PP.

For the evaluation of the kinetic data of crystallization, the rate of growth should be known. No literature data are available for the growth rate of  $\beta$ -modification at higher temperatures since  $\beta$ -spherulites are formed only below a certain temperature ( $T_c \sim 411$  K). According to some reference [5, 15], the growth rate of  $\beta$ -spherulites is higher than that of  $\alpha$ -spherulites. By a stepwise crystallization technique, the growth rates were successfully determined in our laboratory in a wide temperature range, nearly up to the melting point of the  $\beta$ -modification. Evaluating

these experimental data on the basis of the kinetic theory of crystal growth [16, 17], it was established that growth of  $\beta$ -PP proceeded in Regimes Hoffman III and II below and above 406 K, respectively. In contrast to literature data [13], it was found that above a certain temperature, designated  $T_{\beta\alpha}$ , the growth rate of the  $\alpha$ -modification reached or exceeded that of the  $\beta$ -modification [11, 12].

Another interesting phenomenon was observed during the stepwise crystallization. On raising the temperature of a spherulite grown at a low-temperature step above  $T_{\beta\alpha}$ ,  $\alpha$ -nuclei formed on the surface of the growing  $\beta$ -spherulites then grew to  $\alpha$ -spherulite segments. Thus, a  $\beta\alpha$ -bifurcation took place on the surface of growing spherulites. Its probability increases with temperature. The  $\beta\alpha$ -bifurcation was interpreted in terms of a secondary  $\beta\alpha$ -nucleation [11, 12].

Comparing the rate constants of crystallization to the growth rates, the rates of nucleation were determined. The results revealed that nucleation was athermal while the calculated density of nuclei decreased linearly with increasing  $T_c$  [8].

#### *Lower and upper critical temperature limits of formation of $\beta$ -PP*

Analysis of the above observations led to the conclusion that the formation of  $\beta$ -PP had an upper and a lower critical temperature limit ( $T_c^*$  and  $T_c^{**}$ , respectively).

The existence of an upper critical temperature limit was directly demonstrated by the isothermal crystallization experiments, being  $T_c^* = 403$  K. The lower critical temperature limit was derived from the phenomenon of melting memory effect and from the experiences about the critical recooling temperature ( $T_R^*$ ). The lower critical temperature was supposed to be identical with the critical recooling temperature, i.e.  $T_c^{**} = T_R^*$  since the melting memory effect could be interpreted without any contradiction on the assumption that a post-crystallization below  $T_R^*$  produced  $\alpha$ -modification. As a straight consequence, below  $T_R^*$  the formation of pure  $\beta$ -modification would be impossible.

Let us interpret the temperature  $T_{\beta\alpha}$ . This value can be regarded as the theoretical upper temperature limit of the formation of  $\beta$ -modification above which no production of  $\beta$ -modification is possible. If some  $\beta$ -nuclei still formed above  $T_{\beta\alpha}$ , their growth would immediately be accompanied by the  $\beta\alpha$ -bifurcation resulting necessarily in an end-product of  $\alpha$ -modification. Correspondingly, above  $T_{\beta\alpha}$  pure  $\alpha$ -modification, between  $T_{\beta\alpha}$  and  $T_c^*$  mixed polymorphic structure, between  $T_c^*$  and  $T_c^{**}$  pure  $\beta$ -modification, below  $T_c^{**} = T_R^*$  again mixed polymorphic structure is formed.

*The structural stability of the  $\beta$ -modification of polypropylene [7]*

The literature regards  $\beta$ -PP unstable. However, the behaviour of our non-recooled samples is not different from that of the thermodynamically stable ones (e.g. they melt without  $\beta\alpha$ -recrystallization). In spite of this supposed thermodynamical instability,  $\beta$ -modification never transforms into  $\alpha$ -modification in the solid state. Its structural interpretation is implied in the fact that the lattice of  $\beta$ -PP consists of helices with identical convolution (helical chain conformation) while that of the  $\alpha$ -modification, regarded thermodynamically stable, comprises helical chains of both right and left convolution. It is clear that a rewinding of helices (right  $\rightleftharpoons$  left) cannot proceed in the solid state without a collapse of the crystal lattice. As it was demonstrated above,  $\beta\alpha$ -recrystallization took place in the range of the

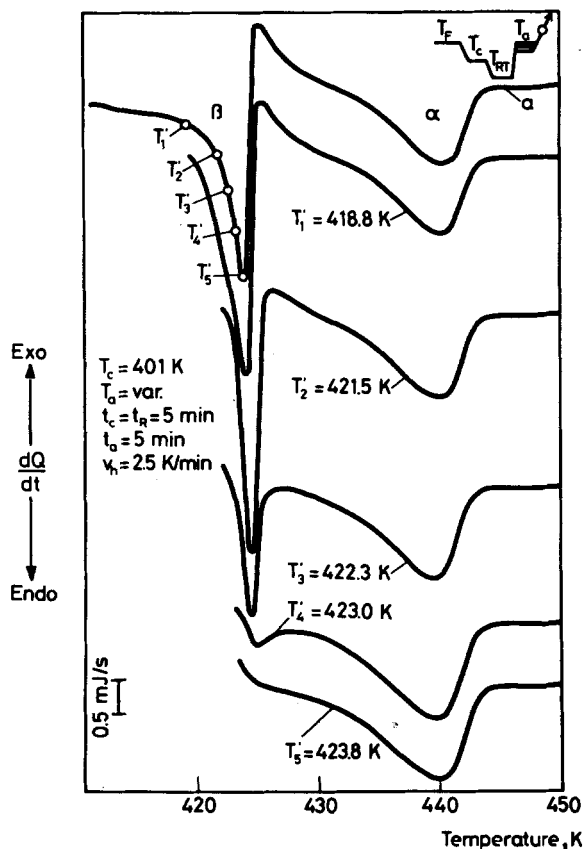


Fig. 4 The effect of annealing temperature ( $T'_1 - T'_5$ ) on the course of melting curves of re-cooled samples (a - melting curve of the non-annealed re-cooled sample)

partial melting of  $\beta$ -modification inasmuch as  $\alpha$ -nuclei had formed in the system due to recooling.

Is it possible to stabilize the  $\beta$ -phase at high temperatures or to eliminate the susceptibility to  $\beta\alpha$ -recrystallization in recooled samples (processed end-products in the practical plastics technology)? To answer this question, a comprehensive study was conducted with thermal treatment of polypropylenes. Annealing of thermodynamically stable modifications led to a perfection of the crystal structure, consequently, to an increased stability. Annealing is usually performed at a high temperature but below the melting point. Different thermal patterns were applied to  $\beta$ -PP. Their results are listed as follows:

(a) The samples were recooled to room temperature after crystallization then

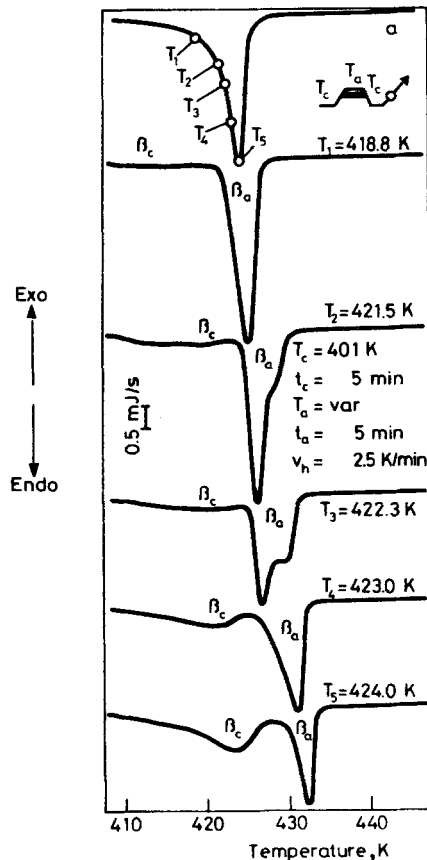


Fig. 5 The effect of the annealing temperature ( $T_1 - T_5$ ) on the course of melting curves started from  $T_c$  (a - melting curve of the non-annealed sample)



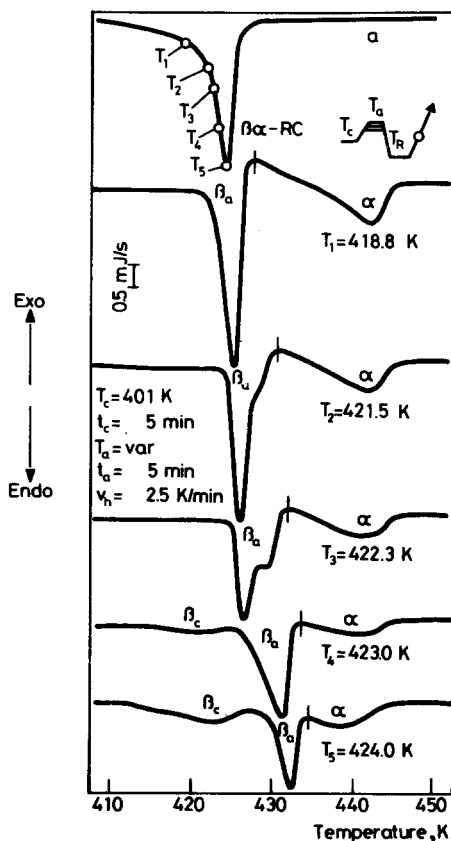


Fig. 6 The effect of the annealing temperature ( $T_1 - T_5$ ) on the course of melting curves of samples cooled to room-temperature after the annealing (a – melting curve of the non-annealed original sample)

annealed below the melting point;  $\beta\alpha$ -recrystallization occurred, the structure transformed into the  $\alpha$ -modification at a great extent or almost completely (Fig. 4).

(b) Annealing started directly from the temperature of crystallization led to a stabilization of a definite proportion of  $\beta$ -phase ( $\beta_a$ ) ceasing the susceptibility to  $\beta\alpha$ -recrystallization. On the other hand, recooling the sample from the temperature of annealing to  $T_c$ , some amount of unstabilized structure ( $\beta_c$ ) was formed due to a post-crystallization. This is illustrated by the experimental results in Fig. 5. The unstabilized proportion,  $\beta_c$ , became susceptible to  $\beta\alpha$ -recrystallization as demonstrated in Fig. 6 by the melting curves recorded after annealing from  $T_c$  followed by cooling to room temperature.

(c) A stepwise annealing was performed at decreasing temperatures; in this way,

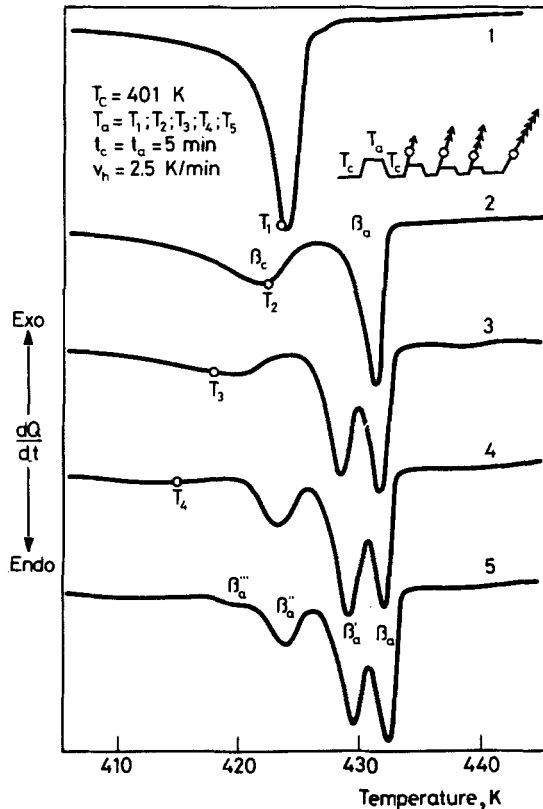


Fig. 7 Melting curves of samples annealed at temperatures decreasing stepwise ( $T_1 - T_4$ ) after each annealing step (annealing temperatures are indicated on the melting curves)

the proportion of the unstabilized material susceptible to  $\beta\alpha$ -recrystallization due to cooling was reduced practically to zero.

Results from the stepwise annealing are shown in Fig. 7. In the first step ( $T_1$ ), unstabilized  $\beta_c$  phase was formed; its proportion decreased in the subsequent steps ( $T_2, T_3, T_4$ ). In this way,  $\beta$ -modification was divided into four individually stabilized components ( $\beta'_a, \beta''_a, \beta'''_a, \beta''''_a$ ). In such a sample, very little if any  $\alpha$ -nuclei would form during the recooling to room-temperature, thus the susceptibility to  $\beta\alpha$ -recrystallization which might arise in the recooling process remained negligible.

It can be established as a summarized conclusion that the characteristics of structural changes during the annealing of  $\beta$ -PP are highly dependent on the thermal history (annealing memory effect). Stability of  $\beta$ -phase of PP can be increased by an appropriate annealing pattern while the susceptibility to  $\beta\alpha$ -recrystallization can be eliminated.

*Manufacturing  $\beta$ -PP-products [9]*

As it was demonstrated above, pure  $\beta$ -PP can be formed by crystallization in a relatively narrow temperature range (100–130°). It is crucial for the production of  $\beta$ -PP-based end-products if these thermal conditions of crystallization can be provided during processing.

Under the processing conditions, crystallization usually proceeds non-isothermally, in fact, the thermal environment may be widely variable in the residence space of the material. In addition, the effects of mechanical (shearing, stretching, compressing) impacts to the melt are also crucial in the crystallization.

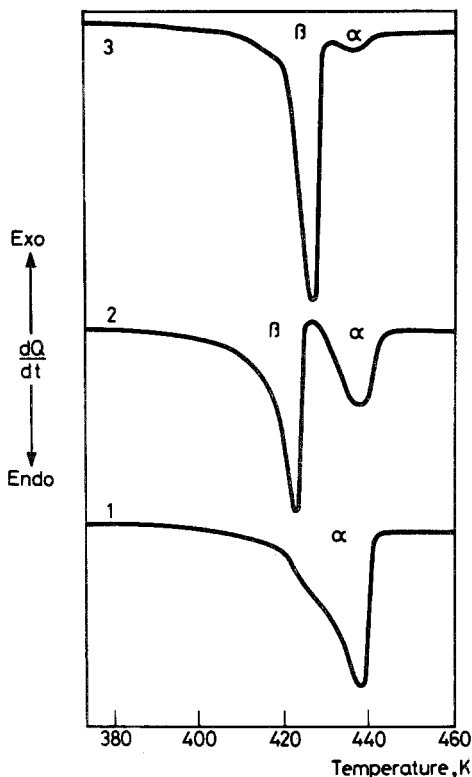
It is demonstrated in the following sections how  $\beta$ -PP based end-products can be produced by various processing techniques under the appropriate thermal conditions.

*Compression moulding.* This is the simplest way to form sheets of different thicknesses without any problem at a compression temperature within 100 to 130°. The melt should be chilled quickly to this compression temperature in order to avoid any crystallization above the upper critical limit temperature of  $\beta$ -PP formation. Especially for thick mouldings, due to the thermal inertia of the polymer, the mould temperature is recommended to set somewhat above the lower limit temperature of  $\beta$ -PP formation, most favourably, between 110 and 115° in our experiences. In our laboratory,  $\beta$ -PP sheets of 1 to 4 mm thickness were moulded. Optical microscopy of microsections from the sheets revealed radial negative  $\beta$ -spherulites. The melting curve of a moulded sheet, cooled to room temperature after moulding, is shown in Fig. 8. It is characteristic of pure  $\beta$ -PP recooled below  $T_R^*$  thus, susceptible to  $\beta\alpha$ -recrystallization (cf. Fig. 1).

As it was presented above, the structure of  $\beta$ -PP can be stabilized by a stepwise annealing started from  $T_c$ . In this way, its susceptibility to  $\beta\alpha$ -recrystallization due to recooling can be eliminated. This result obtained by crystallization and annealing in the DSC sample holder could be reproduced under technological conditions in spite of the large size of the moulding and the high thermal inertia of the mould. Thus,  $\beta$ -PP sheets with *stabilized structure* could be manufactured. Comparing the melting curves of annealed  $\beta$ -PP sheets to those of non-annealed ones, it can be established (Fig. 8) that annealing dramatically reduced the tendency to  $\beta\alpha$ -recrystallization.

The most important mechanical properties of  $\beta$ -PP were determined for moulded sheets with or without annealing and compared to those of  $\alpha$ -PP manufactured in a similar manner.

*Extrusion.* A crystallization temperature pattern favourable for  $\beta$ -PP formation is provided by a high-temperature (above 100°) cooling zone through some modification to the conventional extrusion.



**Fig. 8** Melting curves of sheets compression moulded at 115 °C. 1 – sample of  $\alpha$ -modification; 2 – compression moulded  $\beta$ -PP without annealing; 3 – compression moulded annealed sample of  $\beta$ -PP

It was found in the preliminary experimental profile extrusions that water cooling tubs could not be applied for adjusting the optimum conditions to  $\beta$ -PP formation; in this case, mixed polymorphic products formed though the proportion of  $\beta$ -modification could markedly be increased by elevating the water temperature. Practically pure  $\beta$ -PP can be formed by forced air cooling and by a very low take-off rate. Thick or large-diameter profiles, however, show insufficient quality (lunkers or cracks in the mass, high tolerance in dimensions) due to slow cooling.

Sheets in pure  $\beta$ -PP were successfully produced by means of a Viskosystem laboratory extruder with wide-gap die. The melt is crystallized in the interstices among three superimposed pressure rollers. Temperatures of the rollers can be adjusted in a wide range by separate oil thermostats. If the roller temperatures do not exceed 120°, the molten polypropylene crystallizes in the first roller gap while the third roller can provide posterior annealing.

The effects of the technological variables on the formation of  $\beta$ -PP were determined as follows:

(a) The temperature of the first two compression rollers has crucial importance. It should be set between 105 and 110° for manufacturing high-grade  $\beta$ -PP sheets.

(b) The temperature of the third roller is ineffective on the formation of  $\beta$ -PP but a higher temperature at this point may provide posterior annealing to stabilize the  $\beta$ -phase and to reduce the tendency to  $\beta\alpha$ -recrystallization due to a recooling.

(c) Sheets in pure  $\beta$ -PP are formed at low take-off rates. Both an increased take-off rate and a reduced mass flux lead to straining the melt which shifts the polymorphic composition toward the  $\alpha$ -modification.

Observations (a) and (b) agree with the experimental results for the thermal preconditions and structural stability of  $\beta$ -PP formation.

The observation (c) that a straining load to the melt favours the formation of  $\alpha$ -modification can be ascribed to an altered mechanism of crystallization. Stretching may unbend and fasciculate the globular molecules in the molten phase. Fascicles are then oriented in the stretch direction and act as "row nuclei" below the melting point, inducing oriented crystallization. Such row nuclei form at considerably higher temperature than the thermal nuclei in the unstressed melt [18]. For this reason, a mechanical load (stretch, shear) may cause crystallization at higher temperature, above the upper critical temperature limit of  $\beta$ -PP formation, leading to a mixed polymorphic product.

*Injection moulding.* Under such complex thermal and flow conditions, quite variable in space, where the melt cools quickly and undergoes high shear load along the wall of the mould, an oriented cylindrite morphology is formed in the sheared layer due to the crystallization induced by the high density of row nuclei [19]. In contrast to this skin effect, the core cools more slowly and the melt has time to relax (disorient) before crystallization. The core region of the moulding, therefore, crystallizes into a spherulitic structure [19].

The injection mouldings have non-homogeneous structure which is highly variable with the processing conditions. For PP with high tendency to  $\beta$ -crystallization, the dependence of the polymorphic composition on the thermal and mechanical conditions makes the situation more complicated.

The experimental injection moulding was performed by a Battenfeld machine with a plate mould. Temperatures of the mould and occasionally of the melt were varied systematically. Thickness of the injection moulded plates was 1 or 3 mm.

Cut segments and microsections of the plates were tested by calorimetry and optical microscopy, respectively. The following conclusions were drawn:

— At low mould temperatures ( $T_s = 20$  to  $60^\circ$ ) in the thinner (1 mm) plates, always  $\alpha$ -modification formed regardless of the moulding conditions.

— At low mould temperatures ( $T_s = 20$  to  $60^\circ$ ), the thicker (3 mm) plates have

mixed polymorphic composition where the skin consists of  $\alpha$ -cylindrites while the core comprises both  $\alpha$ - and  $\beta$ -spherulites. The proportion of  $\beta$ -modification increases with the mould temperature while appears to be invariant in the melt temperature.

— As the mould temperature reaches or exceeds the lower critical temperature limit of  $\beta$ -PP formation (100 to 120°), mixed polymorphic structure is formed again. The skin consists of  $\alpha$ -cylindrites but the core contains only  $\beta$ -spherulites. It is remarkable that at high  $T_s$  the injection period ( $t_s$ ) should be increased considerably. The relative proportion of the sheared skin layer of  $\alpha$ -modification is reduced by increasing the thickness of the moulding, consequently, the proportion of  $\beta$ -modification in terms of the total mass of the part increases.

It can be established that no pure  $\beta$ -PP parts can be produced by injection moulding. Since the crystallization on the row nuclei in the high-shear layer at the wall of mould commences still above  $T_c^*$ , the formation of  $\alpha$ -modification is inevitable here. At an optimum mould temperature ( $T_s \geq T_c^{**}$ ), a unique sandwich construction is formed with a core of  $\beta$ -modification and a skin of  $\alpha$ -modification.

#### *Phase stability of $\beta$ -PP under mechanical load*

The stress-strain diagram of  $\beta$ -PP is characteristic of crystalline polymers, consisting of three typical regions: elastic deformation, orientation to necking, and elastic deformation of the necked specimen.  $\beta$ -PP shows a single difference: in the orientation region, necking proceeds with not constant but slightly increasing stress. The mechanical properties of  $\alpha$ - and  $\beta$ -modifications are very close to one another but dependent on the manufacturing conditions and on the test procedures. Its discussion is beyond the scope of this paper.

All the more remarkable is the phase stability and the structural change during the necking process in the  $\beta$ -modification. First of all, let us consider the behaviour of compression moulded sheets stabilized by posterior annealing in the region of elastic deformation (at lower stress levels than necessary for necking). After sixty periodic loading/unloading cycles at a relative deformation range of  $\epsilon = 0$  to 8%, the structural changes were tested calorimetrically. The melting curves of original and periodically loaded samples were practically coincident, i.e. no  $\beta$ - $\alpha$ -recrystallization occurred. It led to the conclusion that  $\beta$ -PP is stable in the initial range of elastic deformation before necking.

In the orientation range, during necking, a marked phase transition takes place. Melting curves of samples taken from the necked part of compression moulded sheets deformed at different extent (designated D III) are shown in Fig. 9. It can be stated that  $\beta$ -modification transforms continuously into  $\alpha$ -modification in the orientation region (decreasing relative size of the melting peak of  $\beta$ -modification)

and the transformation is completed by the break. It should be emphasized, however, that even at a much higher deformation ( $\epsilon = 150\%$ ) than the elongation of necking ( $\epsilon_{\max} = 9.7\%$ ), the necked segment still contains a considerable amount of  $\beta$ -modification. It is remarkable that the moulded sheets were stabilized before testing by annealing started from the processing temperature ( $115^\circ$ ) thus, its susceptibility of  $\beta\alpha$ -recrystallization was eliminated.

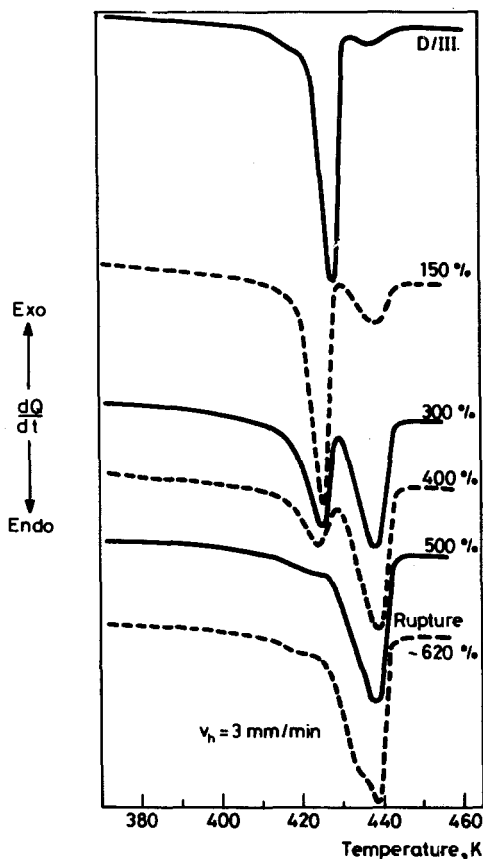


Fig. 9 Melting curves of necked samples from stretched compression moulded sheets, stabilized by annealing, at different degrees of stretching

It was found that the strain rate (in the range of  $V = 3$  to  $600 \text{ mm/min}$ ) in the stress-strain test had no significant effect on the feature of  $\beta\alpha$ -recrystallization during the deformation.

Several models are known [20] for the description of structural changes in the necking region of deformation (for monomorphic polymers). According to

Peterlin's model, these structural changes take place within the solid crystalline phase (one-phasic transformation). On the contrary, Juska and Harrison [21] supposed a melting due to stretching the crystallites followed by a recrystallization (two-phasic transformation). Between these two extremities, several intermediate models were published [22–24] based on local melting or formation of transient amorphous phases.

Since  $\beta\alpha$ -recrystallization of  $\beta$ -PP which requires rewinding of the helical chains is sterically hindered in the solid phase, the  $\beta\alpha$ -recrystallization observed during stretching cannot be interpreted by the one-phase model. On the other hand, the independence of the feature of  $\beta\alpha$ -recrystallization on the strain rate contradicts the two-phase model. The best fit interpretation to the structural change during the deformation of  $\beta$ -PP is the intermediate model of Peterman [23].

#### *Polymer blends with $\beta$ -PP*

Improvement and modification of properties of polymers are achieved in physical and chemical ways. The most important physical methods imply the formation of multicomponent systems, such as polymer blends, filled resins, and composites.

High-grade conventional polypropylenes containing mostly  $\alpha$ -modification have moderate cold resistance and impact strength due to the relatively high glass transition temperature ( $T_g$ ). Since  $T_g$  is a characteristic transition temperature of the amorphous phase, consequently the cold resistance of  $\alpha$ - and  $\beta$ -modifications are identical. The cold resistance of conventional PP is usually improved by blending with various elastomers or polyethylene.

It was concluded on the basis of comprehensive calorimetric studies that blends of  $\beta$ -PP with elastomers [10] or with low-density polyethylene could be prepared under the thermal conditions necessary for the formation of pure  $\beta$ -PP. E.g. introducing elastomers of EPM type or of ethylene/vinyl acetate copolymer (up to 16 per cent) had no appreciable influence on the  $\beta$ -crystallization tendency and spherulitic structure of the polypropylene component. Melting curves of a blend with 16 per cent of Vestopren 2047 elastomer are presented in Fig. 10 as a function of the crystallization temperature. It can be seen that the dependence of the polymorphic composition on  $T_c$  is similar to that for pure  $\beta$ -PP and pure  $\beta$ -PP is formed at  $T_c \leq 400$  K. The presence of the elastomer lowers the upper critical temperature ( $T_c^*$ ) only slightly. It was established by optical and scanning electron microscopy as well as by dynamical mechanical analysis that blends of  $\beta$ -PP with elastomers were two-phase systems in the solid state. Elastomer particles of about 5  $\mu\text{m}$  were dispersed in the continuous  $\beta$ -PP matrix (up to an elastomer content of 16 per cent).



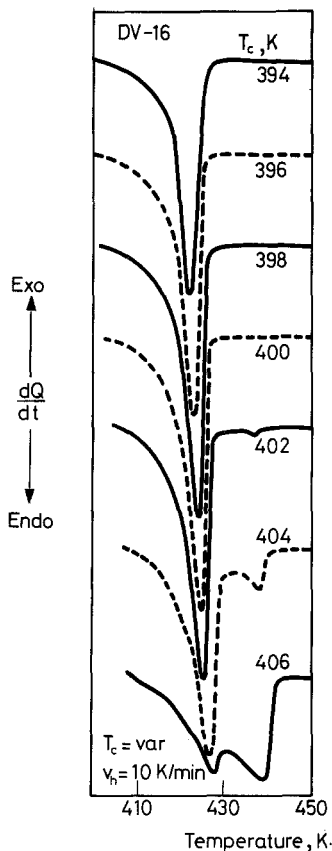


Fig. 10 Melting curves of samples containing 16 per cent of Vestopren 2047 elastomer crystallized at different temperatures

Mechanical testing of compression moulded sheets in  $\beta$ -PP/elastomer blends showed decreasing but still satisfactory strength characteristics (modulus, stress to necking, tensile strength) with the proportion of elastomer. Impact strength, however, improved considerably.

Blends of  $\beta$ -PP with LDPE can be prepared over the whole range of composition without any problem. Like elastomers, LDPE has no influence on the  $\beta$ -crystallization tendency of the polypropylene component as demonstrated by the melting curves of  $\beta$ -PP/LDPE blends with different compositions in Fig. 11. Separate melting peaks of both crystalline components appear in the diagrams. Location of the peaks on the temperature scale is invariant in the composition; their intensities refer to the relative proportions of the components. Melting peaks of

polypropylene appear in the characteristic temperature range of the  $\beta$ -modification and no peak is visible referring to the presence of any  $\alpha$ -modification.

These two separated melting peaks which are invariant in the composition make evident that a heterogeneous mixture of the two crystalline components is present. This heterogeneous structure was proved by optical microscopy as well.

Blends of polypropylene susceptible to  $\beta$ -crystallization with high-density polyethylene (HDPE) are much more complicated. Up to a polyethylene content of 60 per cent, melting curves of blends show separate melting peaks of polyethylene and of both ( $\alpha$  and  $\beta$ ) modifications of polypropylene referring to a mixed polymorphic system. With increasing polyethylene content, the polymorphic pattern of polypropylene shifts toward the  $\alpha$ -modification. Above 60 per cent of polyethylene, the total of polypropylene is of  $\alpha$ -modification. Consequently, no

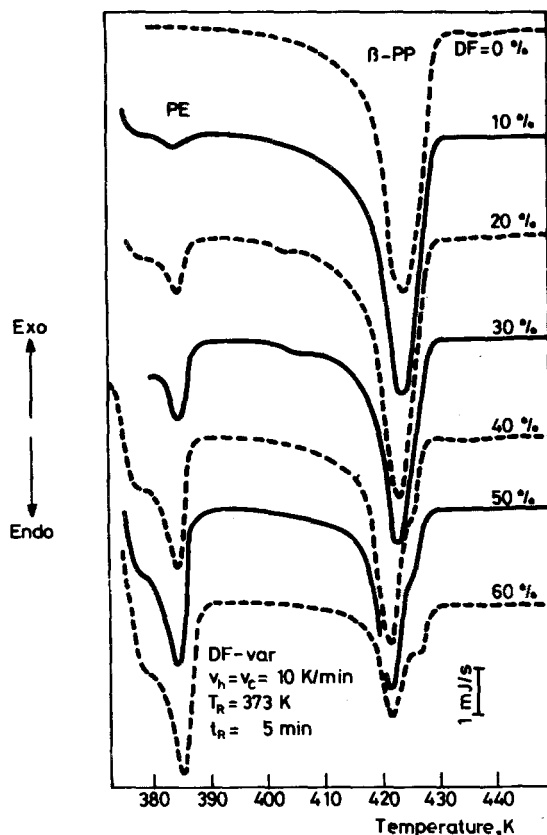


Fig. 11 Melting curves of blends containing Tipolen FA 2210 low-density polyethylene as a function of the composition (Cooling and heating rate: 10 deg/min,  $T_R = 373$  K)

pure  $\beta$ -PP appears in the presence of HDPE. Studying the crystallization of these blends in a wide range of cooling rates has led to the conclusion that the temperature range of crystallization of polypropylene is at a higher level than that of LDPE, thus crystallization of polyethylene commences as that of polypropylene has completed (as indicated by the perfect resolution of the two peaks on the crystallization curves of blends). On the other hand, the temperature ranges of crystallization of HDPE and PP are completely overlapping (crystallization curves of blends have a single peak) thus, both components crystallize together. (It should be noted that, in spite of the simultaneous crystallization, the two components form separate phases as shown by the melting curves.) For this reason, the settled crystalline polyethylene phase may exert an  $\alpha$ -nucleating effect. The diverse effects of the two types of polyethylenes on the  $\beta$ -crystallization tendency of polypropylene in the blend are, therefore, attributed to their different temperature ranges of crystallization.

#### *$\beta$ -PP based composites*

$\beta$ -PP was found suitable for producing filled systems with some minor exceptions. According to our earlier results, inorganic or mineral fillers alter the course of crystallization of polypropylene to different extents. Two extremities can be defined for the fillers with respect to their effect on the crystallization of polypropylene [25]:

(a) *Inactive fillers* that have negligible if any effect on the rate of crystallization and on the supermolecular structure. They include chalk, dolomite and carbon black for polypropylene.

(b) *Active fillers* that are artificial nucleating agents (selective  $\alpha$ -nucleating agents), increasing the overall rate of crystallization and inducing the formation of fine-textured spherulitic structure due to the high nucleus density. Active fillers shift the temperature range of non-isothermal crystallization toward higher levels. The most accepted active filler is *talc* [26].

For this reason, *chalk* and *talc* were selected as typical representatives of the above two groups for the research to preparation of  $\beta$ -PP-based composites (filled systems), applying them at 0.1 to 10 per cent in polypropylene [27].

The melting curves of chalk- and talc-filled samples are shown in Figs 12 and 13, respectively. (Figures on the curves refer to the percentage of the filler.) The melting peaks of chalk-filled samples (Series Dm) lie in the temperature range corresponding to  $\beta$ -PP ( $T_m \sim 430$  K), i.e. the formation of  $\beta$ -PP is unequivocal. Only at chalk content of 10 per cent, a small diffuse  $\alpha$ -peak appears.

The characteristics of the melting peaks of talc-filled samples (Series Dt) are quite different from those of chalk-filled ones (Fig. 13). The high melting peaks are

located in the temperature range of  $\alpha$ -modification. Some small peaks referring to the presence of  $\beta$ -modification appear only at low talc concentrations (0.1, 0.5, and 1.0 per cent).

In the presence of talc, therefore, the formation of  $\beta$ -PP is suppressed due to the  $\alpha$ -nucleating activity of talc. In this case, crystallization starts at a higher temperature and this crystallization range shifts above the upper critical temperature of  $\beta$ -PP formation at the cooling rate applied. On the other hand, chalk has a negligible influence on the rate and temperature range of crystallization. Consequently, the crystallization process in this system is identical with that in the unfilled resin, thus, under the appropriate conditions,  $\beta$ -PP is formed.

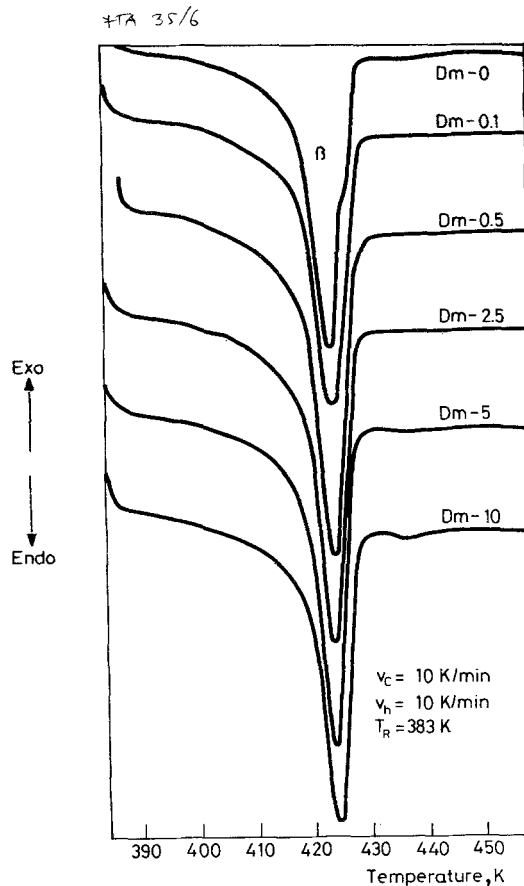


Fig. 12. Melting curves of composites loaded with different amounts of chalk (heating and cooling rate: 10 deg/min,  $T_R = 373 \text{ K}$ )

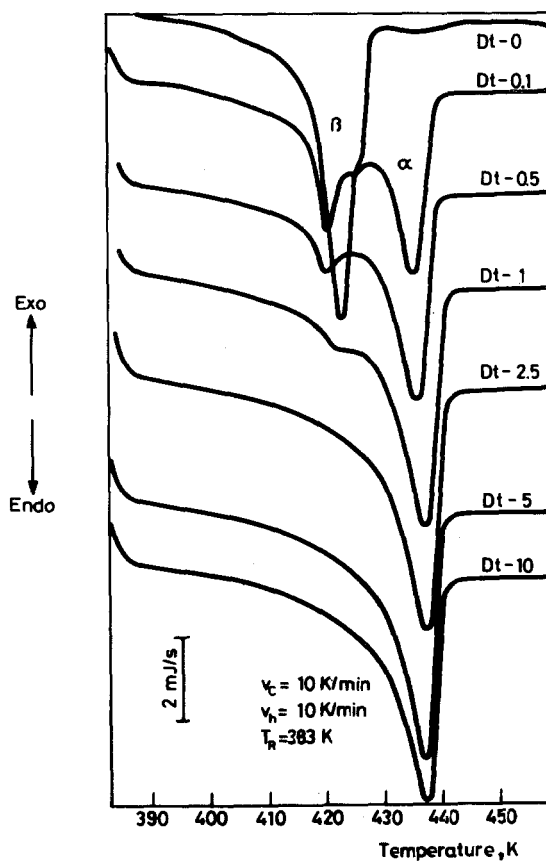


Fig. 13 Melting curves of composites loaded with different amounts of talc (heating and cooling rate: 10 deg/min,  $T_R = 373$  K)

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**Zusammenfassung** – Sowohl unter Laboratoriums- als auch unter Betriebsbedingungen wurden die  $\beta$ -Modifikation und Multikomponentensysteme von  $\beta$ -Polypropylen hergestellt. Hierbei wurden die charakteristischen Wesenszüge von Kristallisation, Schmelzen und Tempern von  $\beta$ -PP beschrieben. Es wird auch der sehr ausgeprägte Memory-Effekt von  $\beta$ -PP bei Schmelzen und Tempern dargestellt. Für die Formierung von  $\beta$ -PP wird die Existenz einer unteren und einer oberen Grenztemperatur verdeutlicht. Es wurde weiterhin die strukturelle Stabilität und die dehnungsinduzierte  $\beta$ - $\alpha$ -Rekristallisation von  $\beta$ -PP untersucht. Herstellung und Eigenschaften von Polymergemischen und Verbundstoffen von  $\beta$ -PP wurden ebenfalls beschrieben.

**Резюме** — В лабораторных и заводских условиях получены  $\beta$ -модификация полипропилена (ПП) и многокомпонентные системы на его основе. Приведены особенности кристаллизации, плавления и термообработки  $\beta$ -ПП. Установлен резко различный характер эффекта памяти при плавлении и термообработке  $\beta$ -ПП. Показано наличие нижнего и верхнего пределов образования  $\beta$ -ПП. Проанализированы структурная устойчивость и ориентационно-наведенная  $\beta\alpha$ -перекристаллизация. Приведены также получение и свойства полимерных смесей и наполненных композитов на основе  $\beta$ -ПП.