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Enhancement of βα-recrystallization in β-form isotactic polypropylene during heating after roll deformation

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Summary

β-form isotactic polypropylene shows βα-recrystallization behavior (recrystallization from β- to α-form) during slow heating. This is enhanced by deformation. β-form specimen with uniaxially oriented lamellae was deformed by rolling, and βα-recrystallization was studied by DSC and x-ray diffraction. The result showed that (1) βα - recrystallization is promoted with the degree of deformation. (2) Deformed specimen shows βα-recrystallization from considerably low temperature compared with the undeformed one. (3) The recrystallized α-form is c-axis-oriented along the roll direction. From these results the βα-recrystallization mechanism was discussed in view of α-nucleus formation by deformation.

Introduction

It is well known that β-form of isotactic polypropylene (β-PP) recrystallizes partly to α-form accompanying premelting (βα-recrystallization) during heating in DSC. This recrystallization is promoted in case that T_c is low or the heating rate is small.

Recently Varga reported an interesting observation in β-PP grown by the addition of nucleating agents [1] : After melt-crystallization in DSC when scanning was begun directly from T_c the thermogram revealed only β-melting endotherm even with a slow heating rate, whereas when the specimen was once cooled to room temperature and thereafter began to scan with the same heating rate, βα-recrystallization was observed to occur. When the βα-recrystallization occurs typically, three peaks appear in the DSC curve, namely β-melting endotherm, α-recrystallizing exotherm and α-melting endotherm. When β-PP is deformed mechanically, the DSC thermogram becomes to show change from the initial stage of deformation owing to βα-recrystallization. In this paper results from DSC and x-ray diffraction for rolled β-PP are reported and discussed in view of α-nucleus formed by rolling deformation.

Experimental

Material used in this investigation is isotactic polypropylene sheet 0.23 mm thick from Chisso Co. Ltd. (M_v=2.55x10^5 , Tacticity =97%) This material was melt-crystallized by the method as in our previous papers, namely by moving the specimen along the temperature gradient.[2, 3,4] Specimen plates thus crystallized show an unidirectional lamellar orientation of β-form along the growth direction. The linear growth rate of lamellae was 0.4 mm/h. This rate corresponds to crystallization temperature around 132°C. Deformation was carried out by rolling the specimen plates at room temperature along the lamellar direction. Draw ratio λ was defined as the ratio of specimen length along the rolling direction after and before rolling. For WAXS experiment, undeformed and deformed specimens were heat-treated by the following way: Heating in DSC with the rate 10°C/min up to a temperature T_p which is below or in the melting range, holding for 1 min, and then cooling to room temperature with the same rate. Thereafter WAXS photographs were taken at room temperature.

Results

The DSC thermogram of β-PP after rolling is illustrated in Figure 1. The β-melting peak becomes smaller whereas α-melting peak becomes larger with λ, and at some stage of rolling, the β-melting peak almost disappears (e). However it does not mean that the original β-crystals have been almost destructed by rolling. As is seen in Figure 2, by use of quicker heating rate, specimen which show such type of thermogram can give rise to the β-melting peak.

In Figure 3 are shown WAXS photographs of specimens as-grown and after rolling (λ=2.8), each of which was thereafter heat-treated. The as-grown specimen (a) shows almost pure hexagonal pattern of β-form with a-axis orientation along the lamellar direction. Accordingly, the c-axis (molecular axis) is perpendicular to this direction. After rolling, rotation of crystals to some extent and also broadening of orientation of β-crystals are seen, but β-form is still domi-

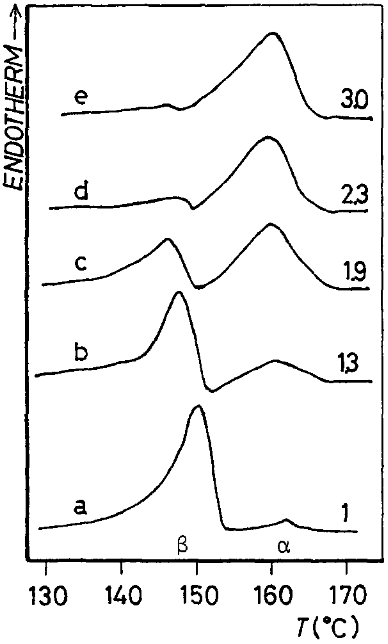


Fig.1 DSC thermogram of as-grown (a), and rolled β-PP for several draw ratio λ (b—e). Heating rate 10°C/min. λ is indicated at each curve.

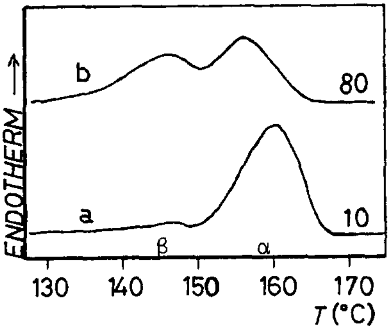
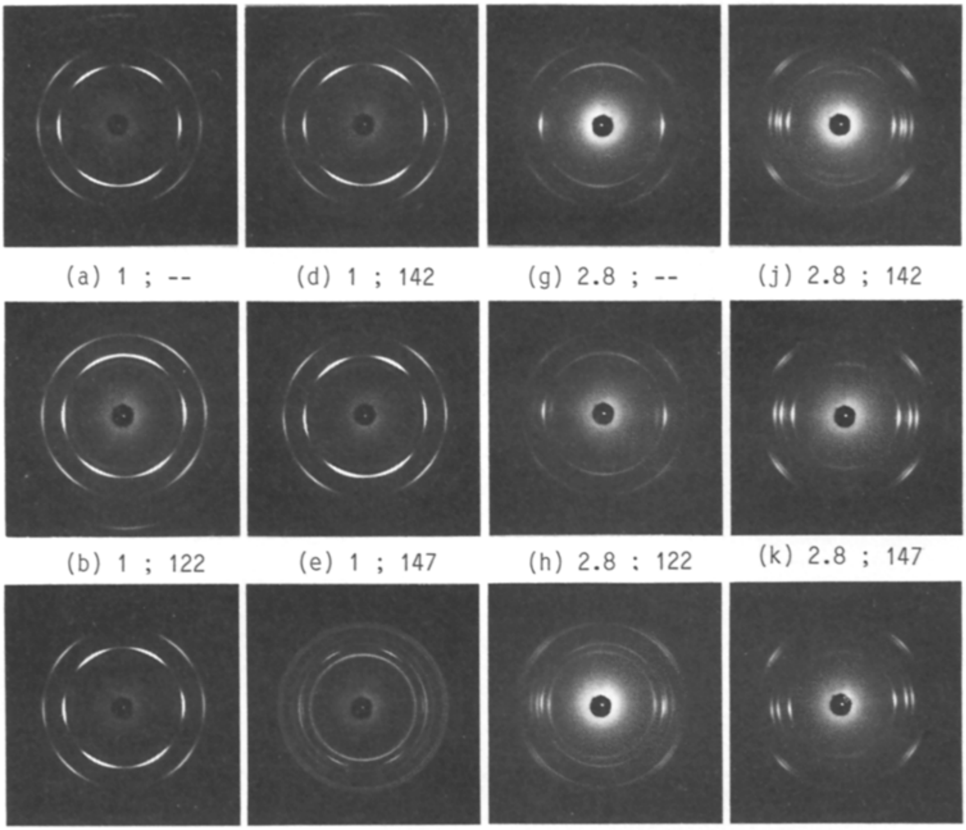


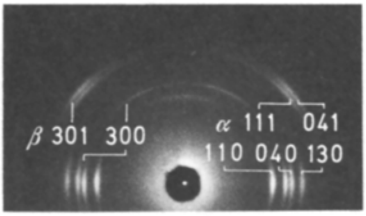
Fig.2 DSC thermogram of rolled β-PP for different heating rates. λ=3.0 Heating rate (°C/min) is indicated at each curve.



(a) 1 ; --
(d) 1 ; 142
(g) 2.8 ; --
(j) 2.8 ; 142

(b) 1 ; 122
(e) 1 ; 147
(h) 2.8 : 122
(k) 2.8 ; 147

(c) 1 ; 132
(f) 1 ; 150
(i) 2.8 ; 132
(l) 2.8 ; 150



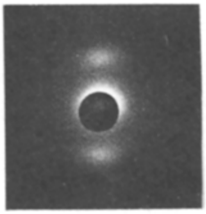


Fig.3 WAXS photographs of undeformed and deformed β-PP before(a,g) and after heating to T_p. (b—f; h— *l*) Two numerals indicated under each photograph are λ (left) and T_p(°C) (right) values. Lamellar axis and roll direction are both vertical in the photographs. X-ray is vertical to roll plane. Main hkl indices of α and β crystals are indicated in the enlarged photograph of (j).

Fig.4 SAXS photograph of deformed (λ =2.8) and heat-treated (T_p=150°C) β -PP, corresponding to Fig.3(*l*). Lamellar axis and roll direction are both vertical in the photograph. X-ray is vertical to roll plane.

nant (g). The molecular axis in β-crystals remain largely inclined to the roll direction. [3] Besides, weak diffuse equatorial reflection can be observed which originates from smectic phase or α-form microcrystallites.

Photographs after the heat-treatment for deformed specimens indicate that:

(1) In the case of T_p=122°C $\beta\alpha$-recrystallization is not observed. The equatorial diffuse reflection splits into separate reflections from α-crystals by annealing effect.(h).

(2) When T_p is set higher, $\beta\alpha$-recrystallization proceeds during the heat treatment and α-reflections become stronger (i—l).

(3) The recrystallized α-crystals have pretty good c-axis orientation along the roll direction, contrary to the case of undeformed one in which orientation is hardly seen (f).

Discussion

(1) The change of melting behavior in Fig.1 is explained as follows. In the case of as-grown β-PP, it is supposed that few α-nuclei are originally contained. Hence some induced time is necessary to the spontaneous formation of α-nuclei in the premelted region of β-PP. Therefore there is a time lag between β-melting and α-recrystallization. Consequently, the $\beta\alpha$-recrystallization during the DSC scan is insignificant except very slow heating. On the contrary, in the case of rolled one, α-form portions are generated in β-lamellae. Therefore $\beta\alpha$-recrystallization can proceed by recrystallization of molten material on these nuclei. The density of generated α-nuclei will increase with λ , so the $\beta\alpha$-recrystallization will proceed more quickly with λ . The seeming disappearance of β-endotherm (Fig.1(e)) is explained in this way as the offsetting superposition of β-melting endotherm and α-crystallizing exotherm with shorter time lag.(Fig.2)

(2) From WAXS series of Fig.3, it is found that in the case of deformed specimens, $\beta\alpha$-recrystallization takes place drastically from considerably low temperature. In (i) where T_p =132°C, which corresponds almost to the starting temperature of endothermic curve of DSC for undeformed specimen (Fig.1 a), recrystallization is found to have already advanced. On the contrary, in the case of undeformed specimen, even the pattern of T_p=142°C (d) remains almost unchanged, by comparing with unheated one. The recrystallization becomes only detectable in (e) where T_p=147°C. As $\beta\alpha$ -recrystallization is not a transformation in the solid state, but it must pass the stage of melting by some crystallographic ground [5], the observed evidence indicates that premelting is taking place even at such low temperature. This circumstance on premelting may be similar for undeformed specimen, in which premelting may be accompanied by subsequent β -recrystallization ($\beta\beta$ -recrystallization) resulting in the thickening of lamellae with the same crystal orientation. This sort of change is, however, not detectable in the Figure. The preferential occurence of $\beta\alpha$ -recrystallization compared with $\beta\beta$ -recrystallization in case that α -nuclei are provided in advance, is due to the difference in T_m of both forms ($T_m(\alpha) > T_m(\beta)$), from which it follows that the growth rate of α -lamella becomes larger than that of β -lamella above the temperature $T_{\beta\alpha}$ (ca. 140°C) [6].

(3) The c-axis-orientation observed in the recrystallized α-form (Fig. 3 (i)—(*l*)) indicates that majority of melted molecules have attached onto the mechanically formed, c-axis-oriented α-nuclei.

Besides the c-axis-orientation, different kind of orientation probably a*-axis-one, is faintly seen. It may result either from branching growth of recrystallized α-lamellae (cross-hatched structure) [4,7], or from epitaxial overgrowth of α-form onto the lateral surface of remaining β-lamellae which is supposed to occur above $T_{\beta\alpha}$ [8].

As a subsidiary experiment, a SAXS photograph was taken on the same specimen as Fig.3 (*l*) as shown in Figure 4. This is a two point pattern on the meridian and not layer line type. Together with Fig.3 (*l*) it is supposed that this pattern reflects the melt-grown structure of developed α-lamellae whose surface normal is parallel to the c-axis of oriented α-nuclei.

(4) The finding of Varga which was referred to in the Introduction may possibly be due to the formation of α-nuclei when β-PP was cooled after the isothermal crystallization. Of course the nuclei formed from such an origin may be small in number and therefore not so efficiently active as in the case of mechanically formed ones.

There may be a variety of conceivable origin of α-nucleus formation in β-PP by cooling after the isothermal crystallization. One is the secondary crystallization of interlamellar amorphous molecules to α-crystallites by cooling, irrespective of the crystalline structure of neighbouring β-lamellae

Another is due to a mechanical effect during cooling and reheating. Contraction and expansion of lamellar stacks in spherulites may exert tensile stress to some of the tie-molecules interconnecting the neighbouring lamellae, which may occasionally yield local unfolding of molecular segments and grow into α-nuclei. This type of nucleus formation has already been proposed by Petermann et al. on the II—I phase transformation of polybutene-1 [9]. They consider that thermal stress can, likewise the external tensile stress, cause the formation of nuclei for the solid state phase transformation. In the case of β-PP, however, α-nucleus formation may be energetically disadvantageous compared to polybutene-1. Accordingly, it is not clear if such way of nucleus formation is also applicable to the case of β-PP, but the possibility may not be eliminated at the present stage.

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