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Study of the β - α Solid-Solid Transition of Isotactic Polypropylene by Synchrotron Radiation

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SYNOPSIS

The transformation of the β-modification into α-modification in isotactic polypropylene was investigated by WAXS, DSC and dilatometric methods. The temperature and time dependent WAXS spectra were made by using high-intensity synchrotron radiation. The β-α transformation was followed by short time exposures. The transformation of the β-modification was found to act toward the increase in the total crystallinity.

INTRODUCTION

Isotactic polypropylene has three crystal modifications, the monoclinic α-modification, the hexagonal β-modification and the triclinic γ-modification. /TURNER JONES et al., 1964; SAMUELS et al., 1972/. The α-modification is the most commonly observed one while the β-modification can be formed beside the α-modification under specific conditions such as

a/ crystallization from the melt at crystallization temperature between 100 and 130°C /TURNER JONES et al., 1964/;

b/ crystallization from an oriented melt /LEUGERING et al., 1973/;

c/ crystallization from the melt in the presence of nucleating agents /MORROW, 1969; LEUGERING, 1967/.

The γ-form of crystalline polypropylene can be produced from low-molecular fractions by slow cooling and from normal commercial polypropylenes by crystallizing under high pressure.

It has been observed that both the β and γ-form tend to convert to the monoclinic α-form when the sample is subjected to mechanical deformation or to appropriate thermal treatment. The most direct way to follow this transition is to perform continuous X-ray diffractometric structure analysis during the transition process. This was carried out first by TURNER JONES et al. /1964/ in the case of the β to α transition and by PAE /1968/ for the γ to α transition. By using conventional X-ray apparatus, however, recording a wide-angle X-ray scattering

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spectrum is a rather time-consuming process which can be performed only at a few selected temperature values or at a very slow temperature rate. More rapid investigations can be carried out by DSC. A very profound study of the melting behaviour of polypropylene containing β-modification was conducted by UHLMANN et al. /1979/, who found a very strong dependence of DSC traces on the heating rate. At lower rates /2-16°C/min/, multiple peaks were observed in the temperature range of 130 to 150°C while, at higher rates, only one endothermic peak was found. UHLMANN et al. supposed that the multiple peaks were connected with the successive melting processes of less perfect crystals and the subsequent recrystallization and that the β-modification is metastable with respect to the α-modification. DSC study can provide, however, only indirect information about structural changes.

The recent development of synchrotron radiation sources and position sensitive counters made it possible to obtain a wide-angle X-ray scattering spectrum for polymers in a few seconds using monochromatized synchrotron radiation /FORGÁCS et al., 1980/. Since a large number of exposures can be made in a short time, the structural changes accompanying phase transition can be followed easily in a direct way. As the heating rate during structural analysis can be as high as in the case of DSC or dilatometric measurements, the microscopic data can be compared with the macroscopic ones obtained under the same conditions.

In this paper, results obtained by using these techniques for investigation of the $\beta-\alpha$ solid-solid transition in isotactic polypropylene are reported. From wide-angle X-ray spectra recorded during a temperature scan or at constant temperature, the change in the relative amount of the β and α-modifications and in the total crystallinity was calculated. In addition, DSC and dilatometric measurements were carried out and their results were compared with the observed structural changes.

EXPERIMENTAL

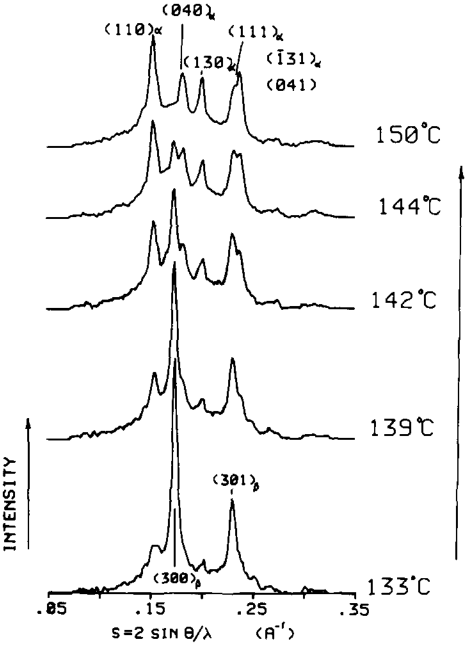
In order to obtain samples with relatively high amount of β-modification, 0.03 w-p.c. of Hostapermrot E 3b /Hoechst AG/ was added to Hercules Co. Ltd. Pro-fax 6523 isotactic polypropylene / $\rho = 0.91$ g/cm^3, $\bar{M}_n = 16 \times 10^3$, $\bar{M}_m = 420 \times 10^3$/. This additive is a very good nucleating agent for producing samples with high β content /MOOS et al., 1981/. 0.5 mm thick samples were prepared in a laboratory press at 200°C and quenched in cold water between 2 mm thick iron sheets. X-ray scattering experiments were carried out by using the synchrotron radiation of the VEPP-3 storage ring at the Institute of Nuclear Physics in Novosibirsk /USSR/. The method is described in detail in an earlier paper /FORGÁCS et al., 1980/. The adjusted wavelength /λ/ was 0.1320 nm and scattering was recorded between the angles of $3.5^{\circ} < 2\theta < 34.0^{\circ}$ which correspond to the limit values of the scattering vector $s = 2 \sin \theta / \lambda$ of 0.02 and 0.46. Counting time for one spectrum was usually 60 seconds and exposures were made at every two minutes.

The DSC measurements were carried out by a Du Pont 910 DSC equipment. Volumetric measurements were made in a mercury filled dilatometer similar to those described by KOVACS /1955/.

In all cases, the temperature scanning rate was 2°C/min.

RESULTS AND DISCUSSION

Typical X-ray spectra obtained in a heating scan are shown in Figs. 1a. and 1b.



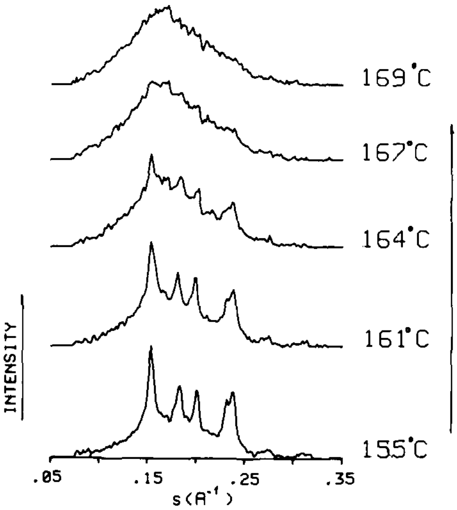


Fig. 1a. Selected WAXS spectra during heating: β - α transition

Fig. 1b. Selected WAXS spectra during heating: final melting

It can be seen that isotactic polypropylene containing β-form crystals melts in two steps. The first one is a solid-solid transition when the β-modification transforms into α-modification and, after that, the final melting of the completely α-formed polymer takes place.

The relative amount of the β-modification can be characterized by the so-called k-value /TURNER JONES et al. 1964/, refered as:

$$k = \frac{I(300)_\beta}{I(300)_\beta + I(110)_\alpha + I(040)_\alpha + I(130)_\alpha} \qquad /1/$$

where $I(hk0)_{\alpha,\beta}$ are the intensities of wide-angle X-ray crystalline reflections for hk0 planes of the α- and β-modification, respectively. The k-value is zero in the absence of the β-modification and unity if only the β-modification is present in the material. The temperature dependence of the k-value during melting process is shown in Fig. 2a. In Fig. 2b., the relative crystallinity is plotted against the temperature.

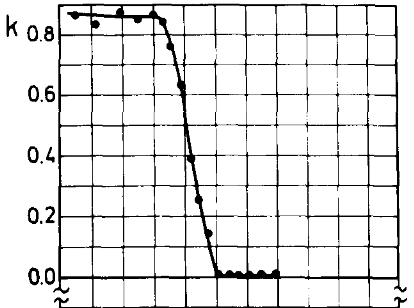


Fig. 2a.
The temperature dependence of the β content during heating

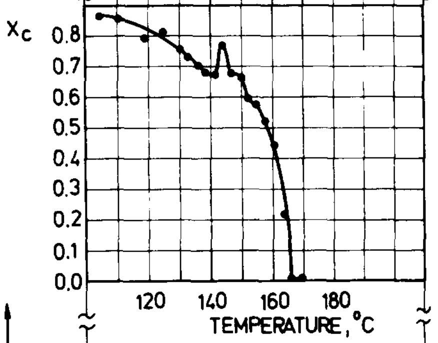


Fig. 2b.
The temperature dependence of the total X-ray crystallinity during heating

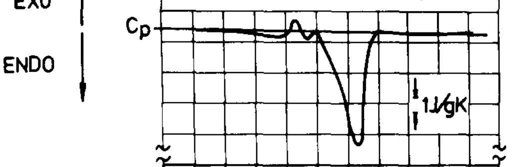


Fig. 2c.
DSC pattern during heating

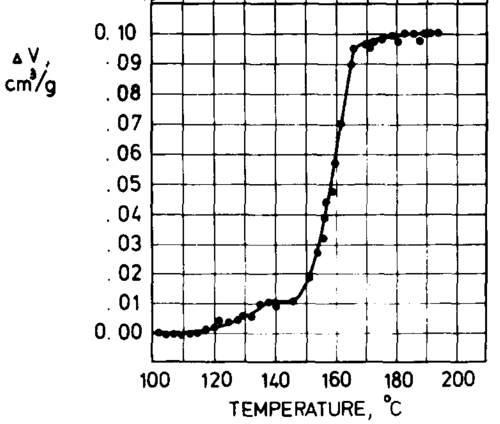


Fig. 2d.
The temperature dependence of the change in specific volume caused by phase transitions

The crystallinity was calculated by the formula

$$X_c = \frac{\int_{0.05}^{0.35} \left(I(s) - I_{am}(s) \right) s^2 ds}{\int_{0.05}^{0.35} I(s) s^2 \, ds} \qquad /2/$$

where I(s) is the total intensity corrected by Lorentz and polarization factors, $I_{am}(s)$ is the intensity of the amorphous content. The shape of $I_{am}(s)$ was choosen to be identical to the shape of spectrum of the melt.

Fig. 2c shows the DSC trace of the melting process while in Fig. 2d the corresponding volumetric data are presented. The change of specific volume plotted on the ordinate, was corrected for the thermal expansion by the subtraction of the latter:

$$\Delta V = V(T) - V_{25^\circ C} - \alpha_{cr} \left(T - 25^\circ C\right) \qquad /3/$$

where V(T) is the measured specific volume at temperature T, $V_{25^\circ C}$ is that at 25°C and α_{cr} is the thermal expansion coefficient at 25°C.

Comparing the plots of Figs. 2a to 2d, it can be seen that the transition of the β -modification starts at about 130°C and is completed by 150°C. The over-all crystallinity decreases markedly with increasing temperature up to about 140°C where at $k \approx 0.55$ its decrease stops. In fact, at about 142°C, it even increases a little. After the β to α transition has been completed $/k = 0/$, the crystallinity starts to decrease again until the complete melting. The observed DSC diagram is very similar to that obtained by ULLMANN et al. /1979/ at the same scanning rate and can easily be explained on the basis of X-ray analysis. During the β to α transition, the heat transfer is relatively small reflecting to the fact that the endothermic process of disappearance of the β -form crystallites is compensated by the exothermic process of formation of monoclinic α -form crystallites. A small exothermic peak at 142.5°C corresponds to the increasing crystallinity revealed by the X-ray diffractometric results /Fig. 2b/ around the same temperature. The volumetric curve is in full agreement with the X_c and DSC curves. During the β to α transition, the increase in volume change stops for a while reflecting again to an increase in the total crystallinity.

The fact that the β to α transition leads to an increase in the total crystallinity was also confirmed by isothermal experiments /Fig. 3./ when the sample was placed into the diffractometer heating oven already set to the temperature of 141.3°C.

TURNER JONES et al. /1964/ also made observations on the isothermal transition of the β -modification to the α -form and found that the conversion was initially rapid then reduced to a slower rate. It may suggest that at every temperature there is a definite k-value corresponding to the equilibrium between the two modifications. If so, it may be expected for a sample containing the both modifications that, upon recooling the relative amount of the β-modification will increase.

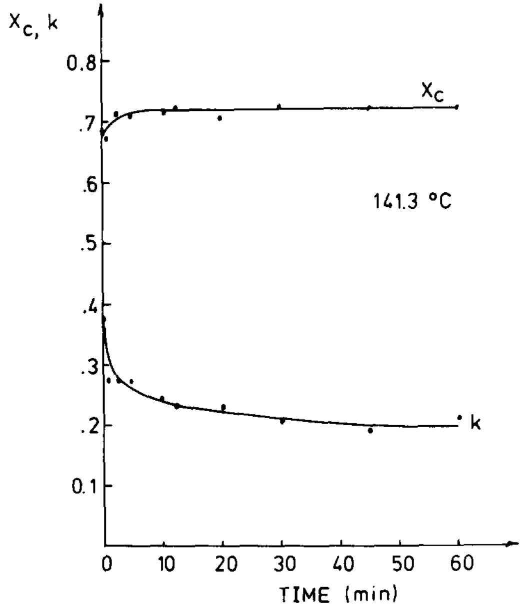


Fig. 3.
β to α transition at constant temperature

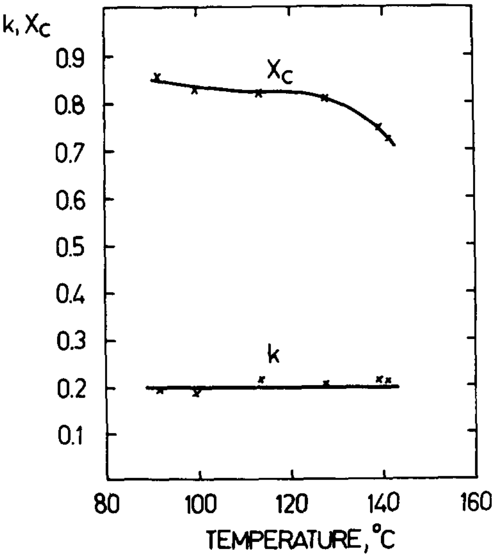


Fig. 4.
Temperature dependence of the β content, /k/ and the total crystallinity, X_c upon recooling from 141°C.

We carried out such experiments by interrupting the heating process at 141°C when both modifications were present and cooling down the sample to a lower temperature again. While crystallinity increased by decreasing temperature, the k-value remained practically constant /Fig. 4./, confirming the statement of ULLMANN et al. /1970/, that the β modification is metastable with respect to the α modification.

CONCLUSIONS

From the presented wide-angle X-ray scattering, DSC and dilatometric data, the following conclusions can be drawn:

/i/ The β-form crystallites transform into α -form in the temperature range of 130 to 150°C.
/ii/ This transition acts toward the increase in total crystallinity.
/iii/ No reversed / α to β/ transition was observed.

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