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Melt Crystallization of Polypropylene: Structure Formation

V. I. Poddubny, V. K. Lavrentyev, V. A. Shevelev, N. V. Mikhailova, A. V. Sidorovich and V. G. Baranov

Institute of Macromolecular Compounds, the USSR Academy of Sciences,
199004 Leningrad, UdSSR

SUMMARY

The steps of order formation during the polypropylene cooling from superheated to supercooled melt were determined by wide-angle X-ray scattering. The symmetrical Gaussian halo at the temperatures higher than 280°C is the manifestation of intermolecular short-range order. Below 280°C the additional halo corresponding to the intramolecular short-range order connected with the helix fragments formation appeared. In the supercooled melt just before the beginning of the crystal formation process the diffractogram profile was similar to that of the paracrystalline form consisting of the long distance one-dimensional order domains. The existence of this metastable form with mesomorphous structure was confirmed by NMR and IR data.

INTRODUCTION

Crystallization of polymers is usually considered as a superposition of two processes. First is the formation of regions exibiting local orientational order. Secondly the turns of single chain segments nessesary for the three-dimensional lattice formation (FRENKEL 1968). As to the first process which is of a purely polymeric nature, it seemed reasonable to assume the existence of such domains in the melt already, i.e. in the amorphous state. Usually the closeness of densities in amorphous and crystalline state is discussed as a prove of such assertion. Experimental investigation and also the broad discussion of the problem of the amorphous polymers structure have shown, however, that the resolution provided by known structural methods usually does not make it possible to observe these regions (FLORY 1976). Nevertheless some experimental data definitely indicate that a structure transition exists in the melts of crystallizing polymers (data usually refer to polypropylene (PP) and poly-4-methylpentene-1) at the temperatures higher than the melting point (SIEGLAFF et al. 1969, WILKES and LEHR 1973, KRÜGER et al. 1980, MATROSOVICH et al, 1980). In other words, there is a temperature range where stable aggregates of probably mesomorphous nature exist and make an effect on the rheological properties of the melt. For PP this assumption is the true because of the calorimetric data from (SMIT 1972).

In the present work we attempted to follow the structure formation in PP on cooling from very superheated melt (300 °C) down to a temperature of 150 °C when crystallization takes place with a pronounced rate.

MATHERIALS AND METHODS

The Daplen PP ($M_w=3\cdot10^5$) was investigated. Wide angle X-ray measurement were done by the use of a diffractometer DRON-1 (USSR). IR spectra were measured with a spectrometer Perkin Elmer 580 B. The free induction signal of protons were measured with an impulse NMR relaxometer RRP-1 (USSR) operating at 16 MHz. All the instruments were equipped with thermoblocks which made it possible to carry out the measurements at high temperatures which control accuracy to within 1 K.

DISCUSSION

Diffractograms of PP taken at various temperatures are shown in Fig.1. The melt scattering curve at a temperatures of more than 280 °C represents a broad (halfwidth $2\theta=6^\circ$) bell-shaped symmetric reflection with its maximum in the range of $2\theta \approx 12.5^\circ$. The corresponding d-spacing value is 7.1 Å (Fig. 1a). If thermal expansion is taken into account, this value corresponds to the mean intermolecular distance in the well-known paracrystalline phase of PP which can be formed on fast chilling of the melt (NATTA et al.1959). It means that in solid state this charasteristic of macromolecular packing can be retained.

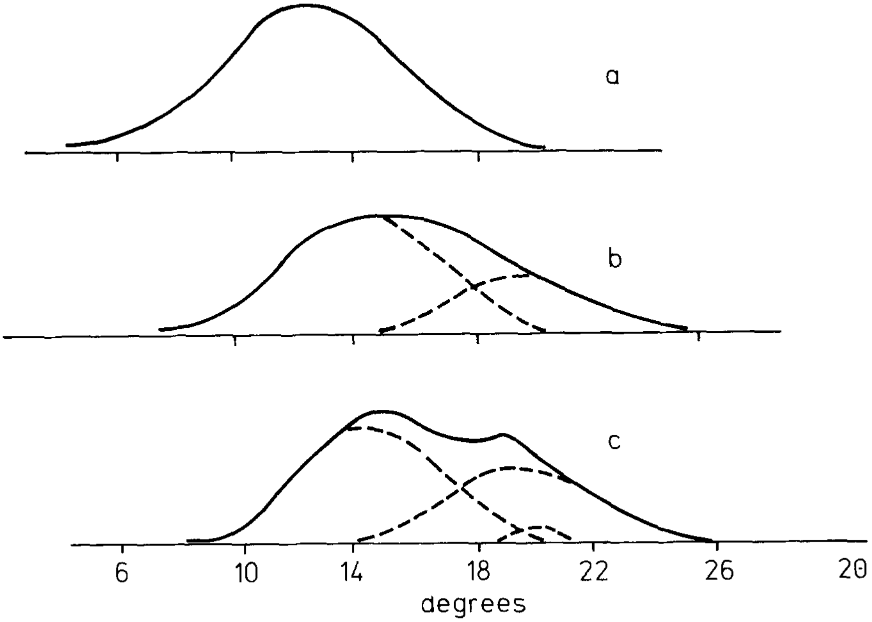

Fig.1. Difractograms of PP melt at 280°C - a; at 280°C - b and just before the beginning of crystal formation in supercooled melt - c.

Below 280°C the reflection shape changes. The symmetry is lost and a "tail" appears in the wide angle range (Fig.1 b). This can be explained due to the presence of a second broad reflection of much lower intensity located in the range of $2\theta=20^{\circ}$. Fig.1b shows the result of computer separation of the scattering curve into two reflections of Gaussian shape. The intensity of the second reflection increases with a decrease in the temperature. The corresponding d-spacing value of this reflection is 0.42nm, which is the characteristic distance along the helical macromolecules of PP (ZANNETTI et al. 1968). Hence it is reasonable interpret this reflection as a manifestation of the short-range intramolecular order. The appearence of this reflection may imply that macromolecules with relatively large fragments exhibiting stable helical conformation have appeared in the melt. The length of these fragments should be no less than three monomer units, i.e. a complete helix turn, On the other hand, judging by a considerable spreading of the reflection, their width can't be very large. The fraction of these self-ordered fragments increases with a decrease in the temperature.

Upon reaching the temperature value lower than that of crystallization the samples were thermostatted at various temperatures in the range of 135-160°C up to the beginning of crystallization. The difractograms showed an increase in the intensity of intramolecular reflection in time. In some cases in a moment immediately preceding the start of crystallization it was possible to obtain diffractograms exhibiting a broad intermolecular reflection and relatively narrow intrachain reflection comparable to the former in intensity (Fig. 1 c). It can be assumed at this moment the melt contains the domains of long parallel fragments of extended macromolecules exhibiting helical conformation. The packing of the chains exhibits the short-range order only. This difractogram is similar to those of PP paracrystalline form and differs from them in a greater half-width of the first reflection, i.e. in the lower degree of order of macromolecular packing and possibly smaller transverse dimensions. It can be assumed that in this case the domains of mesomorphous state occur in the melt. This state is metastable, and short time of the transition from this state to crystalline phase hinders the registration of the mesomorphous nuclei appearance and also the investigation of the kinetic of the process by usual methods.

The method of wide-angle X-ray scattering is unsuitable for the determination of kinetic parameters of crystallization, since the recording of one diffractogram according to which the degree of crystallinity can be determined, takes considerable time, hence requires the selection of temperatures at which crystallization rate is low enough. However the dilatometric method which is usually employed for this purpose cannot provide information on the appearance of the metastable mesomorphous state described above because of probable closeness of the densities of this phase and crystalline phase (by analogy with the paracrystalline form (McALLISTERet al.

1978). As a result the kinetics of crystallization was studied by NMR-relaxometer and IR-spectrometer.

Fig.2 shows the time dependence of amorphous portion in PP crystallization at 140°C. It was determined by signal form of free induction decay at 200 (a) and 500 mcsec (b) after the system had been subjected to 90°-impulse. The shape of SFI is determined by the coexistance of three phases in the system: crystalline, amorphous, and, possibly, mesomorphous. Crystallization is accompanied by a change in the proportion of this components, to be precise, by the appearence and increase in the contribution of a narrow component peculiar to the SFI of crystal.

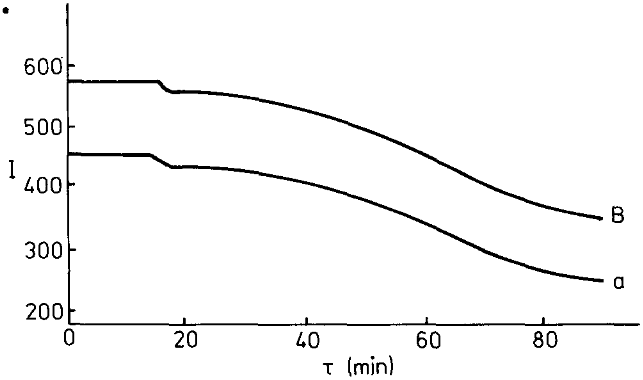

Fig.2. The time dependence of intensity of free induction in supercooled melt at 200 - a and 500 mcsec - b after the signal.

It can be seen that curves exhibit a peculiar feature: a step after completion of the induction period which is usually considered as being related to nucleation. We suggest that this feature generally not observed in usual dilatometric experiments is due to the formation of an intermediate mesomorphous phase before crystallization. Its observation by X-ray diffraction method has been described above.

The precision of the experiment did not allow to choice whether this phase precedes crystallization onlt in the first stage, i.e. in the nucleation, or precedes the formation of crystals throughout the entire crystallization process.

Indirect evidence of the intermediate state existance in the process of PP crystallization is also presented by the data of IR-spectrometry. Melt-crystal transition is accompanied by the appearence of several characteristic absorption bands (KUMPANENKO et al. 1981). The character of appearance is different for two groups of this bands. For example, in Fig.3 time dependence of absorption coefficient for two crystalline bands 998 and 845 cm^{-1} is presented with crystallization of PP melt at 140°C.

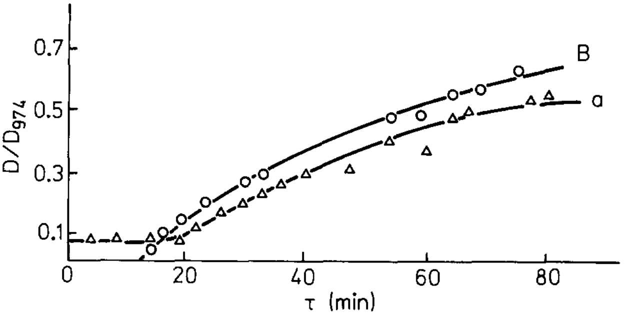

Fig.3. Time dependence of absorption coefficient for the bands 998 (a) and 845 cm^{-1} (b) in supercooled PP melt.

While the band 998 cm^{-1} appeares in the middle of the induction period, the band 845 cm^{-1} appeares early in the beginning of the crystal growth and changes at the same manner as the degree of crystallinity. This result can be interpreted as a manifestation of appearance of the domains with intramolecular order even in the induction period, which makes clear the physical sense of phenomenon (band 998 cm^{-1} corresponds to the defectless spiral fragments longer than 4 turns (KUMPANENKO et al 1981). Band 845 cm^{-1} and also some other crystalline bands absence at this moment can be interpreted as a consequence of the necessity of the compact intermolecular packing for their manifestation. Additional confirmation of such a difference in qualitative attribution of these bands is the difference in the relation of the absorption coefficients of monoclinic and paracrystalline forms, though their spectra almost coincide. While for crystals $D_{998}/D_{845}=1.16$, for paracrystals $D_{998}/D_{845}=1.26$. This fact confirms that the band of 845 cm^{-1} is more sensitive to the quality of macromolecular packing as it has been mentioned above in the explanation of IR-spectroscopy data on PP crystallization, i.e. that intermediate metastable form with mesomorphous structure precedes crystal formation from the melt. The data of (BOLOTNIKOVA et al. 1982) on the rheological properties of the supercooled PP melt also has been indicated the existence of the supermolecular structures in the supercooled melt.

We believe that the existence of this metastable form before crystallization of the unpertubed melt is a general property of all flexible-chain polymers. The problem is only in the possibility of its detection. This possibility is determined by the degree of stability. In the PP case the relatively high stability of this phase is due to the same factor as the existence of the metastable paracrystalline form, i.e. relatively high intramolecular forces acting in this polymer.

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