Polymorphism of the Poly(ethylene oxide)–*p*-Nitrophenol Complex

P. Damman* and J. J. Point

Physico-Chimie des polymères, Université de Mons-Hainaut, 20 Place du Parc, B-7000 Mons, Belgium

Received June 15, 1994; Revised Manuscript Received November 14, 1994®

ABSTRACT: In previous papers, the structure and the spherulitic morphology of the α crystal form of the poly(ethylene oxide)–*p*–nitrophenol molecular complex were described. The observation of another spherulite morphology (*β*) of the same compound was now reported. The spherulitic growth rates were found to be significantly lower than those of α spherulites, and their melting point was observed 30 °C lower. From a polarized FTIR study of these *β* spherulites, it appears that they are made of a new allotropic form of the molecular complex which surprisingly corresponds to the same stoichiometry but shows a different polymer conformation and molecular packing. These changes were attributed to the hydrogen bonds involved between host and guest molecules.

Introduction

Poly(ethylene oxide) (PEO) is known to form crystalline complexes either with inorganic molecules such as mercuric chloride and alkali salts or with organic molecules such as urea, thiourea, *p*-dihalogenobenzenes, and resorcinol.[1] The structure of the α crystal form of poly(ethylene oxide)–*p*–nitrophenol (PEO–pnp) molecular complex stable at room temperature was previously described.[2,3] It corresponds to stacks of pnp molecules which stabilize the macromolecules in the unusual ($t_2gt_2gt_3$) glide conformation. This complex was found to crystallize from the melt as lamellae, revealed by transmission electron microscopy, and small-angle X-ray diffraction.[4] The curve giving the thermal dependence of the linear growth rate of the α spherulites showed two breaks at 58 and 65 °C which were related to a change in the crystallographic orientation of the growth front. The growth face is a (100) facet below 58 °C and above 65 °C, but in between these temperature ranges, the leading facet is a (010) plane.[4] These observations imply that subtle modifications in the structure of the crystals, such as a change of the fold plane, were associated with the kinetics of crystal growth. In this paper we report the observation of a new type of spherulite. Their growth rates are significantly lower than those observed for the α spherulites. By a polarized FTIR study we have shown that these spherulites are made of a new allotropic form of the PEO–pnp compound.

Experimental Section

Preparation of the Samples. The samples were made from PEO and pnp (M_w 6000 and 35 000 from Hoechst) by melting stoichiometric mixtures of the two components. The stoichiometry was previously determined by calorimetry and was found to correspond to 4 pnp molecules for 6 PEO monomeric units.[2] The *β* spherulites may be nucleated at random places by quenching a few seconds in liquid nitrogen samples in the melt phase or at precise places by pressing on the cover slide of the preparation with a fine stylus at liquid-nitrogen temperature.

Polarized Optical Microscopy. Polarized optical microscopy observations were carried out on a Leitz Wetzlar Ortholux microscope, in conjunction with a Mettler hot stage FP54. The hot stage was calibrated with standard melting point substances in the temperature range of interest. Sample films, 10 μm thick, were prepared between coverslips and microscope slides. The growth rates of the spherulites were measured at regular intervals prior to impingement. This procedure was repeated several times for each temperature of crystallization to give growth rates with a standard deviation lower than 5%.

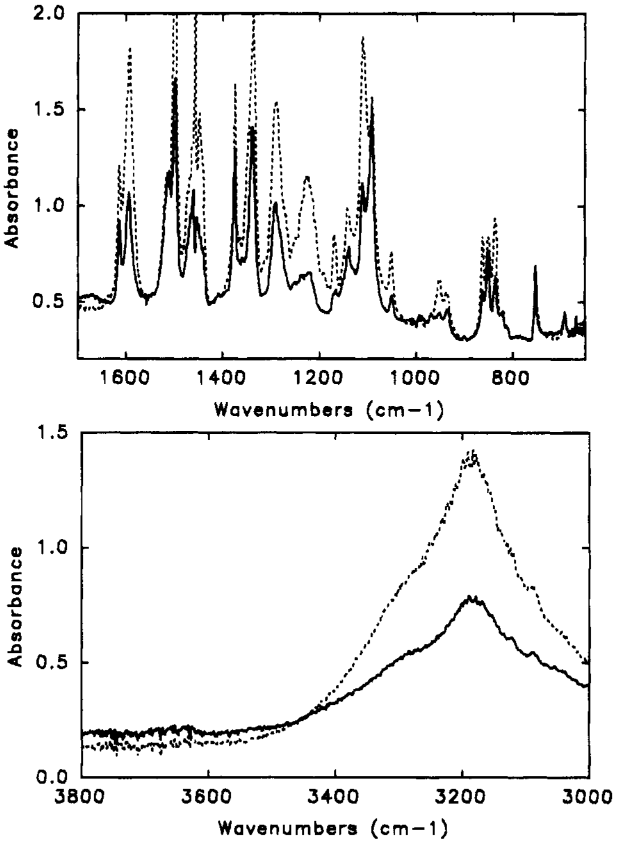

Figure 1. Polarized FTIR spectra of a peripheral part of a PEO (M_w 6000)–pnp *β* spherulite crystallized at 40 °C. Solid (broken) line: polarization parallel (perpendicular) to the spherulite radius.

FTIR Spectroscopy. FTIR spectra were recorded with a Micro FTIR fitted on a Bruker IFS-113V spectrometer. At least 16 interferograms were coadded with a resolution of 2 cm^{-1}. The polarized spectra of peripheral parts of spherulites were recorded with an aluminum wire grid polarizer deposited on a KRS-5 window.

® Abstract published in *Advance ACS Abstracts,* February 15, 1995.

0024-9297/95/2228-2050$09.00/0

Table 1. Wavenumbers and Dichroism Observed for the PEO Vibrations in α and β PEO−pnp Spherulites

PEO (α (100) spherulite)		PEO (β spherulite)	
wavenumber (cm^{-1})	dichroism	wavenumber (cm^{-1})	dichroism
m 457	∥	w 667	∥
sh 841	∥	w 821	⊥
m 871	⊥	s 834	⊥
m 950	⊥	m 934	⊥
s 1032	∥	m 951	⊥
m 1036	⊥	s 1049	⊥
s 1135	∥	s 1140	⊥

Results and Discussion

Conformation of the PEO Macromolecules. Figure 1 gives the polarized FTIR spectra of β spherulites of a PEO (M_w 6000)−pnp complex crystallized at 40 °C. Tables 1 and 2 give the wavenumbers and dichroic behavior observed for PEO and pnp vibrations in α and β samples. From Table 1, the IR spectra of the polymer are found to be completely different in both crystal forms. In the β spherulites, PEO vibrations which characterize the ($t_2gt_2gt_3$) conformation (457 cm^{-1}, for instance) have disappeared and new modes at unusual frequency were observed (667 cm^{-1}, for instance). Thus, the macromolecule conformation in the β form is neither the ($t_2gt_2gt_3$) glide type conformation previously determined for the PEO−pnp α form[3] nor the usual 7/2 helical conformation observed for pure PEO. Unfortunately, the instability of the β spherulites with time did not allow us to record X-ray diffraction patterns suitable to determine the unit cell of the β form.

Table 2. Wavenumbers and Dichroism Observed for the Aromatic Vibrations in a PEO−pnp Crystalline Complex (α and β Spherulites)

symmetry, wavenumber (cm^{-1})	pnp (α spherulite) dichroism	pnp (β spherulite) dichroism
a_1, 1166	∥	⊥
1500	∥	⊥
1589	∥	⊥
1612	∥	⊥
b_2, 694	⊥	∥
755	⊥	∥
851	⊥	
b_1, 3084	⊥	⊥
ν_{OH}[a]	∥	⊥
sciss_{NO_2} 863	⊥	⊥
$\nu_{as\ NO_2}$ 1512	⊥	

[a] The wavenumber depends upon the crystal form; see text.

Orientation of the pnp Molecules. The vibrations of the pnp molecules may be treated with a C_{2v} symmetry point group. The transition dipole moments of the vibrations corresponding to b_2, b_1, and a_1 representations are along *X*, *Y*, and *Z* axes which corresponds to the out-of-plane axis, the in-plane axis normal to the 1−4 axis, and the 1−4 axis, respectively. The attributions of the pnp modes of vibration based on the normal-mode analysis of different aromatic molecules found in the literature[5] and the dichroism observed for differently oriented samples of the PEO−pnp α form[3] are summarized in Table 2. From Figure 1 and Table 2, we can see that the vibrations belonging to a_1 and b_1 symmetries are polarized perpendicular to the spherulite radius. However, the b_2 modes are polarized parallel

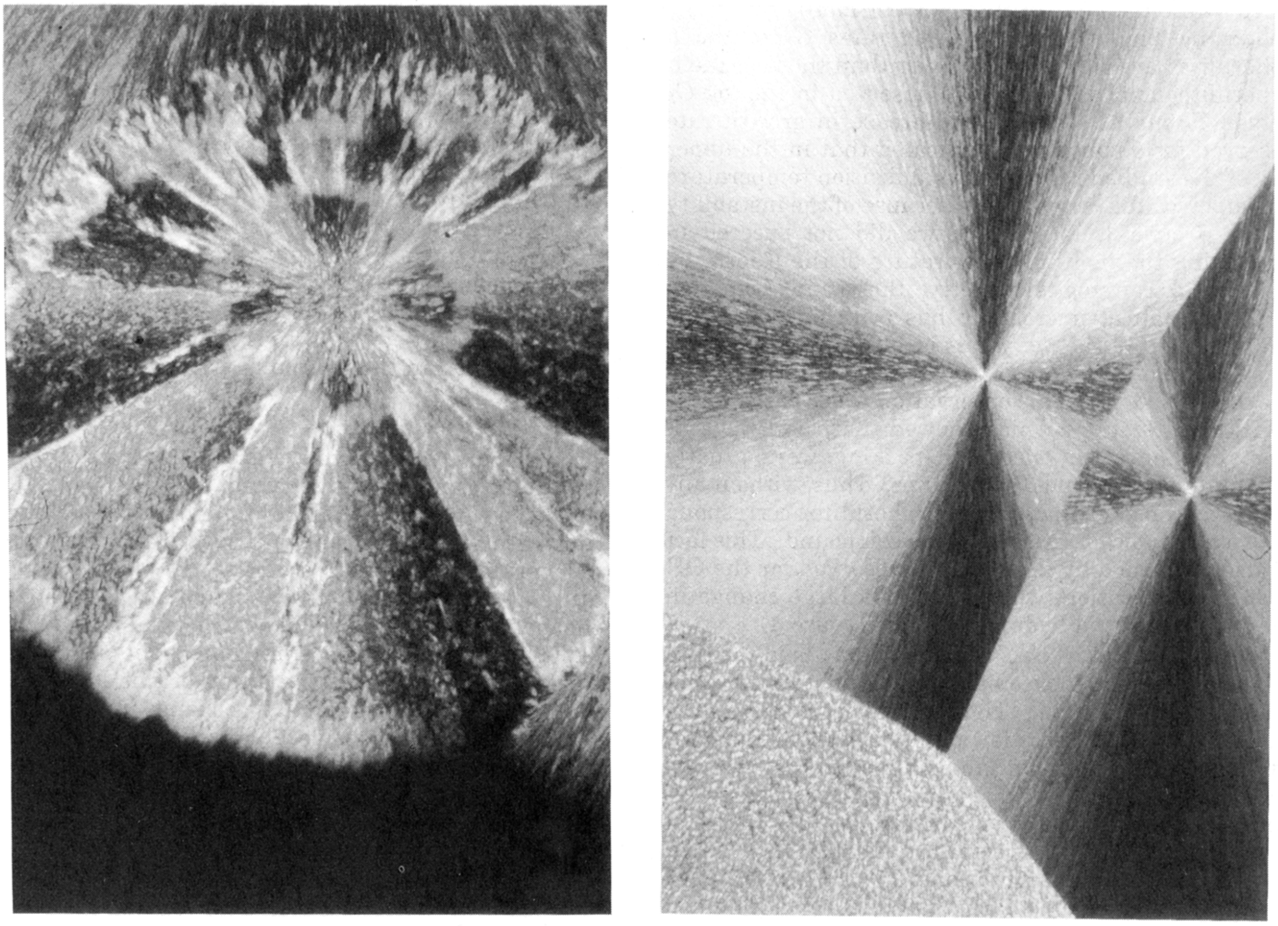

Figure 2. Optical micrographs of α (right) and β (left) spherulites crystallized at 40 °C.

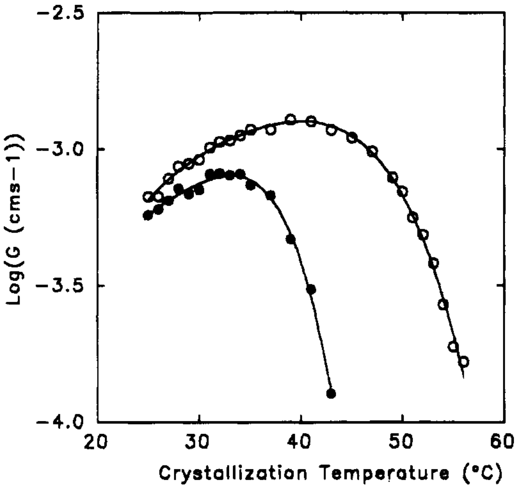

Figure 3. Linear growth rate of α (○) and β (●) spherulites of PEO (M_w 6000)–pnp versus the crystallization temperature.

to the radius. Thus, the dichroic measurements have shown that the out-of-plane axis of the pnp molecules is preferentially oriented along the radius of the spherulite. This molecular orientation is surprisingly different than in both (100) and (010) α spherulites where the plane of the pnp molecules was found to be parallel to the spherulite radii.[3] This change in molecular packing is an additional reason which may account for the large difference in melting point observed for these two crystal forms.

Kinetics of Crystallization. Melting Point. Figure 2 shows the optical micrographs of α and β spherulites crystallized at 40 °C. The α spherulites have a fine fibrous texture and a well-defined Maltese extinction cross, while the β spherulites appear more coarse. As shown by Figure 3, the growth rates G_β of the β spherulites are significantly lower than those of the α spherulites and no breaks are observed in the log G_β versus T_c curve. The sharp decrease in growth rate observed for β spherulites indicated that in the upper end of the studied range of crystallization temperature the supercooling is very low. Because of the instability of the β crystals (see later), we did not succeed in measuring the melting temperature of the β form by differential scanning calorimetry. But visual estimation of T_m by optical microscopy has confirmed that the melting point of the β crystals is surprisingly low. T_m was found to be around 60 °C compared to the T_m of the α form (90 °C). This observation was related to the FTIR investigations which showed that the PEO conformation and the molecular packing were greatly different in both α and β spherulites. Thus, without any doubt we consider that α and β spherulites correspond to two allotropic forms of the same compound. This fact is also confirmed by the red shift observed for the OH stretching vibration, which implies a large change in the strength of the hydrogen bonds (Figure 4).

Metastability of the β Spherulites. As in the case of the PEO–resorcinol complex,[6] the β spherulites were found to be unstable. The β crystals underwent a transformation within a few minutes at room temperature. To determine what kind of process was involved, the FTIR spectra of a β spherulite were recorded before and after the solid-state transformation. Figure 4 clearly shows that the spectra are changed from β to α IR spectra. The PEO vibrations (457, 667, 1036, 1049 cm^{-1}, ...) were particularly suitable to distinguish between both crystal forms. Moreover, the disappearance of the dichroic behavior shows that the solid-state transformation occurs randomly inside the spherulites. This observation greatly differs from the oriented transformation already reported for the PEO–resorcinol complex where a front of transformation similar to a spherulite growth front was observed.[7] The absence of dichroism does not allow characterization of the newly formed α crystals. Finally, we note that the OH stretching wavenumber in the β form (Figure 4) is lower than that in the α form (3272 cm^{-1} for α, 3190 cm^{-1} for β). Despite the metastability of the β crystal form, this shift demonstrates that the hydrogen bonds are more efficient in the β crystal form.[8] This effect is evidently related to the difference in the conformation of the PEO molecules and in the molecular packing.

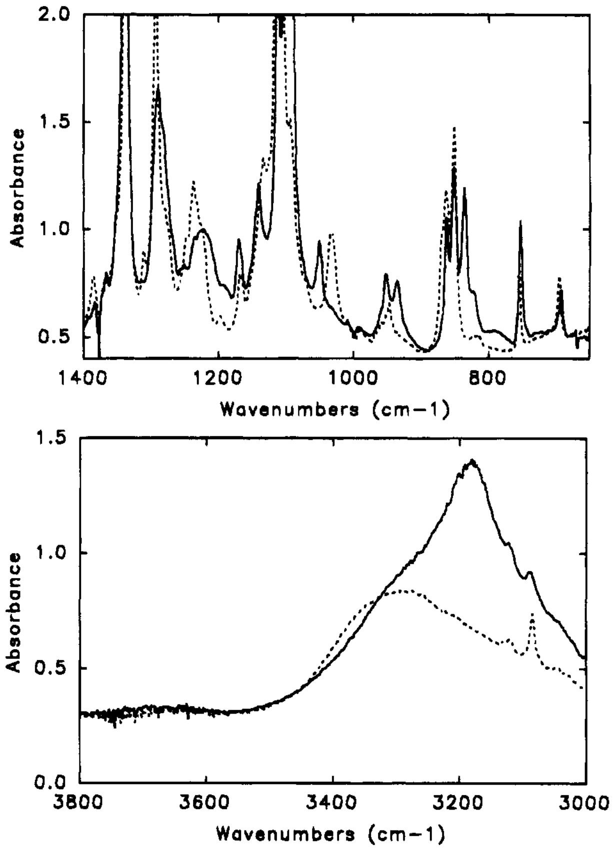

Figure 4. FTIR spectra of a β spherulite before (solid line) and after (broken line) its solid-state transformation.

Conclusions

In conclusion, a new crystal form of the PEO–pnp molecular complex was reported.

The new β form crystallizes from the melt as spherulites with growth rates always lower than those of the α spherulites, previously studied. The melting temperature of the β spherulites was found 30 °C lower than the melting temperature of the α spherulites, and thus explains the kinetic measurements. The FTIR investigations have revealed the origin of this low melting temperature. It was related to a change in the polymer conformation and the molecular packing, both being the clues of the observed polymorphism. Finally, the β spherulites were found to rapidly undergo a solid-state transformation even at room temperature into the more stable α form.

Acknowledgment. P.D. is a Research Assistant of the Belgian National Funds for Scientific Research. This work was supported by the "Ministère de la Région Wallone, programme FIRST" and by the Belgian National Funds for Scientific Research. It was performed in the laboratory of Professor Dosière, who is gratefully acknowledged by the authors.

References and Notes

(1) Iwamoto, R.; Saito, Y.; Ishihara, H.; Tadokoro, H. *J. Polym. Sci., Polym. Phys. Ed.* **1968**, *6*, 1509. Point, J. J.; Coutelier, C. *J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 231.

(2) Point, J. J.; Damman, P. *Macromolecules* **1992**, *25*, 1184.

(3) Damman, P.; Point, J. J. *Macromolecules* **1994**, *27*, 3919.

(4) Damman, P.; Point, J. J. *Macromolecules* **1993**, *26*, 1722.

(5) Garrigou-Lagrange, C.; Lebas, J. M.; Josien, M. L. *Spectrochim. Acta* **1958**, *12*, 305. Evans, J. C. *Spectrochim. Acta* **1960**, *16*, 1382. Stephenson, C. V.; Coburn, W. C.; Wilcox, W. S. *Spectrochim. Acta* **1961**, *17*, 933.

(6) Delaite, E.; Point, J. J.; Damman, P.; Dosière, M. *Macromolecules* **1992**, *25*, 4768.

(7) Villers, D.; Paternostre, L.; Dosière, M. *Macromolecules* **1994**, *27*, 1586.

(8) Pimentel, G. C.; Sederholm, C. H. *J. Chem. Phys.* **1965**, *24*, 639.

MA941311V