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Cooling rate effect on the phase transitions in a polymer liquid crystal: DSC and real-time MAXS and WAXD experiments

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ABSTRACT

The importance of the cooling rate for the structural transformations in a main-chain poly(hexamethylene-4,4′-bibenzoate) has been presented. Detailed analysis of the phase transitions, main structural parameters and their temperature changes has been performed by differential scanning calorimetry, real-time middle-angle X-ray scattering and wide-angle X-ray diffraction methods. The thermodynamic nature of the initial transformation into a smectic A phase has been discussed. The material in the smectic state is supposed to be organized in smectic domains. The crystallization from the smectic phase depends strongly on the kinetics. The crystallization inside the smectic domains results into different final structures determined by the cooling rate applied. At the highest cooling rates, only one crystalline form has been observed. Different possible modifications have been discussed for the case: either a γ-polymorphic form or still some mesophase of high order, as a frozen metastable state. There is a possibility that the phase might be also identified as a condis crystal. At decreasing cooling rates, a new crystalline form, named α*, appears together with the first one. Lowering the cooling rate, the volume fraction of the α*-polymorph gradually increases, at the expenses of the first form. The interesting feature of the new observed α*-polymorph is that it has some similarities with α- and δ-phases of the same material. Contrary to the previous observations, no $\gamma \rightleftarrows \alpha^*$ transformation has been observed neither during the course of single crystallization nor during the subsequent heating. A model describing the gradual transformation of the material during its temperature treatment has been proposed.

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1. Introduction

Thermotropic polymer liquid crystals (TPLC) have been of great interest for many years. TLCPs have high-strength, easy orientation, excellent chemical resistance, ability to incorporate fillers or a great percent of other co-monomers without loosing their liquid crystalline behaviour. Such properties have led to many practical applications of the TLCPs as neat polymers as well as co-polymers or mixtures.

This study deals with poly(hexamethylene-4,4′-bibenzoate) (P6MB), one of TPLC polyesters class. Literature data for P6MB show that at cooling and heating it undergoes two enantiotropic phase transitions [1,2]. At decreasing temperature, the isotropic melt transforms into a liquid crystalline phase–smectic A (SmA) that further on crystallizes. Li and Brisse [3,4] investigated P6MB under some specific conditions (long time annealing, high stretching, or quenching and subsequent annealing and stretching). The authors used a model compound method, as a first step, and then going to the case of the polymer they derived the three possible polymorphs: α, β, γ. They concluded that all crystal unit cells belong to the monoclinic

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system. Form α has $P\bar{1}$ symmetry, six chains form the unit cell and the chains are in face-to-face fashion with faces parallel to the *bc* plane. The unit cell parameters are $a = 1.098$ nm, $b = 1.147$ nm, $c = 1.962$ nm and angle $\beta = 89.7$. Polymorph β has $a = 1.339$ nm, $b = 1.284$ nm, $c = 3.919$ nm and angle $\beta = 84.7$. The chains arrangement is of herringbone type. The interesting feature of the β form is that the unit cell *c*-direction is twice that of α- and γ-polymorphs. Polymorph γ has $P2_1$ symmetry, its unit cell consist of four chains, ordered in a herringbone fashion. The unit cell dimensions are $a = 0.97$ nm, $b = 0.92$ nm, $c = 1.939$ nm and angle $\beta = 83.0$. α- and γ-Polymorphs are assessed to be in *all-trans* spacer conformation, but the dihedral angles, formed between the aromatic rings of the biphenyl groups are 40° and 19°, respectively. Form γ is bulkier than the α one.

Under high pressure, above 100 MPa, a fourth crystalline polymorph – δ – was reported [5,6]. Form δ differs from the others mainly by its *c*-director which is much shorter ($c = 1.57$ nm [5] and $c = 1.76$ nm [6]) than that in the other three forms. That polymorph was obtained from either α- or γ-polymorphs at elevated temperatures and applying high pressure. Once obtained, some of the structure properties were further investigated at lowering the pressure to atmospheric and varying the temperature. Nevertheless, exact crystal identification of form δ was not done.

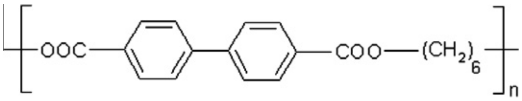
Despite of the comparatively large number of papers devoted to P6MB most of the articles are focused on the final structure attained after some special treatment. There is still a gap in our knowledge about how the structure changes continuously during the treatments and if polymorphs could be observed during the course of simple cooling or heating. Such knowledge is of a great importance for the commercial use of the materials.

The aim of this study is to offer a very detailed and careful analysis of the structural features of P6MB and to show the important effect that exact temperature treatment has on the final formed structure. The results allow one to propose a model of the gradual transformation of the isotropic melt during cooling and consequent heating.

2. Experimental part

2.1. Materials

The investigated material was poly(hexamethylene-4,4′-bibenzoate) belonging to the class of thermotropic main-chain polyesters. It was synthesised at our laboratory by melt transesterification of the diethyl ester of 4,4′-bibenzoic acid and hexamethylene glycol using isopropyl titanate as a catalyst. Consequent purification was made by dissolving the polymer into phenol and tetrachloroethane mixture and precipitating the solution in excess of methanol. The chemical structure of the polymer is shown in Scheme 1.



Scheme 1.

The intrinsic viscosity of the polymer was measured in a phenol–tetrachloroethane mixture at 60 °C, on an Ubbelohde viscometer. A value of 0.9 dL/g was found.

2.2. Methods and experimental details

The thermal analysis was carried out on a Perkin-Elmer DSC-7 apparatus, calibrated with different standards. The sample masses ranged from 5 to 8 mg. DSC (differential scanning calorimetry) thermographs were recorded at different cooling rates (V_c) in the interval from 2 to 40 °C/min. After each cooling experiment, a subsequent heating at a $V_h = 20$ °C/min heating rate was also performed. The heating rate was chosen not too low to prevent a further recrystallization during the heating, and not too high to avoid structure overheating.

Real-time variable temperature X-ray scattering and diffraction experiments were carried out at the beam line A2, HASYLAB (Hamburg, Germany). The wave-length of the X-ray beam was $\lambda = 0.150$ nm. Two linear position-sensitive detectors were used simultaneously. One of them covers the wide-angle X-ray diffraction (WAXD) region (*d*-spacing from about 0.2 to 0.9 nm) and the second one placed at a sample-to-detector distance of 43 cm, middle-angle X-ray scattering (MAXS) region (*d*-spacing range from 1 to 8 nm). The calibration of the spacings was performed with a crystalline PET sample for the WAXD detector and with silver behenate for the MAXS one.

For the X-ray measurements, the samples with a mass of about 20 mg were covered with aluminium foil and placed into the temperature chamber under vacuum. The cooling rates were 2, 4, 10, 20 and 40 °C/min. Subsequent heating was recorded at a heating rate of 4 °C/min.

3. Results and discussion

Previous results [1,2] revealed that under cooling and subsequent heating P6MB melt undergoes two enantiotropic phase transitions: isotropic melt–smectic phase and smectic–crystalline phase. Our DSC (Fig. 1) and X-ray (Figs. 2–8) results confirm generally this sequence. We estimated the transition temperatures from the DCS exo- and endotherms at different cooling rates, varying from 2 to 40 °C/min, as follows:

$$\text{Isotropic\_Melt} \overset{T_{\text{I-Sm}}^{\text{COOLING}}=(232-223)^\circ\text{C}}{\underset{T_{\text{Sm-I}}^{\text{HEATING}}=(243-241)^\circ\text{C}}{\rightleftarrows}} \text{Smectic} \overset{T_{\text{Sm-Cr}}^{\text{COOLING}}=(180-152)^\circ\text{C}}{\underset{T_{\text{Cr-Sm}}^{\text{HEATING}}=(217-208)^\circ\text{C}}{\rightleftarrows}} \text{Crystal}$$

The position of the peak's maximum of the respective thermogram has been used to determine the transition temperature. This value corresponds to the maximal speed of transformation.

3.1. Isotropic melt

Isotropic melt is observed at temperatures above 250 °C. The only feature seen experimentally is a WAXD halo (Fig. 2, $T = 252$ °C). The strong heterogeneity of the

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