Cold crystallization of Poly(ethylene naphthalene-2,6-dicarboxylate) by simultaneous X-ray scattering and dielectric spectroscopy.

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Introduction

Poly(ethylene naphthalene-2,6-dicarboxylate) (PEN) is a semirigid polyester with attractive mechanical properties of potential application for engineering purposes. The crystallization behaviour and microstructure of PEN have been studied by several authors although not so extensively as those of similar copolyesters[1]. Previous studies at HASYLAB have shown that an improvement in the understanding of the crystallization process can be obtained when small and wide angle X-ray scattering experiments (SAXS and WAXS) are accompanied by dielectric spectroscopy (DS) performed simultaneously (SWD)[2]. In a SWD experiment, one may monitor simultaneously, in real time, both, the microstructure development, through SAXS and WAXS, and the dynamic changes occurring in the amorphous phase, by DS.

In the present report we present simultaneous measurements of small and wide angle X-ray scattering and dielectric relaxation spectroscopy (SWD) during isothermal cold crystallization of Poly(ethylene naphthalene-2,6-dicarboxylate) at several temperatures. The general aim of the project is to shed some light on the cold crystallization behaviour by simultaneous characterization of the evolution of both crystalline and amorphous phases in this polymer.

Material

Pelleted PEN (Eastman, Mv ≈ 25000 g/mol) was melted and pressed at a temperature of 290 °C for 2 minutes, under slight pressure. Amorphous films of 0.2 mm thickness were produced by press molding and quenching of the sample in ice water from the molten state.

Techniques

Simultaneous SAXS, WAXS and DS experiments were performed in the Polymer beam-line A2 at HASYLAB (DESY) with a wavelength λ=0.15nm.. Each frame was collected during 60 s. Collected data were corrected for primary beam intensity fluctuations during experiment and background. Complex dielectric permittivity measurements, (ε* = ε ' - i ε '') were performed in the frequency range of 10^3Hz<F<10^6Hz, using a HP 4192 impedance analyzer. Circular electrodes, 3 cm diameter, were employed to prepare a sandwich type capacitor and introduced in an on-purpose designed cell described elsewhere[2].

Results

Fig. 1 presents SAXS-WAXS-DS data during a crystallization experiment at Tc =152° C taken in a simultaneous fashion for different crystallization times. Both, WAXS and Lorentz corrected SAXS intensities are given as a function of the scattering vector q=(4π/λ)sinθ, θ being the scattering angle.
Figure 1: Simultaneous (a) WAXS, (b) SAXS and (c) Dielectric Spectroscopy experiments taken during isothermal cold crystallization of PEN at T= 152°C. The time between consecutive patterns is 10 min..

The \( \varepsilon'' \) data from DS are presented as a function of frequency \( F=\omega/(2\pi) \), \( \omega \) being the angular frequency. The initial amorphous state is characterized by an amorphous halo in the WAXS diagram, a continuous scattering decreasing with \( q \) in the SAXS pattern, due to the liquid-like state, and by the presence of the \( \alpha \) relaxation process centered around a \( F_{\text{max}} \) value of \( 2 \times 10^4 \) Hz in the DS data. The observed relaxation can be identified with the \( \alpha \)-process of PEN[3]. As time increases, the onset of crystallization is denoted by the incipient appearance of Bragg peaks in the WAXS patterns characteristics of the 010,100 and 110 reflections of the triclinic unit cell of the \( \alpha \) crystalline phase of PEN. In the SAXS pattern it is observed an increase of the scattered scattering at lower \( q \)-values that develops into a well defined peak centred around a value of \( q=0.051 \, \text{Å}^{-1} \).

The above mentioned structural features are accompanied by the changes in the dynamics of the amorphous phase as revealed by the simultaneous dielectric experiment. Here, the \( \alpha \)-relaxation exhibits with crystallization time a decrease of its intensity and a shift towards lower frequencies of \( F_{\text{max}} \). The three main features directly derived from our simultaneous experiments support that during primary crystallization the average mobility of the amorphous phase is not notably affected. Upon passing through the cross over time, marking the transition from primary to secondary crystallization the restriction to the mobility of the amorphous phase mainly occurs in the inter-lamellar stacks regions and not in the intra-lamellar stacks amorphous regions. Experiments to further support this hypothesis with other polymers and mixtures of PET and PEN are being prepared for the near future.

References

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