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A near-infrared study of thermally induced structural changes in polyethylene crystal

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Abstract

Thermally induced structural changes of polyethylene (PE) have been studied by means of near-infrared (NIR) spectroscopy in the course of heating up to the melting temperature. NIR bands characteristic of the regular orthorhombic phase, the conformationally disordered hexagonal phase, and the amorphous phase have been successfully identified. It has been found that for the unoriented PE sample, the disordering process of orthorhombic lattice starts above room temperature and that it mostly occurs above 100 °C for the uniaxially oriented PE sample. In the latter case, the enhancement of crystallinity has clearly been detected just below T_m due to the reorganization of crystalline lattice. For the geometrically constrained ultradrawn PE sample, the phase transition from orthorhombic to hexagonal phase has been detected immediately below the melting point. The NIR bands characteristic of the hexagonal phase have been confirmed definitely. Usefulness of NIR spectroscopy has been demonstrated successfully in such a study of thermally induced phase transition behavior of PE samples with appreciable thickness, for which mid-IR spectroscopy is difficult to apply because of the intensity saturation of various key bands.

Keywords: Polyethylene; Near-infrared (NIR); Phase transition

1. Introduction

The structural rearrangement process in semicrystalline polymers on annealing has been a subject of essential importance. Its importance arises not only from fundamental polymer science standpoint but also from industrial point of view. Changes in the aggregation state of the crystalline and amorphous phases during heating are closely related to industrially important properties such as mechanical strength, fatigue life, thermal behavior and appearance. Therefore, a number of investigations were carried out on this matter for more than two decades [1–3]. Among the structural changes occurring upon heating, a phase transition within the crystallite of a polymer has been of particular interest.

When polyethylene (PE) is crystallized from the melt state under elevated pressure, it crystallizes into an orthorhombic phase through an intermediate phase with a hexagonal 'rotator' structure [4–6]. This transition process is known to reversibly occur even under atmospheric pressure in constrained highly drawn PE when it is annealed to the temperature close to T_m [7,8]. The phase transition behavior of PE has been studied mainly by means of X-ray diffraction [9–17]. Differential scanning calorimetry (DSC) [17–22], X-ray imaging [9,18,23,24], and transmission electron microscopy (TEM) [10,13,17,22]. Raman scattering [10,16,18,21,23,25–31] and infrared spectroscopy [9,18,31–38] have also been utilized to explore the phase transition of PE. In vibrational spectra, the bands originating from the monomer sequences in crystalline phase, amorphous phase, and intermediate phase are separately observable. This feature is one of the advantages of vibrational spectroscopy. In addition, polarized vibrational spectroscopy studies enable one to explore the orientation of chain segments with different geometric isomers.

In the research of PE, mid-infrared (MIR) is a very useful technique. However, the transmission measurement of mid-

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IR is limited to a thin sample due to high-absorption coefficient. This limitation requires remarkable sample preparation techniques and skills especially when one studies phase transition behavior of PE under physical tension [18]. Although measurements by Raman spectroscopy generally do not require complexity in sample preparation and measurements, its usefulness is sometimes reduced due to its unsatisfactory S/N and background luminescence that overlaps with Raman signals of interest. Near-infrared (NIR) spectroscopy has advantages over MIR and Raman spectroscopy in the above-mentioned experimental difficulties. Although NIR spectroscopy has been utilized for polymer analysis for more than two decades [31], remarkable progress has been made in the last half decade mainly due to the advances in NIR instrumentation and spectral analysis methods such as chemometrics and two-dimensional (2D) correlation spectroscopy [39]. NIR has been utilized to characterize PE so far. For example, the density of PE has been determined by NIR with multivariate data analysis [40–42]. However, thermally induced structural changes occurring in one of the most fundamental polymer, PE has not been fully studied by NIR yet. Especially, identification of the bands that originate from regular all-*trans* sequence present in orthorhombic phases, those from disordered random sequence of the *trans* and *gauche* rotational isomers in amorphous domains and those due to hexagonal phases have not been reported yet in NIR spectroscopy. In this study, we have succeeded for the first time to identify the bands due to the orthorhombic, amorphous and hexagonal phases by measuring the NIR spectra of thermally treated PE samples as well as the polarized NIR spectra of uniaxially oriented PE. Through this study, we will demonstrate NIR's capability to study the phase transition between orthorhombic and hexagonal phases in PE.

2. Experimental

2.1. Materials

High-density polyethylene Liten MB 62 was the basic material for the present study. The sample was supplied by Chemopetrol Litvínov, Czech Republic. Cold-stretched PE was prepared by drawing the standard dumbbell test piece at 23 °C. The processing conditions for specimen preparation are described elsewhere [43]. The gauge length, width and thickness of the injection-moulded test pieces were 90, 10, and 4 mm, respectively. The obtained draw ratio reached the value of 8.8.

For the preparation of quenched specimen, PE was sandwiched in-between a pair of aluminum foil and melted on a hotplate at 140 °C for 5 min. The melt specimen was quickly cooled in liquid nitrogen. To prepare annealed PE, it was heated to just below its melting temperature, 125 °C and it was kept for 5 min followed by quick cooling in liquid nitrogen.

For the phase transition study, commercially available ultrahigh modulus PE fiber, Dyneema (M_w = ca. 3×10^6 and tensile modulus of ca. 130 GPa, ca. 20 μm in diameter) was used, which was kindly supplied by Toyobo Co. Ltd.

2.2. Measurements

NIR measurements of unoriented and oriented PE samples were performed with a spectral resolution of 4 cm^{-1} by means of a thermo nicolet magna 760 FT-IR/NIR spectrometer. A PbS detector and a CaF_2 beam splitter were used for the measurements in the NIR region. Thirty-two spectra were co-added in each measurement. The spectra were measured for approximate dimensions of ca. $7\times5\times0.5$ mm^3 of the

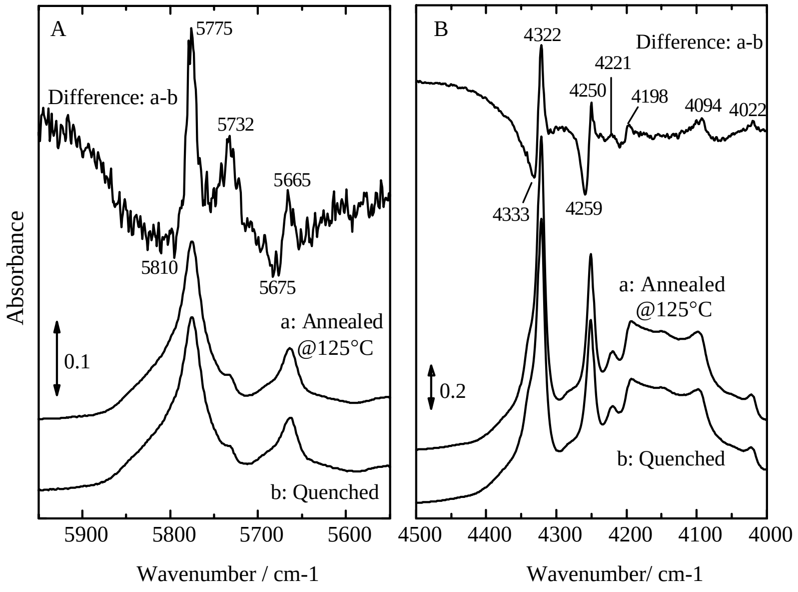

Fig. 1. NIR spectra in the 5950–5600 cm^{-1} (A) and 4500–4000 cm^{-1} regions (B) of unoriented PE after annealing, quenching treatment and their difference spectrum.