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Solid state structure and oxygen transport properties of copolyesters based on smectic poly(hexamethylene 4,4′-bibenzoate)

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Abstract

This study examined the solid state structure and oxygen barrier properties of copolyesters based on smectic poly(hexamethylene 4,4′-bibenzoate) (PHBB) and non-liquid crystalline poly(hexamethylene isophthalate) (PHI). The isophthalate content was varied from 10 to 75 mol%. Differential scanning calorimetry (DSC), wide angle X-ray diffraction (WAXD), dynamic mechanical thermal analysis (DMTA), and atomic force microscopy (AFM) were employed to characterize the polymers. The strong ordering tendency of 4,4′-bibenzoate was demonstrated by the persistence of ordered PHBB structures in copolymers with large amounts of the kinked isophthalate comonomer. Copolymers with up to 50 mol% isophthalate gave evidence of liquid crystalline (LC) character in the precursor melt. Copolymers with up to 75 mol% isophthalate crystallized in the PHBB α-crystal form with only small perturbations of the unit cell. The copolymers provided insight into the low gas permeability of LC polymers. Changes in both solubility and diffusivity contributed to the lower oxygen permeability of the smectic glass compared to the amorphous glass. Smaller free volume hole size of the smectic glass gave rise to lower oxygen solubility and contributed to lower diffusivity. The extended chain conformation in the smectic glass, which reduced the fraction of glycol units in gauche conformations, was a second factor that contributed to lower diffusivity.

Keywords: Liquid crystal polymer; Polyesters; Oxygen transport

1. Introduction

Thermotropic liquid crystalline polymers (LCPs) have been of interest as engineering plastics because of their low viscosity and ease of orientation, their high-strength, and their high barrier performance. The low gas permeability of LCPs stems mainly from low solubility rather than from low diffusivity [1–4]. Other studies reveal the LC glass to have smaller free volume hole size than the amorphous glass [5,6]. If gas solubility is viewed as the process of filling holes of excess free volume, it follows that LC order leads to inherently low gas solubility.

Copolymerization is widely used to extend the structure–property spectrum of polymers in general. Copolymers in which the amount of LC character can be systematically changed are attractive for examining the role of LC character in achieving low gas permeability. This can be readily achieved by copolymerization with a non-mesogenic unit. Of the many possibilities, copolyesters based on 4,4′-bibenzoate offer several advantages. Bibenzoate readily undergoes polycondensation with a variety of diol spacers to form polyesters with smectic order [7]. Moreover, a surprisingly large fraction of a non-LC comonomer can be incorporated before LC behavior is completely lost. For example, poly(ethylene terephthalate-*co*-4,4′-bibenzoate) with up to 65 mol% terephthalate retains some LC-like behavior [8]. Finally, the polymers are tractable and can be fabricated from the melt into films and fibers.

The bibenzoate polyesters often crystallize from the smectic state. Recent studies of polyesters with 5-atom spacers, specifically poly(pentamethylene 4,4′-bibenzoate) (PP5BB) and poly(diethylene glycol 4,4′-bibenzoate) (PDEGBB) found that oxygen transport properties supported a simple two-phase model of impermeable crystallites dispersed in a permeable smectic glass [9,10]. Due to the low crystallite aspect ratio, crystallization only slightly increased the tortuosity of the diffusion pathway. Bibenzoate polyesters with even-numbered spacers crystallize more readily [11]. Poly(hexamethylene 4,4′-bibenzoate) (PHBB) has been well

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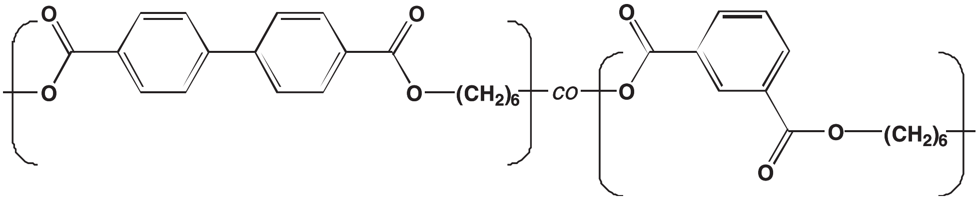
characterized [12,13]. Depending on the thermal history, three crystal forms have been described for PHBB, α, β and γ [14,15]. The present study examines the solid state structure and oxygen transport properties of copolyesters of 4,4′-bibenzoate and isophthalate with the hexamethylene spacer. A structural model is extracted from the combined results of thermal behavior, WAXD, dynamic mechanical response, and morphology by AFM. The structural model is the basis for understanding the oxygen transport properties of this family of polyesters.

2. Materials and methods

Poly(hexamethylene 4,4′-bibenzoate) (PHBB), poly(hexamethylene isophthalate) (PHI) and their copolymers with 10, 30, 50 and 75 mol% isophthalate were provided by KoSa (Spartanburg, SC) in the form of extruded pellets. The chemical structure of the copolymers is



The copolymers are identified as PHBB-*x*I where *x* is the mole percent isophthalate. Randomization of copolymers was virtually ensured under the melt-polymerization conditions that were utilized [5]. The comonomer content is given as the reaction feed.

After the pellets were dried in vacuo for 24 h at a temperature in between ambient and 80 °C depending on the comonomer content, they were compression molded between Teflon-coated aluminum sheets in a press at 150–280 °C to obtain films 180–200 μm thick. Quenched films were taken rapidly from the isotropic melt into ice water. It was not possible to quench PHBB, PHBB-10I, PHBB-30I and PHBB-50I to the amorphous state due to the extremely rapid liquid crystalline and crystalline transitions. It was possible to quench PHBB-75I and PHI to the amorphous state; however, they underwent cold crystallization when stored at ambient temperature due to their low glass transition temperature (T_g), as evidenced by the clear films turning opaque with time. The crystallization was complete in about 3 weeks. Quenched films of copolymers with up to 50% isophthalate were used for characterization unless otherwise indicated. Films used to characterize PHBB-75I and PHI were quenched and aged at ambient conditions for 3 weeks unless otherwise indicated.

Thermal analysis was conducted with a Perkin–Elmer DSC-7 (Boston, MA) calibrated with indium and tin. Dynamic mechanical measurements were carried out in a dynamic mechanical thermal analyzer (DMTA) Mk II unit from Polymer Laboratories (Amherst, MA) operating in the tensile mode, using a frequency of 1 Hz and heating rate of 3 °C min^{-1}.

Wide-angle X-ray diffraction (WAXD) patterns were obtained at ambient temperature with a Philips diffractometer (Natick, MA) in the transmission mode using a slit angle of 1/12 °.

A film specimen for atomic force microscopy (AFM) was vacuum-dried, re-melted under nitrogen, and quenched in air. The surface was etched with 40 wt% aqueous methylamine solution at 23 °C. The optimum etching time was 12 h for PHBB, 1.5 h for PHBB-10I, 35 min for PHBB-30I and PHBB-50I, and 10 min for PHBB-75I and PHI. The etched specimens were washed with de-ionized water and methanol. Initially the specimens were about 35–50 μm in thickness. Etching removed material from the surface to a depth of about 150–400 nm. Images of the etched surfaces were obtained in air at ambient conditions using the Nanoscope IIIa MultiMode head from Digital Instruments (Santa Barbara, CA) in the tapping mode. The procedure was described previously [5,9].

Density was measured at 23 °C with a density gradient column constructed from an aqueous solution of calcium nitrate in accordance with ASTM-D 1505 Method B. Small pieces of film (~25 mm^2) were placed in the column and allowed to equilibrate for 30 min before measurements were taken.

Positron annihilation lifetime spectroscopy (PALS) was performed using a conventional fast–fast coincidence system. The instrumentation and procedures for data analysis were described previously [16].

Oxygen flux $J(t)$ at 23 °C, 0% relative humidity and 1 atm pressure was measured with a MOCON OX-TRAN 2/20 (Minneapolis, MN). The instrument was calibrated with NIST-certified Mylar® film of known oxygen transport characteristics. Specimens were carefully conditioned as described previously in order to obtain the non-steady state oxygen flux from which the diffusivity D was determined [17]. To obtain the diffusivity D and to accurately determine the permeability P, the data were fit to the solution of Fick's second law with appropriate boundary conditions

$$J(t) = \frac{Pp}{l}\left[1 + 2\sum_{n=1}^{\infty}(-1)^n \exp\left(-\frac{D\pi^2 n^2 t}{l^2}\right)\right] \qquad (1)$$

The average thickness l of each specimen was determined as $l = W(A\rho)^{-1}$, where W is the specimen weight, A is the specimen area and ρ is the density. Solubility S was calculated from the relationship $S = PD^{-1}$.

3. Results and discussion

3.1. Slow cooling

The thermograms in Fig. 1 were obtained by cooling from 285 to 0 °C at a rate of 2 °C min^{-1}, followed by heating at a