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Cocrystalline Copolyimides of Poly(ethylene 2,6-naphthalate)

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Supporting Information

ABSTRACT: Copolycondensation of N,N′-bis(2-hydroxyethyl)-biphenyl-3,4,3′,4′-tetracarboxylic diimide (5−25 mol %) with bis(2-hydroxyethyl)-2,6-naphthalate affords a series of cocrystalline, poly(ethylene 2,6-naphthalate) (PEN)-based poly(ester imide). The glass transition temperature rises with the level of comonomer, from 118 °C for PEN itself to 148 °C for the 25% diimide copolymer. X-ray powder and fiber diffraction studies show that, when 5 mol % or more of diimide is present, the α-PEN crystal structure is replaced by a new crystalline phase arising from isomorphic substitution of biphenyldiimide for PEN residues in the polymer crystal lattice. This new phase is provisionally identified as monoclinic, C2/m, with two chains per unit cell, a = 10.56, b = 6.74, c = 13.25 Å, and β = 143.0°.

Semicrystalline aromatic polyesters, notably poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN), have become major industrial materials for fiber, film, and packaging applications since the original discovery of PET in 1941.1 High-temperature applications of PET are, however, limited to some extent by its low glass transition temperature (Tg = 80 °C). This limitation led to the commercial introduction of PEN as a more thermally resistant polyester,2 especially in the form of biaxially oriented film.3,4 Although the Tg of PEN (118 °C) is significantly greater than that of PET, its crystal melting point (268 °C) is only a few degrees higher, so that PEN is still readily processable in the melt.2

Attempts have been made to increase the thermomechanical stability of polyesters still further by introducing rigid diimide comonomer residues.5,6 Although this approach can indeed result in an enhancement of Tg, it has also, until now, invariably led to complete loss of the crystallinity which is essential for achieving biaxial orientation. Even quite low levels of diimide comonomers (as little as 5 mol %) are generally sufficient to destroy the ability of the copolymer to crystallize.5,6

Here we report the synthesis of a new group of copolyester-imides in which biphenyl-3,4,3′,4′-tetracarboximidic residues are incorporated into PET and PEN. Inclusion of this unit in PET at diimide levels above ca. 5 mol % affords only amorphous materials, but copolymers with PEN retain thermal crystallizability across a wide composition range. This result strongly suggests that the biphenyldiimide and naphthalenedicarboxylate (but not terephthalate) units may be isomorphic (Figure 1), enabling their random copolymers to crystallize rapidly even at high levels of diimide.

The novel comonomer, N,N′-bis(2-hydroxyethyl)-biphenyl-3,4,3′,4′-tetracarboxylic diimide (1), was readily obtained from the corresponding dianhydride and 2-aminoethanol (Scheme 1). Copoly(ester-imide)s containing from 2 mol % to 25 mol % of comonomer 1 were synthesized by copolycondensation of 1

Figure 1. Superposition of coplanar models of the bis(2-oxyethyl)-2,6-naphthalate diester (red) and N,N′-bis(2-oxyethyl)-biphenyl-3,4,3′,4′-tetracarboxylic diimide (green) residues, showing their potential for isomorphism.

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Scheme 1. Synthesis of PEN-Based Co(polyester-imide)s (2) via Melt Polycondensation of Bis(2-hydroxyethyl)-2,6-naphthalate with \(N,N'\)-Bis(2-hydroxyethyl)-biphenyl-3,4,3',4'-tetracarboxylic Diimide (1)"
groups adopt the anti-conformation (cf. Figure 1), and the chain itself is thus identical to that found in the $\alpha$-phase of PEN.

Simulation of a powder pattern from this structure gave a promising initial match with experimental X-ray powder data for the copolymers. Energy minimization of the structure using a reoptimized Dreiding II force field, with unconstrained unit cell parameters gave a preliminary unit cell with dimensions $a = 10.82$, $b = 6.75$, $c = 13.27$ Å, and $\beta = 141.6^\circ$. Interactive, manual adjustment of the cell dimensions improved the fit between the simulated and experimental X-ray data very substantially, and the structure was then reminimized with cell dimensions fixed at the derived experimental values ($a = 10.56$, $b = 6.74$, $c = 13.25$ Å, $\beta = 143.0^\circ$).

Examination of the resulting crystal structure (Figure 3) showed it to be consistent with the symmetry operations of space group $C2/m$. Energy minimization in this space group led to a structure giving the simulated powder pattern shown in Figure 3, superimposed on the experimental powder pattern (in red) for the proposed copolymer structure in space group $C2/m$, superimposed on the experimental powder pattern (in blue) for copolymer 2 incorporating 5 mol % of comonomer I.

As shown in Figure 1, the coplanar diester (red) and diimide (green) residues have very similar overall dimensions and so could potentially be accommodated in the same crystal lattice, requiring only that the biphenyl unit also adopts a coplanar geometry. Although a torsion angle of zero at the biphenyl linkage would not represent the energy minimum in an isolated molecule, this geometry is required by symmetry when an inversion center is present at the center of the biphenyl linkage. Indeed, coplanarity is relatively common in the crystal structures of biphenyl-containing molecules, including specifically biphenyl-3,4,3',4'-tetracarboxylic dianhydride. The proposed isomorphism is supported by the uniquely crystalline character of copolymer 2 at high levels of incorporation of monomer I. We have found that analogous PEN copolymers based on other diimide residues, such as diphenylether tetracarboxylic diimide, entirely fail to crystallize once comonomer levels (of 1) exceed ca. 5 mol %.

Oriented film samples of the copolymers 2 gave good X-ray fiber diagrams, with the clearest pattern being obtained from the 20% diimide copolymer. The structure described above, obtained by diffraction modeling of powder data, gave a simulated fiber pattern in very good agreement with the experimental data (Figure 4). It is, however, noticeable that the [0 0 2] reflection on the second layer line in the experimental pattern is displaced slightly above the predicted line. Non-periodic layer lines are characteristically associated with diffraction from copolymer crystallites containing random-
sequence chains and Figure 4 is thus also consistent with the proposed isomorphic character of the two comonomers involved here. We are currently developing more realistic structural models for copolymers that incorporate cocrystal-line biphenyl diimide residues, so that the proposed structure can be refined quantitatively, by Reitveld methods.

Finally, it may be mentioned that we have successfully synthesized PEN copolymers containing up to 20 mol % of comonomer 1 at the 7 kg scale (see SI) and that strong, biaxially oriented film samples have been obtained from these materials using standard polyester processing conditions. Detailed characterization of the new films is now in progress.

**ASSOCIATED CONTENT**

* Supporting Information

Polymer synthesis and characterization information including DSC analyses, 1H and 13C NMR spectroscopic data, GPC chromatograms, and X-ray powder data. Details of computational modeling and diffraction simulation. Atomic coordinates (CIF) for the structural model shown in Figure 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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