# 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)s. 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°.
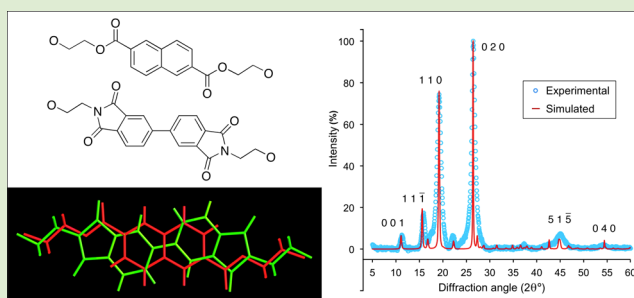
Semicrystalline aromatic polyesters, notably poly(ethylene terephthalate) (PET) and poly(ethylene 2,6-naphthalate) (PEN), have become major industrial materials for fiber, film, and packaging applications since the original discovery of PET in 1941.[1] High-temperature applications of PET are, however, limited to some extent by its low glass transition temperaure (T_g = 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 T_g 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 T_g 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′-tetracarboximide 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 crystalliz-ability 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
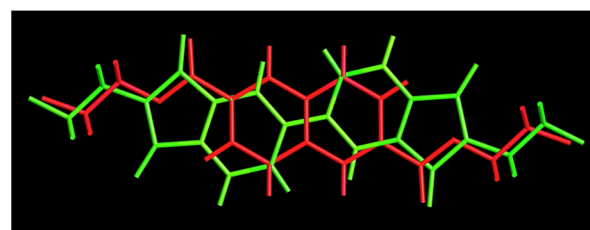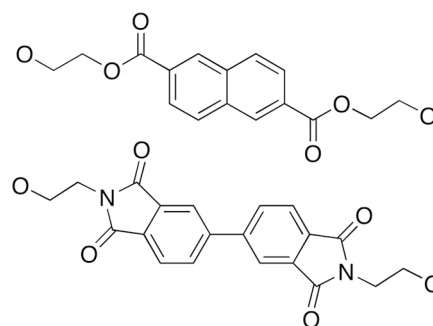
Figure 1. Superposition of coplanar models of the bis(2-oxyethyl)-2,6-naphthalate diester (red) and N,N′-bis(2-oxyethyl)-biphenyl-3,4,3′,4′-tetracarboxylic diimide (green) residues, showing their potential for isomorphism.
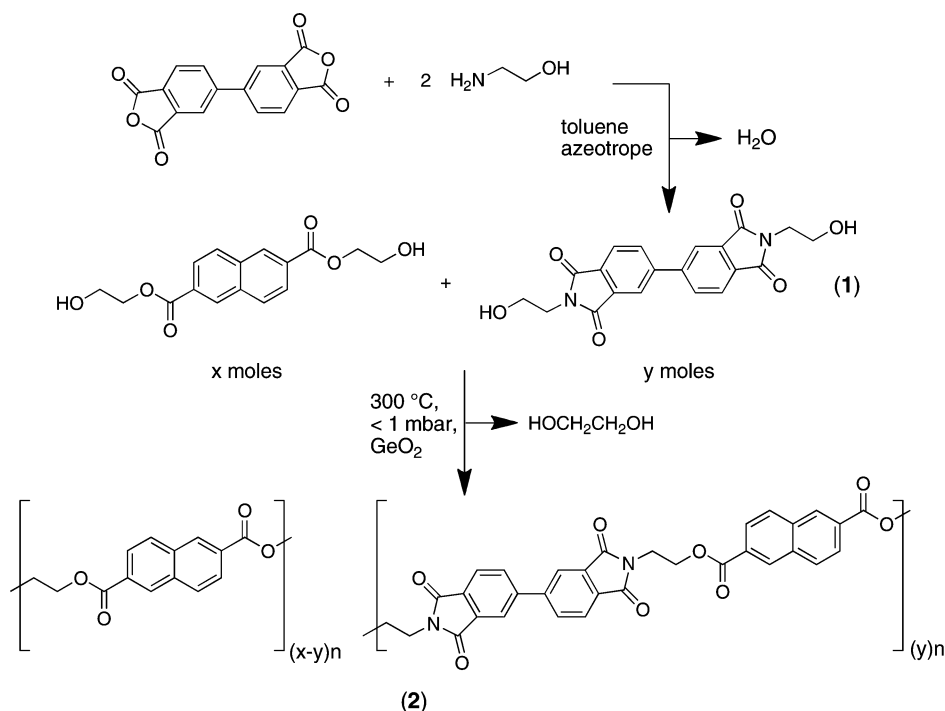
the corresponding dianhydride and 2-aminoethanol (Scheme 1). Copoly(ester-imide)s containing from 2 mol % to 25 mol % of comonomer **1** were synthesized by copolycondensation of **1**

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)[a]

[a]This novel type of polycondensation chemistry requires that y is $\leq x$.

with either bis(2-hydroxyethyl)terephthalate or bis(2-hydroxyethyl)-2,6-naphthalate. Reactions were carried out in the melt, under vacuum, with germanium(IV) oxide or antimony(III) oxide as transesterification catalyst (Scheme 1).

Analysis of the resulting copolymers by ^{1}H NMR spectroscopy showed that, in general, the ratio of diimide to naphthalene-dicarboxylate residues was very close to the monomer feed ratio (see Supporting Information (SI)). Analysis by ^{13}C NMR spectroscopy also showed that the copolymer sequence distributions are entirely random, and size exclusion chromatography gave molecular weights (M_w) in the range 14−18 kDa. As with PET and PEN,[7] postpolymerization in the solid state at 200 °C under vacuum produces a significant enhancement of molecular weight in the new copolymers (e.g., M_w = 16 kDa ⇒ 25 kDa for the 20% copolymer after 16 h of solid-state polycondensation).

Analysis of the new copolymers by DSC (see SI) showed that the ability of PET to crystallize is completely destroyed by the presence of the comonomer at levels of incorporation above ca. 5 mol %. However, PEN responds very differently to copolymer formation, in that substantial crystallinity is retained up to at least 25 mol % of comonomer **1**, at which level the melting point is actually higher than that of the homopolymer. Indeed, the melting point, glass transition temperature, and melt-crystallization temperature *all* increase progressively as the proportion of comonomer **1** rises from 5 to 25 mol %. Although both T_g and T_m increase significantly relative to the corresponding values for PEN, the copolymer melting points remain within the normal processing range for polyester films (280−320 °C). At 20 mol % of **1** for example, the T_g (onset) is 145 °C—an increase of some 27 °C in T_g relative to PEN itself—and the melting point is 286 °C (see also Table 1).

X-ray powder patterns for the new series of PEN copolymers (**2**) are shown in Figure 2, and these confirm that significant

Table 1. Characterization Data for PEN and Its Copolymers with the Biphenyldiimide Monomer 1

polymer	$M_w{}^a$ Da	$M_n{}^a$ Da	$T_g{}^b$ °C	$T_m{}^b$ °C	$T_c{}^c$ °C	$\Delta H_m{}^d$ J g^{-1}
PEN	24 000	5200	118	265	209	37/37
5 mol % **1**	18 000	4100	131	256	192	8/38
10 mol % **1**	19 000	4300	137	262	196	9/34
20 mol % **1**	16 000	3900	144	275	205	15/37
25 mol % **1**	14 000	3700	148	289	236	25/36

[a]By GPC in hexafluoropropan-2-ol. [b]By DSC, second heating scan. [c]By DSC, first cooling scan. [d]Enthalpies of melting before and after annealing at 200 °C for 2 h.

levels of crystallinity are retained for all the compositions investigated (2−25 mol % diimide). Moreover it is clear that, although the α-PEN structure is still present with 2 mol % of diimide comonomer, at 5 mol % the structure transforms abruptly into a new crystal form which is then retained at higher levels of comonomer. A provisional structure for the new crystalline phase has been identified by X-ray powder and fiber diffraction interfaced to computational modeling[8] and is described below.

Because the new crystal form emerges at very low levels ($\leq$5 mol %) of comonomer **1**, the model was approximated as a polymorph of PEN, on the basis that the diffraction pattern simulated from the model would not be greatly affected by the presence or absence of 5% of diimide residues. It was established that the new structure was not the known β-polymorph of PEN as the characteristic β-phase reflections[9] at 2θ = 16.44° and 23.34° (Cu−Kα) are absent from the new pattern. Exploration of possible two-chain cells for the new crystal structure led to a C-centered monoclinic unit cell in which the chain conformation is essentially coplanar. The ester
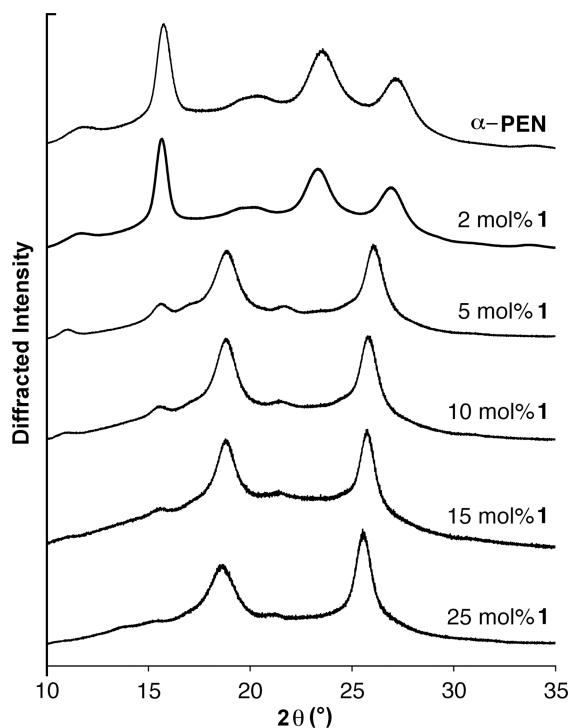
Figure 2. X-ray powder patterns (amorphous background subtracted) of PEN (α-form) and BPDI-PEN copolymers. Samples were cooled from 320 °C and then annealed at 180 °C for 2 h.

groups adopt the *anti*-conformation (cf. Figure 1), and the chain itself is thus identical to that found in the α-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,[10] with unconstrained unit cell parameters gave a preliminary unit cell with dimensions $a = 10.82$, $b = 6.75$, $c = 13.27$ Å, and $\beta = 141.6°$. 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, $\beta = 143.0°$).

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 an experimental pattern for the 5 mol % copolymer **2** from which the amorphous background contribution has been subtracted. Some slight discrepancies remain (perhaps arising from the "homopolymer" approximation in the model), but the agreement in peak positions and relative intensities is clearly very good.

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,[11] 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
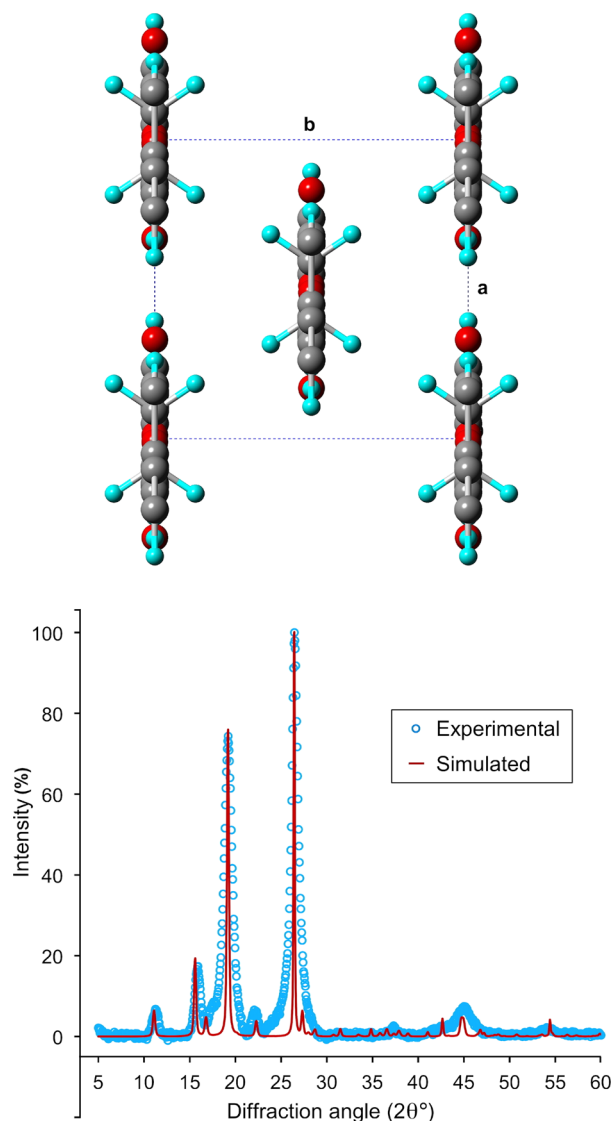

Figure 3. *Top:* provisional crystal structure for copolymer **2**, modeled as a simple polymorph of PEN (monoclinic, $C2/m$, $a = 10.56$, $b = 6.74$, $c = 13.25$ Å, $\beta = 143.0°$, $\rho = 1.42$). Botom: Simulated X-ray powder pattern (in red) for the proposed copolymer structure in space group $C2/m$, superimposed on the experimental powder pattern (in blue) for copolymer **2** incorporating 5 mol % of comonomer **1**.

structures of biphenyl-containing molecules,[12,13] including specifically biphenyl-3,4,3′,4′-tetracarboxylic dianhydride.[14]

The proposed isomorphism is supported by the uniquely crystalline character of copolymer **2** at high levels of incorporation of monomer **1**. 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-
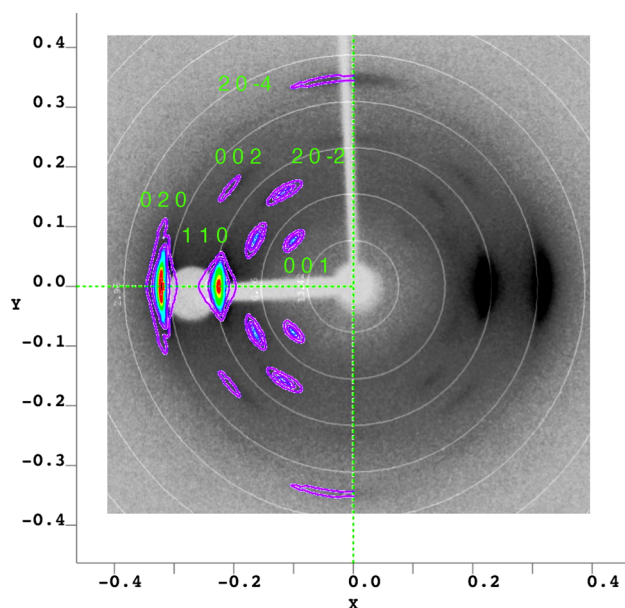
Figure 4. Simulated X-ray fiber pattern (colored contour lines) for the proposed copolymer structure in space group $C2/m$, superimposed on the experimental fiber pattern (greyscale) for a sample of copolymer **2** incorporating 20 mol % of monomer **1**.

sequence chains,[15,16] 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 **2** that incorporate cocrystalline biphenyldiimide 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 ^{13}C 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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■ REFERENCES

(1) (a) Whinfield, J. R. *Nature* **1946**, *158*, 930−931. (b) Whinfield, J. R.; Dickson, J. T. US Patent 2,465,319, 1949 (UK priority date 1941).

(2) Callandar, D. D. In *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*; Scheirs, J., Long, T. E., Eds.; John Wiley: Chichester, 2003; pp 323−333.

(3) Tanabe, T.; Aoki, H.; Murakami, H.; Matsumoto, F. US Patent 3,683,060, 1972 (Japan priority date 1969).

(4) Song, K.; White, J. L. *Polym. Eng. Sci.* **2000**, *40*, 1122−1131.

(5) Park, L. S.; Do, J. H.; Lee, D. C. *J. Appl. Polym. Sci.* **1996**, *60*, 2059−2067.

(6) (a) Xiao, J.; Wan, X.; Zhang, D.; Zhou, Q. F.; Turner, S. R. *J. Polym. Sci., Part A: Polym. Chem.* **2001**, *39*, 408. (b) Xiao, J.; Wan, X.; Zhang, D.; Zhang, H.; Zhou, Q. F.; Turner, S. R. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 852.

(7) Duh, B. *J. Appl. Polym. Sci.* **2007**, *103*, 1075−1084.

(8) (a) Coulter, P. D.; Hanna, S.; Windle, A. H. *Liq. Cryst.* **1989**, *5*, 1603−1618. (b) Colquhoun, H. M.; Williams, D. J. *Acc. Chem. Res.* **2000**, *33*, 189−198.

(9) Lee, W. D.; Yoo, E. S.; Im, S. S. *Polymer* **2003**, *44*, 6617−6625.

(10) Mayo, S. L.; Olafson, B. D.; Goddard, W. A., III *J. Phys. Chem.* **1990**, *94*, 8897−8909.

(11) Barich, D. H.; Pugmire, R. J.; Grant, D. M.; Iuliucci, R. J. *J. Phys. Chem. A* **2001**, *105*, 6780−6784.

(12) Bock, C. P.; Minton, R. P. *J. Am. Chem. Soc.* **1989**, *111*, 4586−4593.

(13) Colquhoun, H. M.; O'Mahoney, C. A.; Williams, D. J. *Polymer* **1993**, *34*, 218−221.

(14) Tong, Y.; Huang, W.; Luo, J.; Ding, M. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 1425−1433.

(15) Gutierrez, G. A.; Blackwell, J.; Chivers, R. A. *Polymer* **1986**, *26*, 348−354.

(16) Sun, Z.; Cheng, H. M.; Blackwell, J. *Macromolecules* **1991**, *24*, 4162−4167.