

# The crystal structure of poly(ethylene furanoate)



Yimin Mao <sup>a,1</sup>, Robert M. Kriegel <sup>b</sup>, David G. Bucknall <sup>a,\*</sup>

<sup>a</sup> School of Materials Sciences and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, United States

<sup>b</sup> The Coca-Cola Company, Atlanta, GA, 30313, United States

## ARTICLE INFO

### Article history:

Received 28 May 2016

Received in revised form

8 August 2016

Accepted 12 August 2016

Available online 16 August 2016

### Keywords:

PEF

Crystal structure

X-ray fiber diffraction

## ABSTRACT

The crystal structure of poly(ethylene furanoate) (PEF) has been determined using X-ray fiber diffraction (XRF) combined with molecular modeling. Analysis of the XRF data suggested the space group was  $P2_1$ , with a monoclinic unit cell where  $a = 5.784 \text{ \AA}$ ,  $b = 6.780 \text{ \AA}$ ,  $c = 20.296 \text{ \AA}$ , and  $\gamma = 103.3^\circ$ , giving a calculated unit cell density of the crystal phase was  $1.562 \text{ g/cm}^3$ . The repeating unit consisted of two monomers related to each other by a  $2_1$  screw axis. It was also shown that two PEF chains were included in each unit cell, with the center-chain being staggered with respect to the corner-chain. Polymer chains were found to be near planar, although careful evaluation showed that the best fit with the data required the cell to contain a mixture of  $3/12$  and  $5/12$  center-chain-staggering.

© 2016 Published by Elsevier Ltd.

## 1. Introduction

Poly(ethylene terephthalate) (PET) is widely exploited in packaging industries and for instance is prominently used for water and soft drinks bottles. However, despite being extremely widely used in such applications, PET has its limitations, particularly in respect of cost as well as issues of finite shelf life of packaged products due to its inherent barrier properties. To this end, initiatives are being explored relating both to the costs, *i.e.*, in generating the polymer from renewable feedstocks for instance, as well as ways to improve its barrier properties. The latter includes multilayer approaches and also inclusion of additives to the PET [1]. An alternative approach is the possibility of replacing PET with another polymer that possesses better barrier properties, and an obvious point to start the search is to explore other polyesters.

Poly(ethylene furanoate) (PEF) is a furan-derived analog of PET, and has the chemical structure shown in Fig. 1. As can be seen, from a structural point of view, the only difference between PEF and PET is that the backbone benzene ring in the PET monomer is replaced by a furan ring in PEF. However, this difference in the primary structure leads to profound consequences in the molecular

dynamics, crystal structure, as well as mechanical and barrier properties of the material [2–7]. With respect to potential applications for plastic beverage bottles, PEF has been found to possess much better gas barrier properties compared to PET, with  $\text{O}_2$  and  $\text{CO}_2$  gas permeability that are 10 times and 19 times lower, respectively [5,7].

The crystal structure of PET was determined more than 60 years ago [8], and consists of a triclinic unit cell with  $a = 4.56 \text{ \AA}$ ,  $b = 5.94 \text{ \AA}$ ,  $c = 10.75 \text{ \AA}$ ,  $\alpha = 98.5^\circ$ ,  $\beta = 118^\circ$ , and  $\gamma = 112^\circ$ . The repeating unit along the  $c$ -axis contains one monomer, with the polymer chain tilted by  $\sim 5^\circ$  with respect to the  $c$ -axis. Whilst the structure of PET has been widely studied the same is not true of PEF, and only a handful of papers have been published describing its crystal structure and crystallization behavior. Part of the reason for this is that compared to other semi-crystalline polymers such as PET, PEF inherently produces solids with a very low degree of crystallinity of at most  $\sim 20\%$ . In addition, the crystallization kinetics are known to be much slower than that of PET, which generates challenges in producing polymers with high enough crystallinity to characterize easily. Some general properties regarding PEF's crystallization kinetics and polymorphism have been recently reported [9–11].

The first, and to the best of our knowledge, the only paper on the crystal structure determination of PEF was reported by Kazaryan and Medvedeva in 1968 [12]. They proposed a triclinic unit cell with dimensions of  $a = 5.75 \text{ \AA}$ ,  $b = 5.35 \text{ \AA}$ ,  $c = 20.10 \text{ \AA}$ ,  $\alpha = 133.3^\circ$ ,  $\beta = 90^\circ$  and  $\gamma = 112^\circ$  based on X-ray fiber diffraction (XRF) results. These authors prepared fiber samples by first stretching the polymer at

\* Corresponding author. Current address: School of Engineering and Physical Sciences, Heriot-Watt University, Edinburgh, EH14 4AS, UK.

E-mail address: [david.bucknall@hw.ac.uk](mailto:david.bucknall@hw.ac.uk) (D.G. Bucknall).

<sup>1</sup> Current affiliations: Department of Materials Science and Engineering, University of Maryland, College Park, MD 20742 United States, and NIST center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD, 20899, United States.

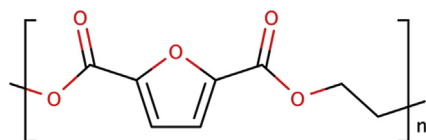


Fig. 1. Chemical structure of poly(ethylene furanoate).

90 °C by a factor of two, and then annealing it at 160 °C for 1 h. In the current paper, we propose a different crystal structure based on XRFD data with improved quality. To prepare aligned crystal with higher quality, the PEF film was annealed at higher temperature for much longer time (see experimental section for details). Careful fiber tilting measurement to examine the meridian diffraction spots was carried out at synchrotron X-ray beamline using a large area detector. More diffraction spots can be resolved owing to these improvements.

Due to intrinsic properties of PEF, such as low crystallinity, small crystal size, and disorder, etc., significant broadening of the measured diffraction spots was observed, making the standard approach of using structure refinement based on the precise determination of peak position and intensity challenging. We report a method that combines crystallographic methods and molecular modeling that ultimately allow us to make direct comparison of simulated 2D diffraction patterns with experimental results, leading to solution of the complex nature of the crystal structure of PEF.

## 2. Experimental methods

### 2.1. Materials and sample preparation

PEF polymer (in the form of melt extruded pellets) was provided by Coca-Cola Company. The glass transition and melting temperature of raw PEF pellet based on Differential Scanning Calorimetry (DSC) data were 86.2 °C and 219.1 °C (endothermic peak position), respectively.

The PEF polymer was dried under vacuum at 140 °C for 3 days before use to remove residual water absorbed by the polymer during storage. The polymer pellets were then melted and pressed into films of homogeneous thickness using a simple mold in a Carver hot press machine with platens set at 240 °C for 5 min, *i.e.*, ~20 °C above its melting point. After pressing, the film was removed from the hot press and allowed to cool down to room temperature. At this stage, the polymer is fully amorphous, due to its slow crystallization kinetics, as verified by both DSC and wide-angle X-ray diffraction (WAXD) measurements. The resulting films had a thickness of 0.8 mm, and were cut into 6 mm × 26 mm rectangular samples using a fine toothed electric saw for subsequent uniaxial stretching treatment.

A Linkam T350 tensile stage equipped with a temperature control unit was used to stretch and anneal the PEF samples. The procedure for preparing oriented crystalline samples for X-ray fiber diffraction experiments is as follows. The sample was mounted in the Linkam stage and heated to 90 °C, then uniaxially stretched at a strain rate of 50 μm/min, until the force reached ~190 N. Whilst holding the sample under constant strain, the sample was then heated up to 180 °C, *i.e.*, ~40 °C below its melting point. Upon reaching 180 °C, the polymer had softened, and the measured force exerted on the sample to maintain a constant strain had dropped to between 30 and 40 N. Once the sample was at 180 °C, it was annealed at this temperature for 4 h maintaining a constant force. After the annealing period the sample was cooled back to room temperature under constant strain.

### 2.2. X-ray fiber diffraction measurements

X-ray fiber diffraction experiments were carried out on the Macromolecular crystallography and BioSAXS beamline F1 at Cornell High Energy Synchrotron Source (CHESS). The experiments were run with a beam energy of 12.686 keV, equivalent to a X-ray wavelength of 0.9773 Å. A Quantum-270 area detector was used to collect diffraction patterns that are stored in 16-bit image files. The sample-to-detector distance was 145 mm, which was calibrated using silver behenate. The X-ray exposure time for each image was 15 s. The sample was mounted as shown schematically in Fig. 2a. The stretched polymer sample was mounted on a frame that was itself attached to a magnetic coupling. This entire piece was attached to a rotatable spindle, so that the tilting angle between the plane of the sample surface and the incident X-ray beam could be adjusted. To ensure correct rotation, the front surface of the polymer film was positioned to intersect the axis of the spindle rotation. The spindle rotation axis was also perpendicular to the incident X-ray direction. Fig. 2b uses the (00*l*) reflection nodes in reciprocal space to demonstrate the scattering geometry. Since the incident X-ray beam direction was initially perpendicular to the fiber axis, to precisely measure the peak position in the meridian direction, the sample needs to be rotated around the spindle axis, so that (00*l*) nodes could intersect with the Ewald sphere. The tilting angle in this intersecting geometry is denoted as  $\delta$ . After projection (see Fig. 2b), the position of diffraction node on the flat detector,  $x$ , is related to scattering angle  $2\theta$  by:

$$\tan 2\theta = x/R \quad (1)$$

and  $R$  is the sample-to-detector distance. To determine the angle of the intersecting geometry,  $\delta$ , the sample was rotated around the spindle axis and diffraction patterns were collected at steps of 1°. The integrated intensity of a given (00*l*) reflection node as a function of tilt angle was then plotted, and the angle at which this intensity reached a maximum corresponds to  $\delta$ . Diffraction patterns shown in this paper were collected at  $\delta=0^\circ$ . More patterns at different tilt angles are shown in the [Multimedia Component 3 of the Supplementary Material](#).

### 2.3. Molecular modeling

Accelrys Materials Studio software was used to construct models of PEF polymer chains in a molecular crystal. The molecular packing within the unit cell and subsequent energy minimization was performed using the Forcite module, utilizing the COMPASS force field. The atomic fractional coordinates were generated after geometry/energy minimization of crystal structures, from which simulated 2D fiber diffraction patterns were generated as described below.

### 2.4. Fiber diffraction pattern simulation

With knowledge of unit cell parameters, atomic positions (in one unit cell), and the polymer chain alignment direction, 2D fiber diffraction patterns can be simulated. The starting point is to determine the structure factor,  $F_{hkl}$  by considering all fractional coordinates of the atoms in a unit cell, ( $p_j$ ,  $q_j$ ,  $r_j$ ), and the corresponding atomic scattering factor,  $f_j$ , using the following equation:

$$F_{hkl} = \sum_{j=1}^n f_j \exp \left[ -i2\pi(p_j h + q_j k + r_j l) \right] \quad (2)$$

where ( $hkl$ ) are the Miller indices defining the nodes in reciprocal

Download English Version:

<https://daneshyari.com/en/article/5178618>

Download Persian Version:

<https://daneshyari.com/article/5178618>

[Daneshyari.com](https://daneshyari.com)