Polymer 54 (2013) 805–811

Contents lists available at SciVerse ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Micro X-ray diffraction mapping of a fluorene copolymer fibre

Christian Müller [a,b,*], Morteza Esmaeili [c], Christian Riekel [d], Dag W. Breiby [c], Olle Inganäs [a]

[a] Biomolecular and Organic Electronics, Department of Physics, Chemistry & Biology, Linköping University, 58183 Linköping, Sweden
[b] Department of Chemical and Biological Engineering/Polymer Technology, Chalmers University of Technology, 412 96 Göteborg, Sweden
[c] Department of Physics, Norwegian University of Science and Technology, Høgskoleringen 5, 7491 Trondheim, Norway
[d] European Synchrotron Radiation Facility (ESRF), B.P. 220, 38043 Grenoble Cedex, France

ARTICLE INFO

Article history:
Received 23 May 2012
Received in revised form
8 August 2012
Accepted 3 October 2012
Available online 4 December 2012

Keywords:
Conjugated polymer fibre
Synchrotron X-ray diffraction
Liquid-crystalline polymer

ABSTRACT

Using raster-scanning wide-angle X-ray scattering, we investigate oriented fibres of the low bandgap conjugated polymer, poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (F8TBT), that was developed in particular for polymer solar cells. For the first time, structural data are provided for F8TBT. Our results demonstrate that the nano-scale structure of this polymer is closely related to the externally observable features of the fibre, and thus emphasise the importance of having full control over the local molecular conformation. Liquid-crystalline phases are observed at elevated temperatures, and the molecular alignment in the drawn fibres yields scattering patterns that are dominated by broad peaks of equatorial diffuse scattering. The significant degree of preferred orientation facilitates the analysis, leading to estimates of (average) nearest-neighbour packing distances and coherence length of this macromolecule. In particular, we observe a pronounced broad signal assigned to packing of the conjugated backbone with an approximate spacing of 4.00–4.39 Å that is coherent over 5-6 polymer segments.

1. Introduction

The field of polymer-based electronics has developed to the point of commercialisation during the past few years, not least because of an improved understanding of the molecular structure and its ramifications on the electronic properties. The conjugated polymer poly[2,7-(9,9-dioctylfluorene)-*alt*-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)] (F8TBT; in the literature also abbreviated as APFO-3 or PFDTBT) has received considerable attention for a variety of opto-electronic applications such as organic photovoltaic (OPV) devices [1–11], field-effect transistors (FETs) [4,8] and organic light-emitting diodes (OLEDs) [12]. In particular the promising performance of OPV devices based on bulk-heterojunction blends of the electron-donating F8TBT and an electron acceptor—usually the small-molecular [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) [1–9], but also CdSe [10] and ZnO nanoparticles [11]— has resulted in significant research efforts. Moreover, when paired with the conjugated polymer poly(3-hexylthiophene) (P3HT), F8TBT can also act as the electron acceptor in bulk-heterojunction solar cells [11]. Structural investigations have largely focused on aspects concerning phase separation in OPV blends since the resulting nanostructures are of immediate relevance for the attainable power conversion efficiency [3,6,9].

In contrast, the organisation of the neat F8TBT macromolecule has attracted lesser attention and only few structural characteristics have been explored. For instance, polarised optical microscopy studies have revealed that F8TBT thin films can display distinct liquid-crystalline textures at elevated temperatures, and thermal studies have indicated a high glass transition temperature in excess of 120 °C [2,8,9]. However, nano-structural features and ordering on the molecular level have not been elucidated in much detail, despite the fact that these attributes are highly relevant for the photo-physical properties of a conjugated polymer such as F8TBT.

Here, we exploit the ability of high molecular-weight F8TBT to form macroscopic fibres that feature pronounced uniaxial alignment. The presence of oriented domains reduces the ambiguity that complicates the interpretation of scattering data from weakly scattering isotropic or multi-domain materials, which until now has precluded structural characterisation of F8TBT. Thus, we utilised raster-scanning Wide-Angle X-ray Scattering (WAXS) to map the macromolecular anisotropy, molecular separation distances and average liquid-crystalline domain size in an F8TBT fibre. We anticipate that knowledge of these characteristics will aid to better understand the interplay between the structure and opto-electronic properties of F8TBT, of related liquid-crystalline conjugated polymers as well as of relevant binary mixtures.

---

* Corresponding author. Department of Chemical and Biological Engineering/Polymer Technology, Chalmers University of Technology, 412 96 Göteborg, Sweden.
E-mail address: christian.muller@chalmers.se (C. Müller).

0032-3861/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.polymer.2012.10.059

2. Materials and methods

2.1. Materials chemistry and processing

F8TBT (number-average molecular weight $M_n \sim 38$ kg mol^{-1}; weight-average molecular weight $M_w \sim 69$ kg mol^{-1}) was studied; for details of synthesis see Ref. [1]. The chemical structure of F8TBT is displayed in Fig. 1. Fibres were drawn from a solid piece of F8TBT after swelling in chloroform.

2.2. Differential scanning calorimetry (DSC)

DSC was conducted under nitrogen from 0 to 320 °C at a scan rate of 10 °C min^{-1} with a TA Q2000 instrument, using a sample mass of ~4 mg. The glass transition temperatures, T_g, and liquid-crystalline/isotropic transition temperatures, T_i, were extracted from inflection and peak temperatures, respectively.

2.3. Optical characterisation

Polarised optical microscopy was carried out with an Olympus BH2 polarising microscope. Polarised photoluminescence emission spectra of F8TBT fibres, excited at 525 nm, were recorded through a linear polarising filter using an Oriel liquid light guide and a Shamrock SR 303i spectrograph coupled to a Newton EMCCD silicon detector.

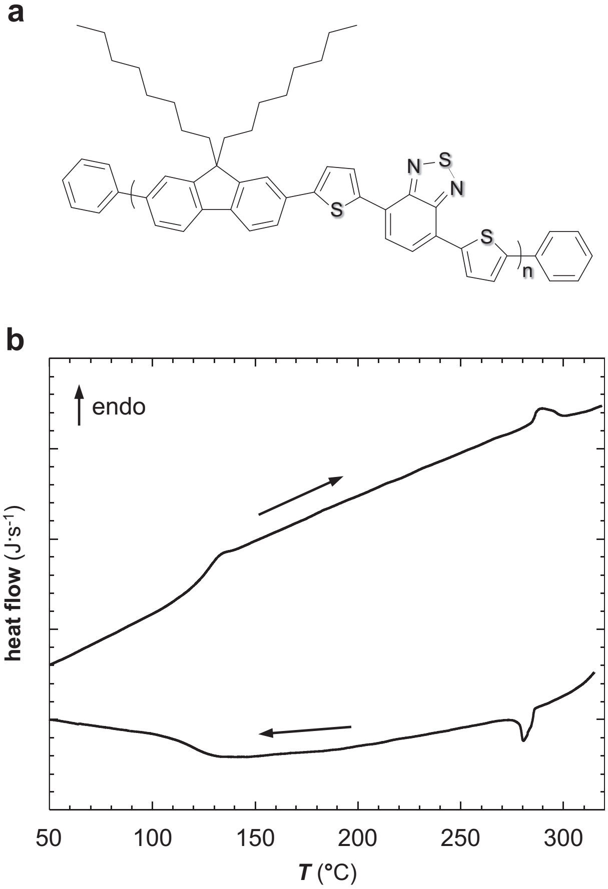

Fig. 1. (a) Chemical structure of F8TBT. (b) Differential scanning calorimetry (DSC) second heating and cooling thermograms of F8TBT.

2.4. Synchrotron micro X-ray diffraction

Diffraction experiments were performed at the ESRF-ID13 beamline using a monochromatic beam of wavelength $\lambda = 0.995$ Å [13]. The fibre was mounted on a MiTeGen Kapton support that was fixed to the beamline scanning goniometer. During the diffraction experiments, the fibre was kept at a temperature of 100 K by an Oxford Cryosystems nitrogen cryo-flow system; no icing was observed during the experimental period. The beam was focused by (crossed) Kirkpatrick-Baez X-ray mirrors to a spot size of about 1.0 × 0.8 μm^2 at the sample position. A 2 × 2 binned Frelon CCD detector with 100 mm converter screen, 2 K × 2 K pixels of 200 × 200 μm^2 size and 16 bit readout was used [14]. The sample-to-detector distance was determined to 94.35 mm using an Al_2O_3 calibration sample. Data collection was done by 2D raster-scans using step lengths of 1 μm across and 2 μm along the fibre. At every raster-step a WAXS pattern was collected, using an exposure time for each diffraction pattern of 1.0 s. Scattering measured outside of the fibre was subtracted as background. In this paper, we use momentum transfer $q = 4\pi \sin\theta/\lambda$, where θ is the Bragg angle. In-house *Matlab* code [15] as well as the program FIT2D [16] were used for the data reduction.

3. Results and discussion

3.1. Liquid-crystallinity of F8TBT

The thermal behaviour of F8TBT was investigated by means of differential scanning calorimetry (DSC; Fig. 1b). Upon heating, F8TBT displayed a glass transition temperature $T_g \sim 128$ °C and liquid-crystalline/isotropic transition temperature $T_i \sim 289$ °C; whereas DSC cooling thermograms yielded $T_g \sim 119$ °C and $T_i \sim 280$ °C. The low enthalpy of fusion $\Delta H_i \sim 1.4$ J g^{-1} (deduced from heating and cooling thermograms) is consistent with a transition between liquid-crystalline ordering and an isotropic state. Whereas the stiffness of the fluorene and benzothiadiazole units gives rise to the liquid-crystalline behaviour, the high T_g can be rationalised with the crank-shaft motion and associated reduction in rotational degree of freedom that arises from the kinked backbone of the macromolecule (*cf.* Fig. 1a) [17].

3.2. Optical anisotropy of F8TBT fibres

The high T_g of F8TBT complicates processing at ambient temperature. Therefore, we swelled the polymer in chloroform, which is a non-solvent for higher molecular-weight F8TBT because chloroform-soluble material was removed during purification. This treatment reduced the T_g sufficiently to facilitate fibre drawing. We have previously reported that such fibres exhibit a considerable degree of optical anisotropy [8], as evidenced by the polarised optical micrograph and polarised photoluminescence spectra shown in Fig. 2. The photoluminescence is predominantly polarised parallel to the fibre axis. This observation corroborates (partial) orientation of polymer chains with the drawing direction since photoluminescence originates from the conjugated backbone of the macromolecule. Incomplete polarisation may arise from imperfect molecular orientation but also from an angular offset between the emitting dipole and the polymer chain. The kinked nature of F8TBT (*cf.* Fig. 1a) may be the origin of this behaviour.

At the peak photoluminescence wavelength $\lambda_p \sim 715$ nm we find a dichroic ratio $R \sim 5.4$. The obtained optical anisotropy is similar to that observed for thin films deposited on rubbed alignment layers [12]. The orientation factor S is defined as [18]: