Polymer 54 (2013) 1251–1258

Contents lists available at SciVerse ScienceDirect

Polymer

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

Insight into lamellar crystals of monodisperse polyfluorenes – Fractionated crystallization and the crystal's stability

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ARTICLE INFO

Article history:
Received 6 October 2012
Received in revised form
18 December 2012
Accepted 20 December 2012
Available online 25 December 2012

Keywords:
Fractionated crystallization
Thermal stability
Solvent annealing

ABSTRACT

Polymer crystals of monodisperse poly (9,9-dioctylfluorene)s (PFOs, named as Fn) on mixing both components (F16 and F64) in different ratios are grown from chloroform/ethanol solutions. In these crystals, lamellar thicknesses corresponding to relevant components can be observed by utilizing atomic force microscopy (AFM). Crystallization of these polymers is accompanied by fractionated crystallization where saturation solubility of different components remarkably affects the crystallization process. Moreover, we report on the stability of the crystal under thermal annealing and solvent annealing. The crystal is thermally stable, but can be eventually dissolved at the good solvent which takes advantages of the slow crystallization process to accomplish the process.

1. Introduction

Organic semiconductor crystals have received wide attention with the rapid development of organic electronics [1–3]. Nowadays, another class of materials, conjugated polymers, has also become a key building block in the device applications such as field-effect transistors (FETs) and photovoltaic cells [4–9]. It is mainly attributed to the availability of their low-cost solution processing and excellent optoelectronic properties. Solution deposition, albeit simple and low-cost, produces inhomogeneous films on the macroscopic scale. Consequently, post-treatment procedures such as thermal annealing [10–13] and solvent annealing [14–17] are frequently applied to promote crystallinity in the fabrication process. Therefore, as the performance of devices strongly depends on the crystallization process and post-treatment procedures, extensive research has been carried out on the two aspects.

On one hand, polymer crystallization [18–20] is viewed as a more complicated process which involves regioregularity, the molecular weight, and crystallization conditions. The first detailed attempt to describe the kinetics of crystal growth was exclusively on the classical growth model of small molecules. The advances in crystal growth of a macromolecule can be summarized by two basically different mechanisms, one leads to predominant chain folding, and the other to little folding in a fringed micelle structure [21]. At the same time, fractionated crystallization, a chain-sorting mechanism, is also observed in some polymers [22–27]. Although concerns about the reality of this crystallization process have been raised [28–36], it is still difficult to draw definite conclusions from the mass of information collected on the growth of crystals, because few of the aspects have been investigated from all sides. This renders the mechanism of polymer crystallization remain obscure. On the other hand, in the case of post-treatments, the crystal's stability is required to be explored.

To further investigate the behavior of PFO chains, it is simple to use monodisperse molecules of different lengths, which can be mixed in controlled ratios, similar to what has been done with *n*-alkanes [25]. Thus, monodisperse PFOs [37–41] are chosen to be an ideal model for this study. In our previous study, PFOs are known to crystallize into extended-chain lamellar single crystals in which the backbones are perpendicular to the lamellae [42]. Herein, on mixing both components (F16 and F64) in different ratios and crystallizing that fully extended chain crystals resulted, two distinct lamellar thicknesses could be observed, corresponding to the two components of the mixture. Together with electron diffraction (ED) and atomic force microscopy (AFM) images, lamellar distribution is analyzed in details and the morphology shows if the molecular weight distribution is not uniform fractionated crystallization will take place and lead to stacking of lamellae which are essentially composed of pure components. In the crystallization process, saturation solubility of different components plays an important

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http://dx.doi.org/10.1016/j.polymer.2012.12.054

role, where species of lower saturation solubility crystallize first. In addition, we also attempt to explore the effects of post-treatments on single crystals of F16. Experimental data indicate that the crystal grown from dilute solution is the thermodynamically stable form either at room temperature or high temperature. However, the crystals will be eventually dissolved at the good solvent.

2. Experiments

2.1. Materials

The synthesis of monodisperse poly (9,9-dioctylfluorene)s (PFOs, named as Fn) was reported previously [43], where *n* represents the number of fluorene units. The exact molecular weights obtained from MALDI-TOF mass spectrometry of F16 and F64 are 6220 and 24874 Da, respectively. The corresponding contour length of F16 and F64 are 13.3 nm and 53.1 nm, which are calculated according to the repeat distance of 0.83 nm [38]. Chloroform and ethanol and carbon disulfide were purchased from Beijing Chemical Works and used without further purification.

2.2. Sample preparation

The solution of F16 was carried out by first dissolving the sample in chloroform followed by the addition of ethanol very slowly. The solvent mixed ratio of chloroform to ethanol was 1/3 (v:v) and the final concentration was 0.005 mg/mL. The substrate was put inside a cylinder container with a radius and height of 1.5 and 3.0 cm, respectively. The solution was deposited onto the glass and the container was then carefully sealed. The same method was applied to the samples blended with two compositions (F16/F64 = 1/2 and 2/1 (w/w)), respectively.

Thermal annealing was performed by using a THMS 600 hot stage (Linkam) connected to a TMS 94 temperature controller. Prior to annealing under nitrogen, the chamber of the hot stage was purged several times with nitrogen.

For the solvent treatment, a certain quantity of CS_2 was dropped onto the sample repeatedly.

2.3. Characterizations

Transmission electron microscopy (TEM) experiments were performed using a JEOL JEM-1011 with an accelerating voltage of 100 kV for bright field TEM and selected area electron diffraction (SAED) modes. The samples for TEM were floated away from the substrate in 10% HF solution and then picked up with a copper grid. The camera length was calibrated with Au to calculate the *d*-spacing of the observed electron diffractions.

Atomic force microscopy (AFM) images were obtained using an SPA-300HV instrument with an SPI3800N controller (Seiko Instruments Inc., Japan) in tapping mode. A silicon microcantilevel (spring constant = 15 N/m, resonant frequency ≈ 130 kHz, Olympus, Japan) was used for the scanning.

The scanning electron microscopy (SEM) images were obtained using FEL XL 30.

Differential scanning calorimetry (DSC) measurement was performed on TA Q100 thermal analyzer at a heating rate of 10 °C/min.

3. Results and discussion

3.1. Fractionated crystallization

In this study, fractionated crystallization is investigated in great details by mixing F16 and F64 in different ratios. An important way

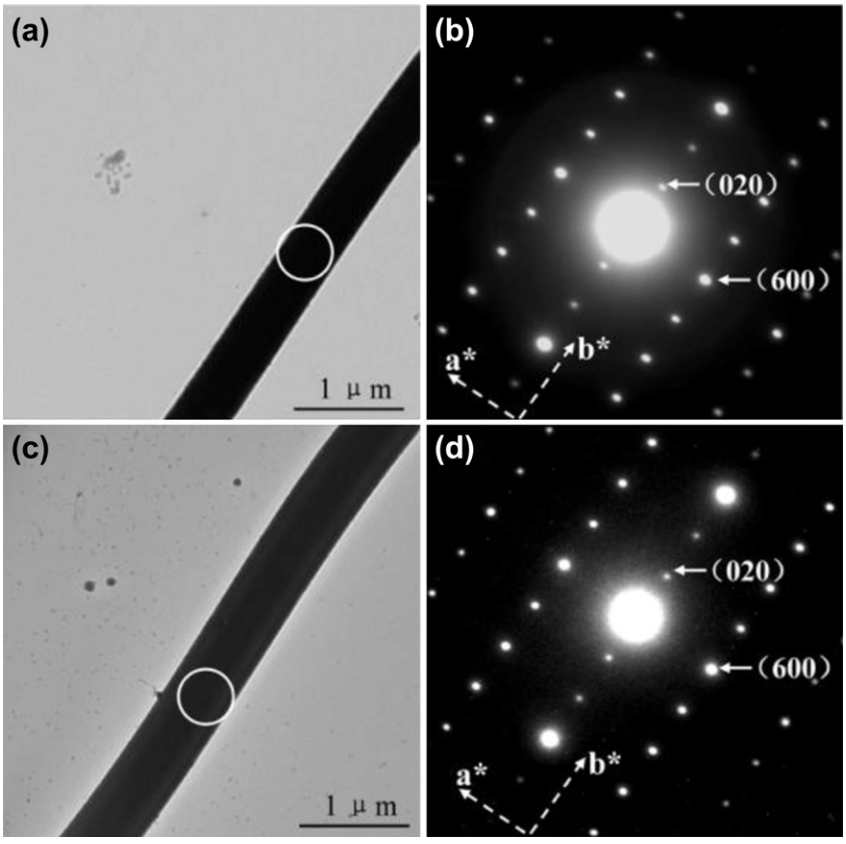

Fig. 1. The TEM images and the SAED patterns of a typical crystal prepared from samples blended with F16/F64 = 1/2 (w/w) (a and b) and F16/F64 = 2/1 (w/w) (c and d).