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Fractionated crystallization of polydisperse polyfluorenes

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ABSTRACT

Lamellar crystals of polydisperse poly (9,9-di-n-octyl-2,7-fluorene)s were obtained from dilute solution. By means of scanning electron microscopy (SEM) and atomic force microscopy (AFM), we found that polymer chains formed lamellar single crystals through fractionated crystallization, in which components of the largest mass fraction crystallized first and remained extended in the first lamella. With the depletion of the species, other components continued the crystal growth and deposited on the already formed surface, which gave rise to the variation in lamellar thicknesses. Therefore, our study not only confirmed the feasibility of our previously crystallization mechanism of the binary mixture on the polydisperse Fn but also provided an extension of the research on the crystallization behavior.

1. Introduction

Due to their potential applications in electronic devices, poly (9,9-di-n-octyl-2,7-fluorene)s (PFOs, named as Fn) have received wide attention [1–3]. The control of the morphology and structure has been considered as a vital step towards the optimization of the performance of electronic devices [4,5]. It is well known that the morphology and structure greatly depend on the crystallization process. A large number of studies about the crystallization process have been carried out and are in progress [6–19]. However, the detailed knowledge about it is still deficient. Particularly, it is of great significance to make it clear that how long entangled polymer chains grow into crystals during the crystallization process. Among these, most of the current work is focused on fractionated crystallization [20–25]. In our previous study, fractionated crystallization was investigated in great details by mixing F16 and F64 in different ratios [26]. It was found that in the stable crystalline phase, as in the case of binary mixtures, polymer chains were extended and packed into lamellae. The study of binary mixtures may serve only as a first approximation of the solids formed from multicomponent assemblies. As a matter of fact, the occurrence of polydisperse aggregates is much more common than the existence of pure compounds in a broad spectrum of natural products. Here we extend our studies on Fn with a broad molecular weight distribution which are expected to contribute to a better understanding of the crystallization behavior in this system.

On crystallizing polydisperse Fn [27–30] from dilute solution, lamellar crystals can also be grown. More importantly, fractionated crystallization is still observed in the polydisperse system. Our results demonstrate the thickness of the first lamella within crystals is close to the extended chain length (ca. 80 nm) of the species of the largest mass fraction. Hence, it is proposed that species of largest mass fraction crystallize first and remain extended during the crystallization. As the first extended-chain crystal forms successfully, it depletes the surrounding solution and thus triggers the attachment of other components on the crystal surface, leading to the stacking of lamellae on top of one another. Therefore, this crystallization behavior of polymer chains results in various thicknesses in the lamellar crystals. In this way, experimental data manifest that the previous crystallization mechanism of the binary mixture is also applicable in the polydisperse Fn.

2. Experimental section

2.1. Materials

Fn was synthesized by Kumada catalyst transfer polycondensation (KCTP) method with 0.1 mol% $Ni(acac)_2$/dppp as the catalyst according to the reference [31]. The obtained polymer was purified by precipitation in methanol and then Soxhlet extraction with acetone.

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The number-average molecular weight (M_n) and polydispersity index (PDI), determined by gel permeation chromatography (GPC) using polystyrene as the standard and tetrahydrofuran (THF) as the eluent, are 100,957 g/mol and 1.71, respectively. The GPC measurement was given in Supplementary Material, Fig. S1. The DSC heating and cooling scan of the powder sample was provided in the Supplementary Material, Fig. S2. There is a clear final melting around 168 °C. The exothermic event near 103 °C and 131 °C are also shown in the curve, demonstrating the crystallization during programmed cooling. Chloroform and ethanol were purchased from Beijing Chemical Works and used without further purification.

2.2. Sample preparation

The solution of Fn was obtained 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.

2.3. Characterizations

The optical images were obtained using Zeiss Axio Imager A2m equipped with the polarizer. Transmission electron microscopy (TEM) experiments were performed using a JEOL JEM-1011 with an accelerating voltage of 100 kV for 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 scanning electron microscopy (SEM) images were obtained using FEL XL 30. 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 microcantilever (spring constant = 15 N/m, resonant frequency ≈ 130 kHz, Olympus, Japan) was used for the scanning. Differential scanning calorimetry (DSC) measurement was performed on TA Q100 thermal analyzer at a heating rate of 10 °C/min.

3. Results and discussion

As shown in Fig. 1a, the rod-like crystals were obtained with the slow evaporation of the solvent. Fig. 1b and c show the typical transmission electron microscopy (TEM) image and the selected area electron diffraction (SAED) pattern of the crystal. The sharp reflexes in the SAED pattern indicate the formation of well-ordered crystals containing unique oriented polymer chains. In the electron diffraction diagram, the d-spacing along the two perpendicular directions is 0.64 nm and 0.36 nm indexed as (020) and (600) on the basis of the lattice constants [30]. Keeping the previous results in mind, the pattern of polydisperse Fn is the same with that of monodisperse Fn. It is noteworthy to point out that polymer backbones are still perpendicular to the lamellae with side chains in the growth direction.

Fig. 2 depicts SEM images of several typical crystals, which provides a wealth of information. To the best of our knowledge, the crystal morphology is a marker which probes the deposition process itself and it is also the closest possible witness of the crystallization process. In large magnification, distinctive lamellar structures with various thicknesses can be clearly observed in the lamella crystals, as depicted in Fig. 2a. It is noted that the thickness of lamellae has distribution but each lamella is quite uniform.

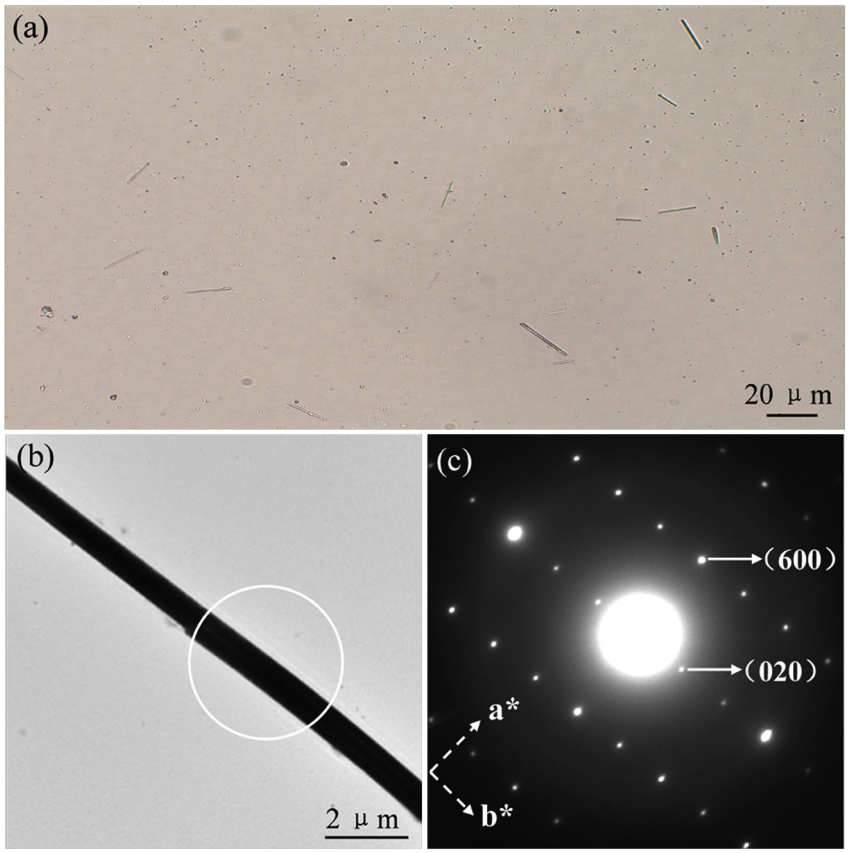

Fig. 1. (a) Optical image of rod-like crystals from mixed solution. (b) TEM image and (c) The selected-area electron diffraction pattern from the area marked in (b).