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Organic crystallizable solvent served as template for constructing well-ordered PPE films

Zicheng Zuo [a,b], Xiaodong Yin [a,b], Chunjie Zhou [a,b], Nan Chen [a,b], Huibiao Liu [a], Yongjun Li [a], Yuliang Li [a,*]

[a] Beijing National Laboratory for Molecular Science (BNLMS), CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, PR China
[b] Graduate University of Chinese Academy of Sciences, Beijing 100080, PR China

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ABSTRACT

Tuning the solidification of the crystallizable solvent naphthalene, well-patterned conjugated polymer poly(phenyleneethynylene) (PPE) films with well-defined nanostructures of 0D nanodots, 1D lamellas, and 2D texture nanostructures have been prepared by several strategies. The nanostructures have been characterized and the formation mechanisms for the morphologies have been discussed.

1. Introduction

The regular patterned and large-scale films have shown many exciting physical properties, and have been applied in many research fields, such as thin film organic field-effect transistors [1], templates for inorganic nanostructures [2], phononic and photonic crystals, electronic devices [3], magnetic recording devices [4], and biological technologies [5]. The preparation of patterned films has drawing extensive attention during the past decades, and scientists have developed many patterning technologies to manipulate the morphology of well-patterned inorganic, organic and polymer films. The patterned nanostructures of organic charge-transfer complexes were synthesized by chemical vapor deposition [6,7]; the high-throughout and high-resolution patterns were prepared by nanoimprint lithography [8]; tailed domain orientation of polymer films were fabricated by using magnetic field [9], electric field [10,11], templated methods [12,13] and so on [14,15]. Among these methods, great efforts have been dedicated in investigation of patterned polymer films obtained from the microphase separation in block copolymers [16–20]. Because of their mutual repulsions among the chemically distinct macromolecules linked by covalent bonds, dissimilar blocks tend to segregate into nanostructures to reach the thermodynamically stable state. The spatial extent of the domains fabricated from copolymers is greatly limited by the constraint imposed by the chemically linked blocks and the molecular weight [21]. By tuning the molecular weight and the chemical structures of the blocks, different patterned nanostructures with diverse chemical and physical properties have been produced from this method [22].

With the improvement of epitaxial crystallization (EC), many crystallizable organic solvents have been introduced as the substrates to induce the epitaxial crystallization of various normal polymers [23,24]. The EC provided a potential method to produce large-scale and low-cost periodic nanostructures that is not available by traditional optical lithography. The epitaxial structures of polymers on crystallizable organic substrates are mainly induced by the two-dimensional lattice matching between polymers and organic substrate crystal plane in contacts. Successive studies had been implemented to produce patterned films with well-aligned, vertically oriented microdomains of semicrystalline block copolymers by this method [25–28]. Although the epitaxial crystallization of some block copolymers on the crystallizable organic solvent substrates has been investigated, homopolymer films prepared by crystallizable organic solvent have been freshly studied, especially for the well-patterned nanostructures of semiconductor π-conjugated polymers.

Because of the good optical and electrical properties, π-conjugated polymers like polythiophenes, poly(phenyleneethynylene)s and poly(p-phenylenevinylene)s have many potential applications in organic optoelectronic devices, such as organic field-effect transistors and organic solar cells [29,30]. Many reports have shown that the film structures of functional polymer have a great influence in the efficiency of microelectronic devices [31,32]. In this paper, the directional freezing property of crystallizable naphthalene [33] is applied to prepare large-scale PPE films with well-patterned

* Corresponding author. Fax: +86 10 82616576.
E-mail address: ylli@iccas.ac.cn (Y. Li).

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nanostructures which may have great potential in constructing polymer optoelectronic devices.

2. Materials and methods

2.1. Materials and preparation of films

The conjugated polymer PPE is synthesized according to the literature [34] and the macromolecular structure is shown in former paper [33]. For the preparation of regular patterned PPE films with well-defined structures, the naphthalene is chosen as the solvent since it is known to be an excellent solvent for conjugated system [33]. The preparation of well-patterned polymer films with different morphologies involves four following steps: Firstly, the PPE naphthalene solution is prepared by dissolving PPE in the melting naphthalene at 110 °C. In brief, 5 mg PPE powder is well dissolved in 1 g naphthalene under stirring at 110 °C. Secondly, the melting solution is dropped onto a clean glass slide (20 mm × 20 mm). Then a clean glass coverslip is located on the droplet, so that the melting solution is sandwiched between two clean glass slides. Little pressure is imposed on the two glass slides, and make sure the conjugated polymer solution uniformly spreads in the sandwiched structure and the air bubbles are driven away. This process is necessary to prepare uniform films and it is helpful for the following uniform solidification of solvent. Thirdly, the sandwiched structure is frozen by different freezing methods for the various morphologies. The last step, after the freezing process, 10 h heat treatment at 60 °C is exerted to relax the molecular strains induced by the slow movement of long macromolecular chains and the rapid crystallization of naphthalene. After removing the coverslips, the naphthalene is slowly evaporated away at 50 °C. In this paper, four freezing operations are adopted for the preparation of different patterns. The first freezing method is to adopt the freezing direction perpendicular to the glass plane which is called vertical freezing (VF). The second method called horizontal freezing (HF) is to freeze the sandwiched structure along the direction parallel to the plane of glass slides. The third method is a combination method in which VF cooperates with HF and it is abbreviated as VH. The forth method is to naturally freeze the samples in air at room temperature which is abbreviated as ART.

2.2. The characterization of morphologies

The PPE films with different morphologies are characterized by the field-emission scanning electron microscopy (FE-SEM) Hitachi S-4300 at an acceleration voltage of 10 kV and an electrical current of 8 mA. Before the SEM characterization, all samples are sputter-coated gold for further investigation of the film nanostructures. Because of the good optical properties of PPE, the samples with different morphologies are characterized with the confocal laser scanning microscopy for further investigating the as-prepared nanostructures (CLSM the FV1000-IX81). The 3D images of the nanostructures are also obtained by the measurement of CLSM.

3. Result and discussion

3.1. The SEM characterization of nanodots

The films morphologies prepared by rapid freezing operations are characterized by scanning electronic microscopy (SEM). In Fig. 1S, it is obviously observed that the films with disordered nanodots and aligned nanodots are produced by applying VF and VH freezing methods, respectively. Fig. 1Sa shows that PPE films with disordered nanodots are produced in a large area and it is indicated that the PPE nanodots are isolated from each other. The magnified image (Fig. 1Sb) shows that the diameter of nanodots is non-uniform and distributes largely from 200 nm to 700 nm. The wide size distribution of nanodots is caused by the rapid vertical freezing. By this solidification method, thin sandwiched structures can be rapidly solidified according to the vertical direction. Then, naphthalene crystals with wide sizes distribution are quickly produced without any directional freezing parallel to film. By the formation of naphthalene crystals, PPE molecules are separated out and aggregated together to randomly disperse on glass substrate. By the sublimation of naphthalene, PPE films with disordered nanodots are produced. When the vertical freezing is combined with directional freezing, the nanodots are forbidden in the orientation of directional freezing. The image 1Sc shows that film with oriented nanodots are obtained in large-scale, and the isolated nanodots are well restricted in lines. In Fig. 1S, the parallel arrows indicate the crystallization direction of naphthalene, and the image shows that the distance between two neighboring lines is about 5 μm. The inset image in Fig. 1Sd shows the well-aligned nanodots are about 400 nm in diameter. Comparing to the disordered film, the size distribution is more uniform in ordered film because of the confinement imposed by directional freezing. By further characterizing the nanodots in disordered and ordered films, the insets in Fig. 1S show that many nanodots are of hollow nanostructures. This is attributed to the rapidly freezing process, in which the macromolecular PPEs cannot move as quickly as small molecular naphthalene, and the intramolecular and intermolecular strain are saved in PPEs nanodots. By the following heat treatments, the stretched PPE molecules were shrunk to the stable conformations, and the hollow structure is formed. The hollow structure is the structural defect by the vertical freezing operation.

3.2. The characterization of parallel and cross-oriented lamellas

By adopting UF methods, films with parallel oriented morphologies have been achieved. In Fig. 1a, the large-scale film with one-dimensional oriented lamellas has been prepared by UF. The well-defined lamellas are paralleled to the orientation of solidification which is represented by the blue arrows in Fig. 1a and b.[1] The inset in Fig. 1b shows that the average thickness of well-aligned lamellas is about 100 nm. Two neighboring lamellas have an intersection at the tail of lamellas. This is due to the slow movement of PPE macromolecules with long main chains. When the unidirectional freezing process has been applied within a short time and the entangled long main chains have not been completely loosen along the freezing direction. Then the intersections are solidified by the crystallization of naphthalene. The distance between two parallel lamellas is about 100 nm in the magnification images.

In Fig. 1c and d, the large-scale films with cross-orientated texture structure have been achieved by solidifying the sandwiched naturally at room temperature. The cross-oriented texture is composed of well-defined PPE lamellas edge-on the substrate, and the inset in Fig. 1d shows the uniform lamella with a thickness of about 80 nm. The arrows in Fig. 1d show that PPE lamellas are predominately oriented along two directions with 90° angle. The right angles are almost the same as the α angle in naphthalene crystal unit. Because of the hydrocarbons are isostructural in the [0 0 1] plane which, given the weak end to end interactions between layers, is an easy cleavage plane and the predominant growth face of the plate-shaped crystals [23]. During the formation process, because of the intensive π–π stacking between PPE and naphthalene molecules, the PPE chains have great interaction with the [1 0 0] and [0 1 0] plane in the monoclinic unit cell of naphthalene. Then

[1] For interpretation of color in Fig. 1, the reader is referred to the web version of this article.