



Crystallization of thiophene/phenylene co-oligomers by dropping of their solutions into poor solvents



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ARTICLE INFO

Available online 14 August 2013

Keywords:

Thiophene/phenylene co-oligomer
Crystal
Solvent

ABSTRACT

We prepared thiophene/phenylene co-oligomer (TPCO) crystals through an efficient method, the dropping of its solution onto a poor solvent droplet on a substrate. In the present study, 2,5-bis(4-biphenyl)thiophene (BP1T) and chlorobenzene are used as one of the TPCOs and a solvent, respectively. We obtained sub-millimeter sized BP1T crystals using *N,N*-dimethylformamide as poor solvent. Furthermore, we employed four kinds of solvents, hexane, benzene, 1,4-dioxane, and toluene, as poor solvents. The size of the BP1T crystals obtained using 1,4-dioxane was 55 times larger than that using hexane.

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1. Introduction

Organic crystalline solids have received much attention because of their high performance in electronic and photonic devices due to their orderliness. Furthermore, their dense packing of molecules leads to excellent robustness [1]. There have been a number of reports on the characteristics of organic materials in their crystalline phase [2–4]. Among these compounds, thiophene/phenylene co-oligomer (TPCO) consisting of thiophene and benzene rings exhibits excellent performance for light emission and electronic mobility [5]. Many groups have investigated efficient preparation processes of TPCO single crystals and device characteristics using TPCO single crystals [6].

We have been studying the preparation process of TPCO crystals using vapor deposition [7,8]. Vapor deposition is one of the practical processes for the fabrication of organic electronic devices, and can be utilized for covering the entire surface of a substrate with organic material. Thermal treatments can be appropriately controlled to crystallize and grow the crystal domain. We proved that the mechanism of increase in crystal domain size is the divergence of strain energy stored in the grain boundaries of its domain through vapor deposition. We also confirmed that thermal treatment assisted the divergence.

Recently, Minemawari et al. reported a crystallization process using an ink-jet method [9]. They demonstrated that mixing fine droplets of a poor solvent and a solution of an active semiconducting component can

trigger controlled formation of exceptionally uniform single-crystal or polycrystalline thin films that grow at liquid-air interfaces. This process was efficient; therefore, if it is applicable for the crystal preparation of TPCO, we can expect to realize a practical photonic and electronic device using TPCO.

The active compound used in their study was 2,7-dioctyl[1]benzothieno[3,2-b][1]benzothiophene (C8-BTBT), whose octyl substituent can increase its solubility. On the other hand, a number of TPCOs do not have a long alkyl substituent, and thus it is necessary to confirm that the reported method is suitable for the preparation of TPCO crystals. Here, we report the crystallization of TPCOs by using the mixture of a poor solvent and its solution. The morphologies of the prepared crystals are described in detail.

2. Experiment

One of the TPCOs used in the present study was 2,5-bis(4-biphenyl)thiophene (BP1T), whose chemical structure is shown in Fig. 1. BP1T was crystallized as follows (see Fig. 2). We first dropped a poor solvent onto a $1 \times 1 \text{ cm}^2$ glass substrate to cover its surface. Three droplets of a chlorobenzene solution of BP1T were then consecutively dropped onto the poor solvent, mixing the poor solvent and the BP1T solution. After that, the poor solvent and chlorobenzene were evaporated at room temperature (approximately 22 °C) or by heating the substrate, yielding the BP1T crystal on the substrate. In the present study, the poor solvents used were *N,N*-dimethylformamide (DMF), 1,4-dioxane, hexane, benzene, and toluene.

The morphology of the deposited films was examined under a polarizing microscope (Olympus Model IX-71). The X-ray diffraction measurements were made with a RIGAKU RU-300 X-Ray diffractometer using Cu-K α radiation.

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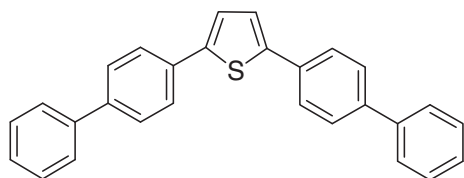


Fig. 1. Chemical structure of BP1T.

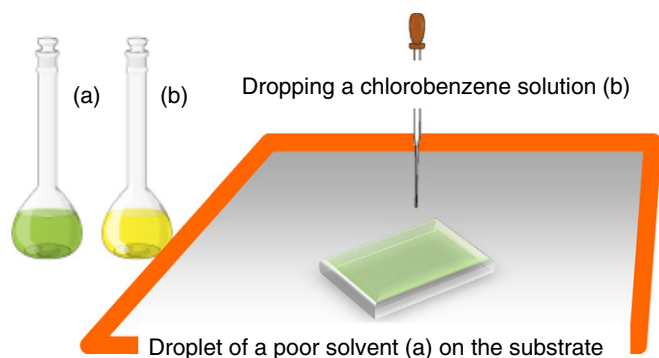


Fig. 2. Brief overview of experimental flow: a) Poor solvent; b) BP1T chlorobenzene solution. First, a droplet of the poor solvent covered a glass substrate. Then, BP1T chlorobenzene solution was dropped onto the poor solvent.

3. Results and discussion

3.1. Usage of DMF as a poor solvent

BP1T consists of symmetrical thiophene and benzene rings, therefore, aromatic solvents are the first alternatives for BP1T dissolution. We employed chlorobenzene, which is one of the well-used aromatic solvents, as a good solvent. However, the thiophene and four benzene

rings of BP1T have no substituent, and BP1T shows relatively high molecular weight, leading to high melting point, less polarity, and low solubility. Accordingly, we could not dissolve an appropriate amount of BP1T using chlorobenzene at room temperature. The solubility of chlorobenzene for BP1T was 4.1 mM at 110 °C. Meanwhile, DMF was used as a poor solvent: it has no benzene ring and a high dielectric constant of 37.6 [10]. The dielectric constant represents the polarity of a solvent, and the higher dielectric constant of a solvent shows that it has a larger polarity. In the study by Minemawari's group, DMF was also used as a poor solvent; the reason why they employed DMF was its big difference in solubility for C8-BTBT as compared with dichlorobenzene as a good solvent. In addition, these two solvents are mutually miscible.

We investigated the dependence of substrate temperature in the 50 °C to 90 °C range. It took over 2 h to dry the solvent mixture of chlorobenzene and DMF below 50 °C, because the boiling temperatures of DMF and chlorobenzene are 153 °C and 131 °C, respectively. Fig. 3 shows a series of polarizing micrographs of BP1T crystals. The temperature of the chlorobenzene solution droplet was 110 °C. At the substrate temperature of 50 °C, we obtained 100 μm-sized crystals, and their features were plain and feathery. The forms of the resulting BP1T crystals resembled the reported crystals; the crystals were prepared by squeezing and displacing the melting BP1T that was sandwiched between the two substrates [11]. The size of the BP1T crystals increased with increasing substrate temperature; plain crystals over 700 μm in size were obtained at substrate temperatures of 70 °C and 80 °C. The thickness of the obtained crystal was approximately 650 nm. The size of the plain crystals did not markedly increase with substrate temperature over 80 °C. Meanwhile, many micro-crystals of BP1T formed on the tops of the larger plain crystals.

We visually confirmed that early-stage growth in the BP1T crystal occurred at the surface between the air and mixed solvent, and even the density of BP1T, at 1.33 g/cm³ [12], is larger than those of DMF and chlorobenzene, of 0.94 g/cm³ and 1.11 g/cm³, respectively.

Fig. 4 shows a series of polarizing micrographs at various solution temperatures. This experiment was performed at a fixed substrate

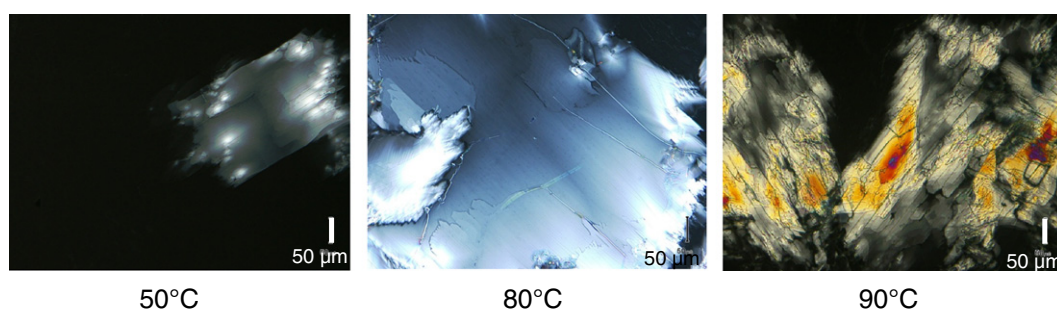


Fig. 3. A series of polarizing micrographs of BP1T crystals obtained by dropping chlorobenzene solution onto DMF droplets. Temperatures shown in the lower row are those of the substrate.

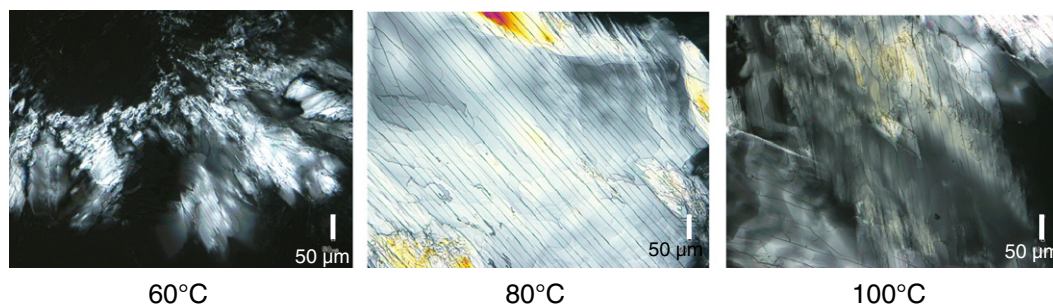


Fig. 4. A series of polarizing micrographs of BP1T crystals obtained by dropping a solution at various temperatures onto DMF droplets. The temperatures shown in the lower row indicate those of the solution droplet.

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