

Polymer Communication

# Extended-chain lamellar packing of poly(3-butylthiophene) in single crystals

Zhiyong Ma, Yanhou Geng, Donghang Yan\*

*State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Graduate school of Chinese Academy of Sciences, Renmin Street 5625, Changchun, Jilin 130022, People's Republic of China*

Received 17 June 2006; received in revised form 23 October 2006; accepted 24 October 2006

Available online 20 November 2006

## Abstract

We developed an approach, i.e. solvent-assist crystallization (SAC), for growing high quality single crystals of head-to-tail regio-regular poly(3-butylthiophene) (P3BT). By means of atomic force microscopy, electron diffraction and X-ray diffraction, we found that P3BT macromolecules formed lamella single crystals through gradient crystallization, and in the single crystals, molecules packed normal to the lamella with extended-chain conformation with alkyl side chains in the growth front during crystallization.

© 2006 Elsevier Ltd. All rights reserved.

*Keywords:* P3BT; Single crystal; Solvent-assist crystallization

## 1. Introduction

Organic electronics and optoelectronics based on organic semiconductors have become an enormous impetus for the advancement of science and high technologies. The property of charge transport of organic semiconductors in solid state closely relates with ordered molecular packing and the regularity of molecules [1–3]. However, people have little knowledge on the morphology of rigid-chain polymer compared with flexible counterparts because of their high melting point or lack of proper solvent [4–7]. Since the discovery of head-to-tail regio-regular poly(3-alkyl thiophene)s (P3ATs) in the mid-90s of last century [8,9], these conjugated polymers have become magic wand to realize high performance organic solar cells and organic field-effect transistors because of their good charge transport properties [1,10]. Here we show that lamella single crystals of P3BT in millimetre long are grown by means of solvent-assist crystallization (SAC). The P3BT crystal structure is the superstructure of fibers from thermal

extrusion or solution casting films after annealing [8,11]. Molecular conformation in the crystals is an extended-chain that was found in crystals of flexible polymers crystallized at high-pressure [12]. Alkyl side chains are in growth front of lamella, which indicate that interaction of alkyl side chain between P3BT molecules is stronger than that of molecular backbones during crystallization. Our results demonstrate that highly ordered morphology could be obtained for conjugated polymers than for flexible polymer. Property of charge transport related with  $\pi$ – $\pi$  stacking between molecules could be controlled by sophisticated molecular design and proper solvent selection to control the strength of interactions between alkyl side chains and molecular backbones during crystallization.

## 2. Materials and methods

### 2.1. Materials and sample preparation

The polymer RR-P3BT was purchased from Aldrich and used without further purification. The given regio-regularity is 97%. The weight-average molecular weight and

\* Corresponding author. Tel.: +86 431 5262165; fax: +86 431 5262266.  
E-mail address: [yandh@ciac.jl.cn](mailto:yandh@ciac.jl.cn) (D. Yan).

polydispersity index, determined by gel permeation chromatography (GPC) using polystyrene as the standard and tetrahydrofuran (THF) as the eluent, are 16,000 g/mol and 1.51, respectively.

Keep 0.2 wt% RR-P3BT THF solution at 70 °C for 5 h, then slowly cool to room temperature. Drop-cast RR-P3BT thin-films on surface of glass substrate or Mica coated with amorphous carbon thin-films and slowly evaporate the solvent. Then the RR-P3BT thin film was dipped into a mixture of nitrobenzene and THF (3:1 in volume) for several days until the solvents were evaporated. We called this crystallization method as solvent-assist crystallization (SAC).

## 2.2. Methods

X-ray diffraction patterns were recorded using Rigaku D/MAX 2500 PC X-ray Diffractometer. The radiation was Ni-filtered  $\text{CuK}\alpha_1$ ,  $\lambda = 1.54058 \text{ \AA}$ , generated at 250 mA and 50 kV. Optical microscope and SEM micrographs were obtained using Leica DMLP and FEI XL 30, respectively. For TEM measurements, carbon thin-films with single crystals were carefully floated away from mica surface on water surface, and transferred onto copper grid. The crystals were imaged using a JEOL 2010 microscope operating at 200 kV.

## 3. Results and discussion

The diagram of solvent-assist crystallization (SAC) is shown in the inset of Fig. 1. The good THF solvent could help RR-P3AT molecules move easily while the bad solvent nitrobenzene kept the crystallization environment. In consequence, the large crystals visible with neat eyes formed on glass substrate. Needle-like single crystals with the length up to millimetre could be clearly identified under optical microscopy, as shown in Fig. 1. Single crystals were then selected

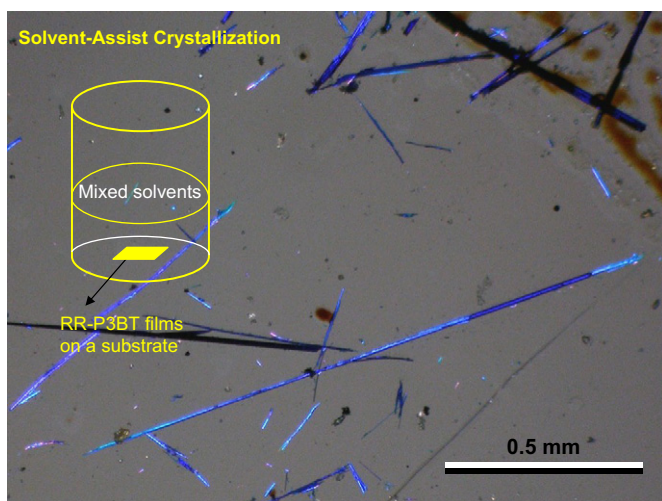


Fig. 1. Micrograph of P3BT single crystals from solvent-assist crystallization under polarizing optical microscope. Schematic diagram of solvent-assist crystallization is shown in the inset.

and put on SEM sample plate using tweezers for SEM observation.

Powder X-ray diffraction of collected crystals shows 14 peaks (Fig. 2). Accordingly, the unit cell parameters were subtracted to be  $a = 1.42 \text{ nm}$ ,  $b = 2.53 \text{ nm}$ ,  $c = 1.56 \text{ nm}$  and  $\alpha = \beta = \gamma = 90^\circ$ . These parameters are commensurate with references to index (111) and (030) reflections [8,11], parameters  $a$  and  $b$  were exchanged in order to assign  $\mathbf{b}$  as crystal growth direction of lamellar crystals, based on electron diffraction of the single crystals as depicted in the following text.

Fig. 3 exhibits the SEM photograph of a typical single crystal. In large magnification, lamella structures with the thickness of 104–15.6 nm can be clearly observed in the lamella crystals edged on the substrate. It is surprising that thickness of lamella has distribution but each lamella is quite uniform. Based on the gel permeation chromatographic (GPC) measurements, the molecular length of RR-P3BT was estimated to be in the range of 7–130 nm by taking into account the deviation of measured molecular weight from real value [13,14], which is consistent with the thickness variation of lamella structures. These indicate that, in the single crystals, RR-P3BT molecules are likely packed with the extension chain conformation in a gradient crystallization process.

In order to understand the molecular packing mode in these lamella crystals, small single crystals were prepared on amorphous carbon thin-films for electron diffraction investigation. Selected area electron diffraction was carried out with gold as the calibration. The single crystal and the corresponding bright-field image are given in Fig. 4, respectively. Electron diffraction shows rectangular pattern, and the  $d$ -spacing along the two perpendicular directions is 0.63 nm and 0.71 nm, respectively. Combining with powder X-ray diffraction results, it is indexed as [001] zone. Molecules are parallel to the lamella normal and normal to the growth direction  $\mathbf{b}$ . Schematic structure of RR-P3BT molecules packing in the lamella crystals is represented in the inset of Fig. 3. It is surprising that the alkyl chains are on the growth front of the lamella based on X-ray diffraction [8]. This result indicates that surface energy of the growth plane (010) with interpenetrated alkyl chains may

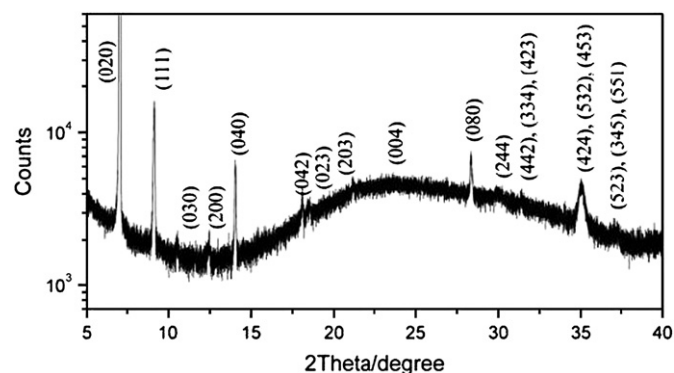


Fig. 2. Powder X-ray diagram of RR-P3BT crystals from solvent-assist crystallization. Unit cell parameters are commensurate with Refs. [1,2], parameters  $a$  and  $b$  were exchanged in order to assign  $\mathbf{b}$  as crystal growth direction of lamellar crystals based on electron diffraction.

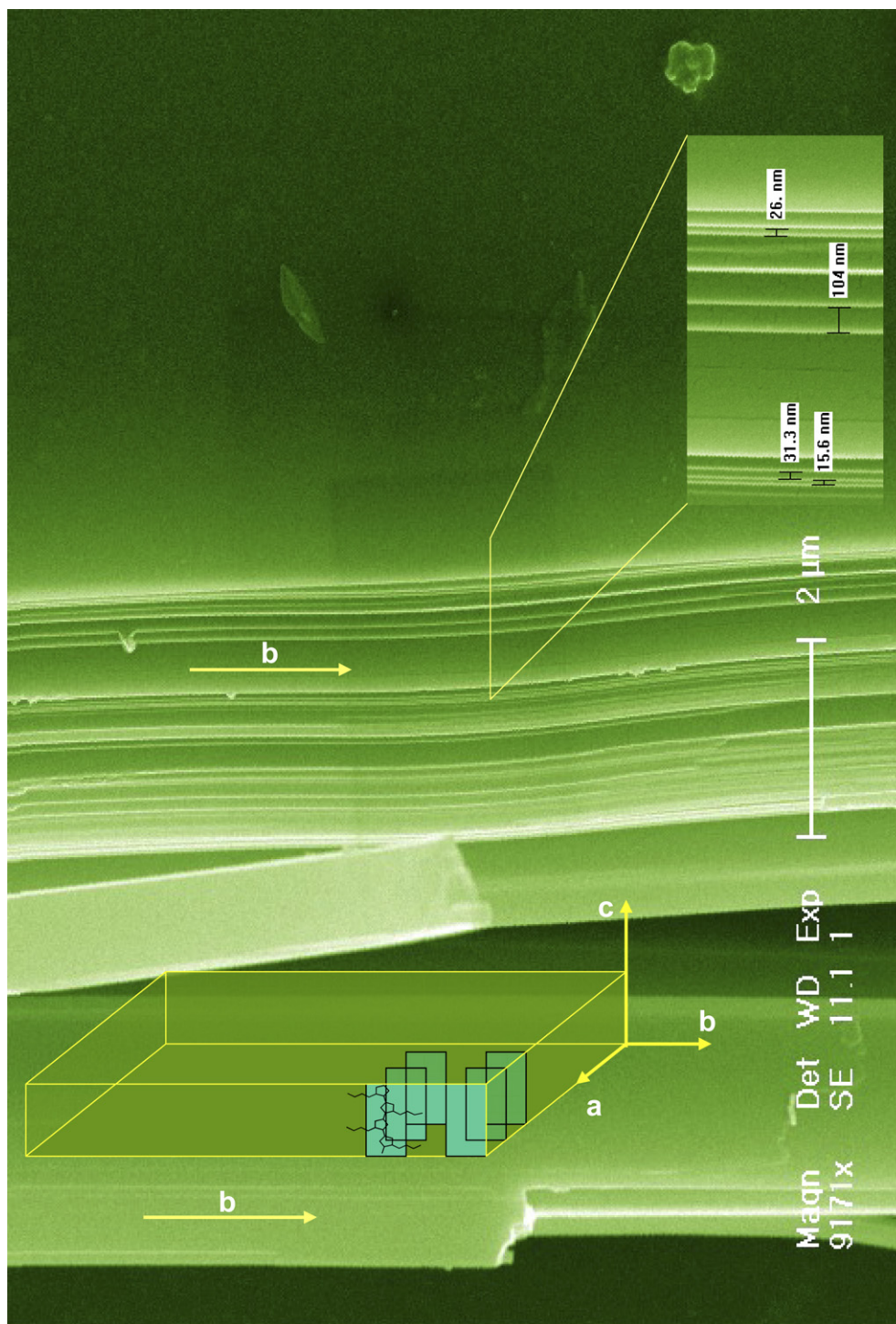


Fig. 3. Micrograph of a typical P3BT single crystal from solvent-assist crystallization under scanning electron microscopy. Lamellar thickness varying between 15.6 nm and 104 nm can be identified from enlarged inset picture in up-right corner. Schematic diagrams of molecular packing in the lamellar crystals, molecular-chain direction **c** and growth direction **b** are also included as the inset.

be higher than that of  $\pi$ – $\pi$  interaction between two RR-P3BT rigid-chains in the solvent at room temperature. The packing mode of the RR-P3BT molecules suggests that the charge carrier transport along lamella should be more difficult. In fact, the field-effect transistors fabricated with Au source and drain electrodes along the P3BT single crystal needle-direction exhibited no field effect.

#### 4. Conclusion

Needle-like RR-P3BT lamellar single crystals with the length up to millimetre have been grown by means of solvent-assist crystallization. Gradient crystallization of the macromolecules with the different molecular weight results in non-uniform lamellar thickness in the range of 15.6–104 nm.

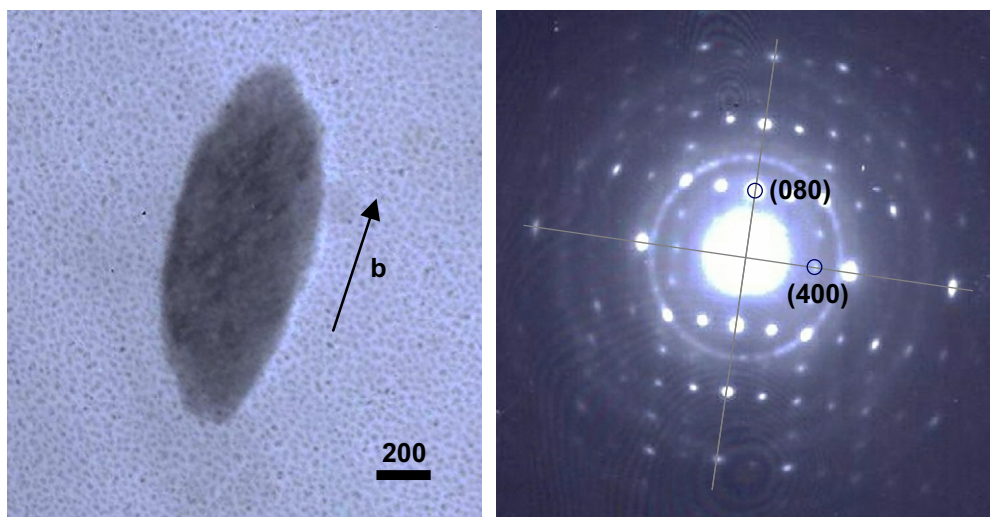


Fig. 4. Bright-field micrographs of P3BT single crystals (left) and the corresponding selected area electron diffraction (right).

In the single crystals, RR-P3BT molecules packed normal to the lamella with extended-chain conformation. Alkyl side chains are in the growth front during crystallization. We demonstrated that solvent plays a key role in controlling ordered morphology of comb-like conjugated polymer. This is helpful for molecular design and fabrication method optimization.

#### Acknowledgements

This work was financially supported by the Special Funds for Major State Basic Research Projects (2002CB613400) and by the National Natural Science Foundation of China (90301008, 20474064, 20521415).

#### References

- [1] Sirringhaus H, Brown PJ, Friend RH, Nielsen MM, Bechgaard K, Langeveld-Voss BMW, et al. *Nature* 1999;401:685–8.
- [2] Wittman JC, Smith P. *Nature* 1991;352:414–7.
- [3] Amundson KR, Sapjeta BJ, Lovinger AJ, Bao Z. *Thin Solid Films* 2002;414:143–9.
- [4] Ihn KJ, Moulton J, Smith P. *J Polym Sci Part B Polym Phys* 1993;31:735–42.
- [5] Mena-Osteritz E, Meyer A, Langeveld-Voss BMW, Janssen RAJ, Meijer EW, Bauerle P. *Angew Chem Int Ed* 2000;39:2679–84.
- [6] Chen SH, Chou HL, Su AC, Chen SA. *Macromolecules* 2004;37:6833–8.
- [7] Shrotriya G, Li V, Huang J, Yao Y, Tommoriarty EK, Yang Y. *Nature Mater* 2005;4:864–8.
- [8] McCullough RD, Lowe RD. *J Chem Soc Chem Commun* 1992;13:70–2.
- [9] Chen T-A, Wu X, Rieke RD. *J Am Chem Soc* 1995;117:233–4.
- [10] Ma W, Yang C, Gong X, Lee K, Heeger AJ. *Adv Funct Mater* 2005;15:1617–22.
- [11] Tashiro K, Kobayashi M, Kawai T, Yoshino K. *Polymer* 1997;38:2867–79.
- [12] Wunderlich B. *Macromolecular physics, crystal structure, morphology, defects*, vol. 1. New York: Academic; 1973. p. 178.
- [13] Grell M, Bradley DDC, Long X, Chamberlain T, Inbasekaran M, Woo EP, et al. *Acta Polym* 1998;49:439–44.
- [14] Izumi T, Kobashi S, Takimiya K, Aso Y, Otsubo T. *J Am Chem Soc* 2003;125:5286–7.