

The Crystallization of Poly (3-dodecylthiophene) in an Oriented Solidification Environment

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Abstract: The crystallization behaviors of poly (3-dodecylthiophene) (P3DDT) under two different oriented solidification conditions, *i.e.*, two different relative relations (90° and 180°) between the directions of gravity and solidification, were investigated. X-ray diffraction results reveal that although similar layered structures are formed, under the condition of the relative relation 180°, temperature gradient has greater effects on the perfect degree of the layered structures of P3DDT. It also can be concluded that after recrystallization, the layered structures of P3DDT can be improved at relative relation 90°, but the orderly degree of the arrangements of alkyl side chains are not improved yet, even is reduced for both of the oriented solidification conditions.

Keywords: Crystallization, poly (3-dodecylthiophene), oriented solidification.

Poly (3-alkylthiophenes) (P3ATs) have made up of a family of conductive polymers which are soluble, fusible and processable, since the introduction of flexible alkyl side chains^{1,2}. It is generally accepted that P3ATs can form similar layered structures, in which the thiophene rings possess planarity and the side chains act as spacers³⁻⁵. When the number of carbon atoms of alkyl side chains is more than 10, some orderly arrangements will occur for side chains between the layers⁴. It has been well known that crystallization has great effects on the mechanical properties of polymeric materials during industrial applications. In this case, the investigations of the crystallization behavior of polymers under different experimental conditions turn out to be of great significance and value. In our previous work, nonisothermal crystallization behaviors of poly (3-dodecylthiophene) (P3DDT) and poly (3-octadecylthiophene) (P3ODT) have been studied using differential scanning calorimetry (DSC)⁶. In this paper, P3DDT was chosen for the investigations of the crystallization behavior in an oriented solidification environment, which will contribute to open up a new research field of the family of P3ATs.

The experiments were performed in an oriented solidification temperature gradient oven which is able to revolve, as shown in **Figure 1**. Temperature gradient originates

from the effects of cooling circulating water. The sample, which is sealed in quartz tube in vacuum, is fixed in a sustaining frame. When the sample is cooled from the molten state, crystallization occurs firstly at the end near cooling circulating water, *i.e.*, at cooling end. While crystallization occurs finally at the end far from cooling circulating water, *i.e.*, at heating end. The part having been crystallized is called solid phase, the part having not been crystallized is called liquid phase, and the direction of solid-liquid interface movement is called solidification direction. For this instrument, the relative relation between the directions of solidification and gravity can be regulated from 0 to 180 degree. In this study, the relative relations (90° and 180°) between the gravity direction and solidification direction were adopted, as illustrated in **Figure 2**. In each experiment, the sample was first heated up to 160°C , and held there for 30 minutes, then cooled naturally to 90°C which approaches the crystallization peak temperature for isothermal crystallization, and then cooled to room temperature naturally.

Figure 1. The schematic graph of an oriented solidification temperature gradient oven

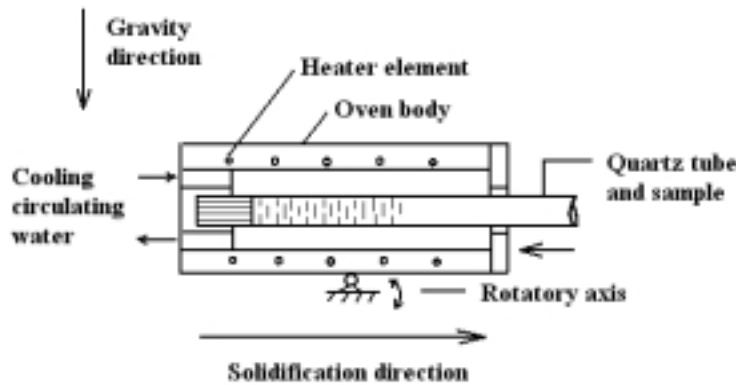
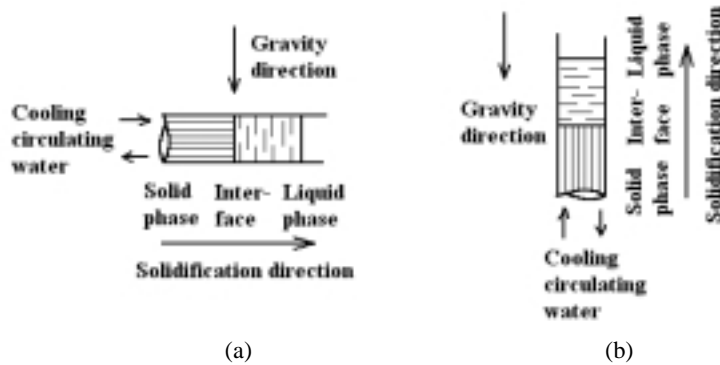


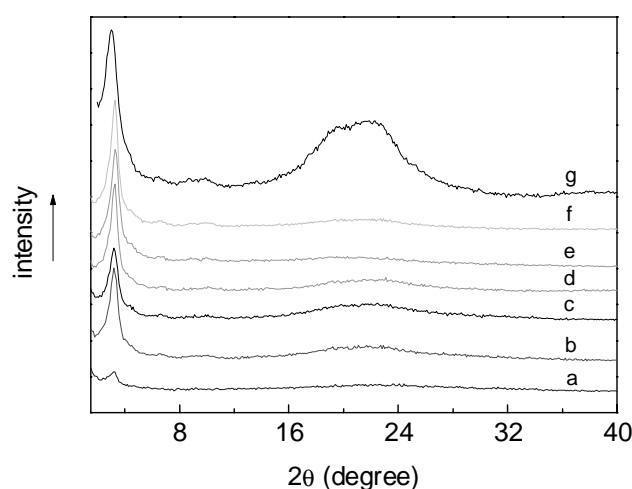
Figure 2. The illustrations of the relative relation between the directions of solidification and gravity (a: relative relation 90° ; b: relative relation 180°)



From X-ray diffraction results, many detailed structural information can be

obtained. In order to make detailed analysis of the effects of experimental conditions on the crystallization behavior of P3DDT, the prepared samples are divided into three parts for measurements: heating end and cooling end, as mentioned above, in addition of the center part between the two ends. And each part of the prepared sample is analyzed using Wide Angle X-ray Diffraction (WAXD). Shown in **Figure 3** is the X-ray diffraction patterns of the three parts of the sample prepared under the two different relative relations between the directions of solidification and gravity, and the X-ray diffraction result of the original sample is also shown in the figure. For X-ray diffraction results of P3ATs, the peaks at small angle corresponding to the first and higher-order diffractions originate from the diffractions of the layered structures, while the peak at wide angle can imply the orderly degree of the packings of alkyl side chains. From **Figure 3** we can find that under those experimental conditions P3DDT can form similar layered structures, and the arrangements of alkyl side chains are relatively disorderly. However, for the relative relation 180° , there is great difference in the intensity of the peaks at small angle, that is to say, temperature gradient has great effects on the perfect degree of the formed layered structures of P3DDT. While for the relative relation 90° , temperature gradient has almost no effects on the intensity of the peaks at small angle yet. Compared with the original sample, the layered structures of P3DDT are improved when being recrystallized at the relative relation 90° , from the considerations of the relatively sharper peaks at small angle of this prepared sample. However, for both of the two oriented solidification conditions, the orderly degree of the arrangements of alkyl side chains has not been improved yet, even is reduced.

Figure 3. The X-ray diffraction patterns of P3DDT under different experimental conditions (a: heating end at relative relation 90° ; b: center part at relative relation 90° ; c: cooling end at relative relation 90° ; d: cooling end at relative relation 180° ; e: center part at relative relation 180° ; f: heating end at relative relation 180° ; g: the original sample of P3DDT)



Acknowledgment

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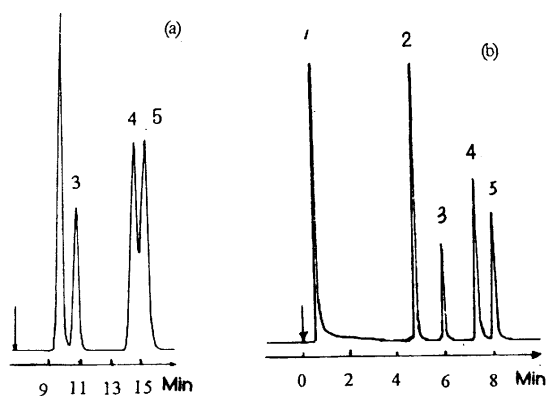
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Erratum: CCL Vol. 11, No. 3, pp. 226, **Figure 1** was corrected in No. 11, 364.

Figure 1. Chromatograms of phenol and three cresol isomers



- (a) Column No.1 column temperature:140°C, carrier gas linear velocity: 17.71cm/s
(b) Column No.2 column temperature:120°C, carrier gas linear velocity: 58.48cm/s

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1: acetone, 2: phenol, 3: *o*-cresol, 4: *p*-cresol, 5: *m*-cresol