

Preparation and characterization of self-assembled conducting polymer nanofibers

Sadaki Samitsu¹, Takeshi Shimomura², Kohzo Ito³

¹Department of Physics and Astronomy, Graduate School of Science, Kyoto University, ²Graduate School of Bio-Applications and System Engineering, Tokyo University of Agriculture and Technology, ³Department of Advanced Materials Science, Graduate School of Frontier Sciences, The University of Tokyo

Abstract

We prepared one-dimensional nanofibrillar structure of poly(3-alkylthiophenes) (P3ATs) via whisker precipitation in anisole. P3ATs self-assembled into nanofibers whose height and aspect ratio was 5 nm and on the order of 10^3 , respectively. UV-Vis absorption spectra showed the relationship between the change of absorption spectra and nanofiber formation in P3ATs solutions. X-ray diffraction measurements showed P3AT nanofibers involve microcrystalline structures. The results indicate that crystallization of P3ATs in a solution, which was driven by strong π - π^* interaction between polymer backbones, plays a crucial role in nanofiber formation.

アニソールを溶媒としたウィスカー法を使用して、ポリ(3-アルキルチオフェン)のナノファイバーを作製した。原子間力顕微鏡の観察からこのナノファイバーは高さが 5 nm と細く、アスペクト比が 10^3 にも達する非常によい 1 次元性を有することを確認した。紫外可視吸収スペクトルの変化がナノファイバーの形成過程とよい相関を示し、X線回折測定により結晶性ナノファイバーであることが明らかになったので、溶液中での高分子の結晶化がナノファイバーの形成の駆動力であると結論付けた。

Introduction

Poly(3-alkylthiophenes) (P3ATs) are conducting polymers that provide higher carrier transport property and better stability to air exposure than other conventional conducting polymers, and have attracted widespread interest in scientific research and industrial application of organic electronics. They offer high solubility in common organic solvents due to alkyl side chains, and therefore, can be applicable to cost-effective solution-based preparation of conducting polymer nanofibers that is a most promising nanostructured material due to their one-dimensionality [1-9]. We present here the effective production of P3AT nanofibers by means of whisker method using anisole as a solvent. P3ATs self-assembled into nanofibers in a solution during cooling to room temperature. We examined the effect of alkyl chain length of P3AT on nanofiber formation and investigated their morphological and electrical characteristics.

Experimental

Chemical structure of regio-regular P3ATs were shown in Fig. 1. A P3ATs solution in a solvent mixture of anisole and chloroform (4:1 v/v) was gradually cooled to 20°C and further held for 12 hours, resulting in nanofiber formation in a solution.

Results and Discussions

Figure 2 shows atomic force microscope (AFM) images of P3ATs nanofibers on SiO₂/Si substrates. The P3ATs nanofibers were uniformly distributed, showing dense network morphology and had one-dimensional nanofibrillar structure with typical height and width of 5 nm and 20 nm, respectively. The length of the P3ATs nanofibers was longer than several μ m, indicating that their aspect ratio was on the order of 10^3 . Characteristic color change of P3ATs solutions in anisole was observed

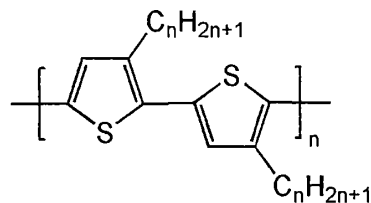


Figure1. Chemical structure of regio-regular P3ATs: P3BT (n=4), P3HT (n=6), P3OT (n=8), P3DT (n=10).

during cooling, and therefore, we investigated relationship between the absorption spectra of P3ATs solution and nanofiber formation. At 70 °C, UV-Vis absorption spectra of P3ATs solutions exhibited a single peak with λ_{max} of 445 nm, which was the same wavelength as that of P3ATs solution in chloroform, which is a good solvent for P3ATs [10]. The result indicates the complete dissolution of P3ATs in the solution. On the other hand, the absorption spectra of the solutions markedly changed during cooling, resulting in occurrence of vibronic structure at the longer wavelength (500-620 nm) at 20 °C for all of the P3ATs investigated. An isosbestic point around 480 nm was exhibited on the absorption spectra at temperatures ranging 70-20 °C. The absorption spectra show that there can be two different states of P3ATs in the solutions at the temperatures. The one is an isolated single chain of P3AT with coiled conformation that exhibits the absorption peak at 445 nm, and the other is a P3ATs aggregate that exhibits the absorbance peaks at longer wavelength of 500-620 nm. X-ray diffraction measurements of P3ATs nanofiber thin films showed clear two peaks at a lower diffraction angle of 3-7° and at a higher angle of 23°. The peak at 3-7° shifted to lower angles and the corresponding inter-layer spacing was increased with increasing alkyl chain length. The result indicates that the peaks at lower diffraction angles correspond to the direction along to the alkyl chain. The other peak at a higher angle was almost constant at 23° and the corresponding inter-layer spacing was 3.8 Å, independent on the alkyl chain length of P3ATs. The result indicates that the inter-layer spacing corresponds to the stacking of polymer backbones. The X-ray diffraction spectra were almost similar to that of thin films or powder of P3ATs in a previous study [10], suggesting that P3AT nanofibers involve microcrystalline structure similar to that observed in thin films or powder of P3ATs.

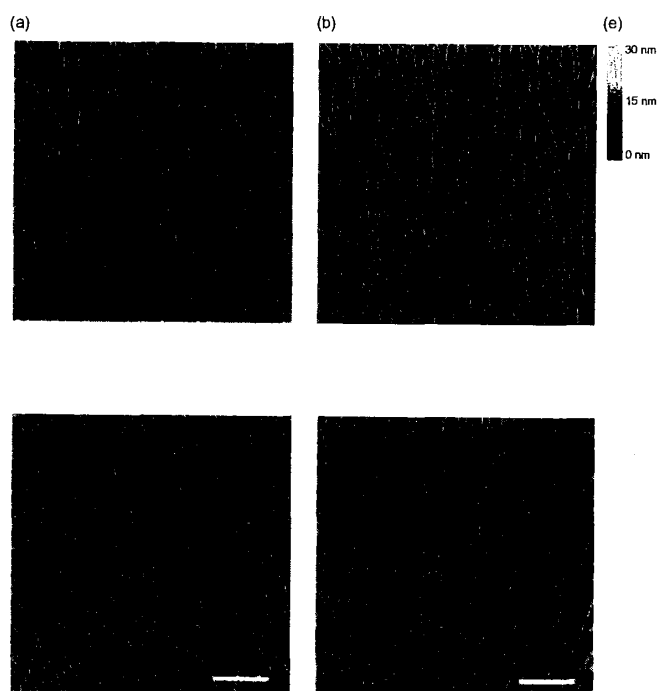


Figure 2. AFM images of P3ATs nanofibers spin-coated on a SiO₂/Si substrate: (a) P3BT, (b) P3HT, (c) P3OT, (d) P3DT nanofibers. (e) Height scale bar is 30 nm.

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References

- [1] C. R. Martin, *Acc. Chem. Res.* 28 (1995) 61 and references therein. [2] A. G. MacDiarmid, *Angew. Chem., Int. Ed.* 40 (2001) 2581. [3] J. X. Huang et al., *J. Am. Chem. Soc.* 125 (2003) 314. [4] B. W. Maynor et. al., *J. Am. Chem. Soc.* 124 (2002) 522. [5] T. Bjørnholm et. al., *Adv. Mater.* 11 (1999) 1218. [6] Y. F. Ma et al., *J. Am. Chem. Soc.* 126 (2004) 7097. [7] A. N. Aleshin, *Adv. Mater.* 18 (2006) 17 and references therein. [8] K. J. Ihn et. al., *J. Polym. Sci. Part B: Polym. Phys.* 31 (1993) 735-742. [9] J. A. Merlo et al., *J. Phys. Chem. B* 108 (2004) 19169. [10] T. A. Chen et. Al., *J. Am. Chem. Soc.* 117, 233 (1995).