3230 *Macromolecules* **1993,** *26,* 3230-3231

Structure/Properties of the Conjugated Conductive Polymers. 3. Copolymers of 3-Alkylthiophenes

Show-An Chen* and Jui-Ming Ni

Chemical Engineering Department, National Tsing-Hua University, Hsinchu, Taiwan 30043, China

Received January 24, 1992
Revised Manuscript Received March 18, 1993

Introduction

In the preceding paper,[1] we have proposed the structures of poly(3-alkylthiophene)s (P3ATs) with alkyl side chains having the carbon numbers 4, 8, and 12 at glassy, glass-transition, and molten states. In the glassy region, the ordered phase is composed of planes formed by stacking coplanar subchains with aligned side chains filling in the space between two neighboring planes; while the disordered phase is composed of subchains with soft conformons, where the torsion between two neighboring subchains of the same chain is distributed over several repeat units. As the glass-transition region is traversed, the soft conformons become localized conformons.

This work is undertaken to examine whether the proposed layered structures for P3ATs are valid for their corresponding copolymers. Characterization by use of X-ray diffraction and ultraviolet-visible spectroscopy indicates a positive result. In addition, such a layered structure with side chains of different lengths along ordered subchains leads to a decreased coplanarity.

Experimental Section

The copolymers of 3BT (3-butylthiophene)/3OT (3-octylthiophene), 3BT/3DDT (3-dodecylthiophene), and 3OT/3DDT were synthesized by continuous feeding of the monomer mixture (1/1 and in addition for 3BT/3OT at 1/3 by weight) for 2 h into the reaction vessel filled with a 100 mL of 0.4 N $FeCl_3$ solution in chloroform at room temperature under a dry nitrogen atmosphere. These copolymers are designated as P3BOT, P3BDDT, and P3ODDT, respectively. The total monomer added was also 0.1 M as for the synthesis of the pure P3AT.[1] The purification and film preparation procedures and the methods of characterization for the copolymers are the same as those for the P3ATs as described in the preceding work.

Results and Discussion

1. Elemental Analysis and Average Molecular Weights. The number- and weight-average molecular weights, $\bar{M}_n$ and $\bar{M}_w$, and compositions of the copolymers are listed in Table I. The $\bar{M}_w$'s are on the order of 10^5, which is sufficiently high to be considered as high MW. The MWDs are rather broad, having a polydispersity of about 10. The compositions of the copolymers are close to those of the feeds. Results of dynamic mechanical analysis (DMA) and differential scanning calorimetry (DSC) of the copolymers exhibit a single T_g for each copolymer, indicating that the copolymers have a more or less homogeneous composition distribution.

2. X-ray Diffractions. X-ray diffraction patterns of the three copolymers with the comonomer ratio 1/1 by weight and of P3BOT with the comonomer ratio 1/3 by weight are shown in Figure 1, and their corresponding values of *d*-spacing calculated using Bragg's law are listed in Table II. Each of the four copolymers exhibits weaker first-order and higher diffraction intensities at lower angles in comparison to those of the pure P3ATs. At the wide angle of about $2\theta = 23.5°$, the diffraction peaks associated with the intraplanar spacing are also much weaker. These results would indicate that the degree of ordering in the ordered phase is less than those of the pure P3AT as also evidenced in DSC results (in which no melting peak for the ordered phase appears) and in the UV-vis results (in which the energies of the absorption maxima for the entire temperature range are higher than those of the pure P3ATs) shown in the later section.

Table I. Average Molecular Weights and Compositions of the P3AT Copolymers[a]

copolymer[b]	$\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-5}$	feed, mole ratio
P3BOT (1/1)	1.3	1.2	BT/OT, 58.3/41.7
P3BOT (1/3)			BT/OT, 68.1/31.9
P3BDDT (1/1)	1.2	1.6	BT/DDT, 64.2/35.8
P3ODDT (1/1)	1.0	1.2	OT/DDT, 56.2/43.8

[a] $\bar{M}_n$ and $\bar{M}_w$ are relative to polystyrene standards. [b] The ratio in parentheses is the weight ratio of the comonomers in the feed and is close to that in the final copolymer (since the copolymerization was nearly complete).

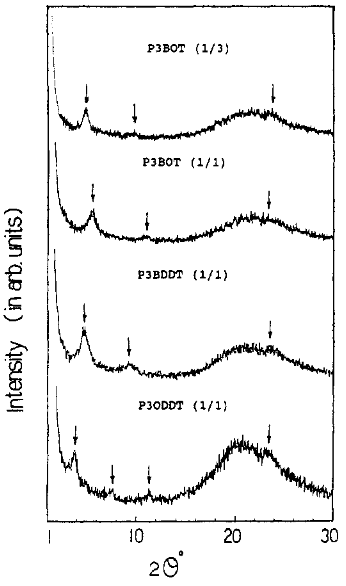

Figure 1. X-ray diffraction patterns of the 3AT copolymers.

Table II. X-ray Diffraction Maxima and Calculated *d*-Spacings of the 3AT Copolymers

	2θ (deg)/ *d*-spacing (Å)				calcd values[a] of *d*-spacing
	small angle			wide	
copolymer[b]	first	second	third	angle	first
P3BOT (1/1)	5.7/15.6	11.0/8.0		23.3/3.8	15.6
P3BOT (1/3)	4.9/17.8	9.9/9.0		23.8/3.7	17.2
P3BDDT (1/1)	4.8/18.5	9.1/9.7		23.6/3.8	16.3
P3ODDT (1/1)	3.7/23.7	7.6/11.6	11.3/7.8	23.4/3.8	21.9

[a] Calculated from eq 1. [b] The ratio in parentheses is the weight ratio of the comonomers in the feed.

Let us calculate the *d*-spacing of the copolymer d_{12} using the molar additivity rule with *d*-spacings of pure P3ATs:

$$d_{12} = x_1 d_1 + (1 - x_1) d_2 \qquad (1)$$

where *x* and *d* are the mole fraction of the comonomer in the copolymer and the *d*-spacing of pure P3AT, respectively. The calculated results are listed in Table II. The calculated values are very close to the experimental values, deviating by only 0.0, 0.6, 2.2, and 1.8 Å for P3BOT (1/1 and 1/3), P3BDDT (1/1), and P3ODDT (1/1), respectively, while the experimental values of the intraplanar spacing

---

* Author to whom correspondence should be addressed.

0024-9297/93/2226-3230$04.00/0

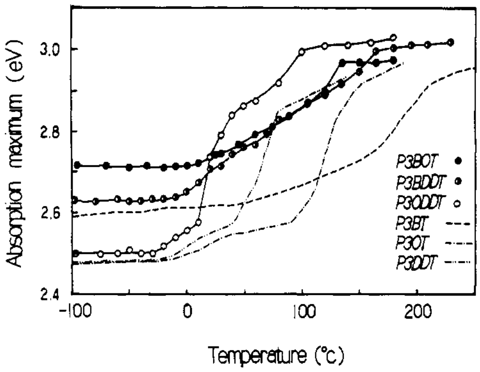

Figure 2. Plots of the energy of absorption maximum in the UV-vis spectra versus temperature for thin films of the 3AT copolymers and the corresponding pure P3ATs.

of the copolymers remain the same as those of the pure P3ATs. For the second-order peaks, the value of the *d*-spacing of each copolymer is about half of that of the first-order peak, indicating that the one-layer packing of the side chains also appears in the ordered phase. The results above are in agreement with the layered structure in the ordered phase of P3ATs revealed in the preceding paper.

3. Ultraviolet-Visible Spectroscopy (UV-Vis). UV-vis spectra of the three copolymers with the composition 1/1 by weight from -95 to +250 °C were measured, and the plots of the energy of absorption maximum versus temperature of the spectra as well as those of the pure P3ATs at similar molecular weight taken from the preceding work are shown in Figure 2. For each copolymer, the entire curve is at a higher energy level than that of its corresponding homopolymers. In addition, the melting transition region shifts to a much lower temperature level. These results would indicate that the conjugation lengths in the copolymers are lower than those in their corresponding pure P3ATs and that the degree of ordering in the ordered phase is also lower as indicated in the absence of an endothermic peak or presence of a very insignificant endothermic peak in the DSC scans.

Conclusion and Structure of the Copolymers

X-ray diffraction results suggest an ordered layered structure for the copolymers as in the homopolymers, P3ATs, but the space between two planes formed by stacking of copolanar subchains is filled with aligned long-long, short-short, and long-short side chains. This results in a reduced coplanarity of the main chains as reflected in the increase of the energy of absorption maximum to a level higher than those of the corresponding homopolymers. Thus the structure of the ordered phase of the copolymer could be proposed as shown in Figure 3.

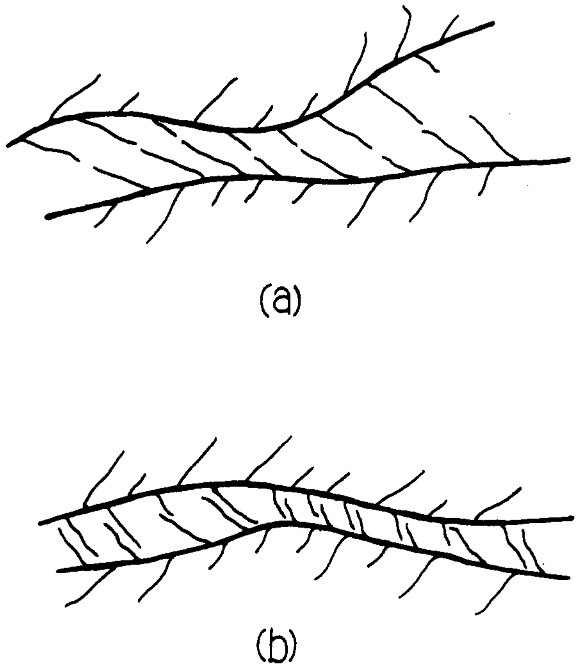

Figure 3. Schematic diagram of the layer structure of the 3AT copolymers: (a) ordered two-layer and (b) ordered one-layer structures.

Acknowledgment. We thank the National Science Council of ROC for financial aid through the project Studies on Soluble Conjugated Conducting Polymers: Structure/Properties and Electrochemical Phenomena, NSC 80-0416-E007-01.

References and Notes

(1) Chen, S. A.; Ni, J. M. *Macromolecules* **1992**, *25*, 6081.