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Comparative Structures of Thiophene Oligomers

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Using X-ray diffraction and electron microscopy, we have examined the structures of specially synthesized, highly purified oligomers of poly(thiophene) that show exceptionally high semiconductor mobilities and current on/off ratios. The tetramer, hexamer, and octamer all show the same planar conformation and herringbone-type molecular packing as has been determined earlier for the hexamer (α-6T) through detailed analyses. Thin films evaporated onto Si substrates for device applications also show the same morphologies (consisting of irregular grains ≤100 nm in diameter) and molecular orientations (essentially perpendicular to the substrates).

Polythiophene and its substituted analogues have been the objects of much research as a result of their electrical conductivity and related electrical properties. Of increasing interest very recently have been the low-molecular-weight analogues of polythiophene, not only as model compounds but most directly as very promising active semiconducting materials. This follows the very extensive and pioneering work by Garnier and his colleagues (see, e.g., refs 1−3). We have recently reviewed these materials and their applications.[4]

In this brief article, we provide comparative X-ray diffraction evidence on three consecutive even members of the oligothiophene homologous series and draw some general conclusions. These homologues are the α-tetra-, α-hexa-, and α-octathienyl (α-4T, α-6T, and α-8T, respectively). For α-6T four detailed structural reports have appeared,[5−8] which are in many respects divergent and whose specific differences have been summarized in detail in a recent review.[4] These materials were synthesized in our laboratories in a highly pure form using improved synthetic and purification procedures as described in detail previously.[9,10] The resulting α-6T and α-8T have higher melting points than previously reported,[5,11] while α-4T was in the same range.[5] In terms of their electrical performance, these materials exhibit some exceptional characteristics,[9] including pure intrinsic behavior (α-6T), high mobilities (especially for α-6T and α-8T), and very low off-currents (α-4T and α-6T).

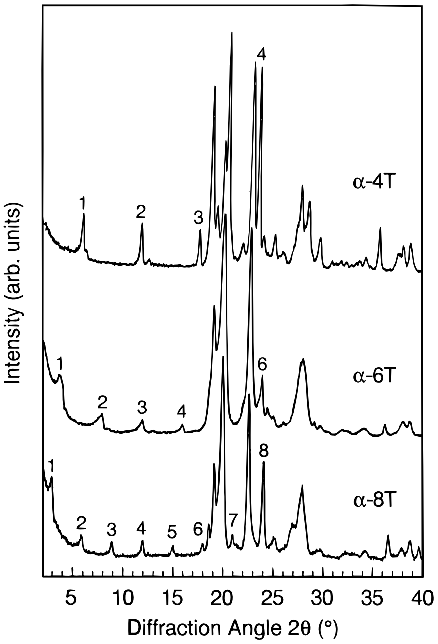

Figure 1. X-ray diffractograms of α-4T, α-6T, and α-8T following synthesis and purification as described in the text.

To understand this performance in terms of their molecular and crystalline structures, we studied X-ray diffractograms of these materials following synthesis and purification, as well as after their deposition onto Si substrates for device applications. The diffractograms were obtained in the reflection geometry using Ni-filtered Cu Kα radiation at a scanning rate of 0.5° 2θ/min. For the bulk oligomers following purification, typical diffractograms are seen in Figure 1. These are dominated by a set of very similar strong peaks in the 19−29° 2θ region and by a set of lower-angle reflections, which are numbered in Figure 1. The diffractograms for α-6T and α-4T exhibit many common features with those presented by Porzio et al.,[6] although the fine features of the latter were very variable depending upon how the specimens had been crystallized, ground, mixed with collodion, etc., and displayed strong effects of preferred orientation.[6] For α-8T we could find no previous structural reports.

It is clear from Figure 1 that the low-angle peaks are successive orders of reflections corresponding to the

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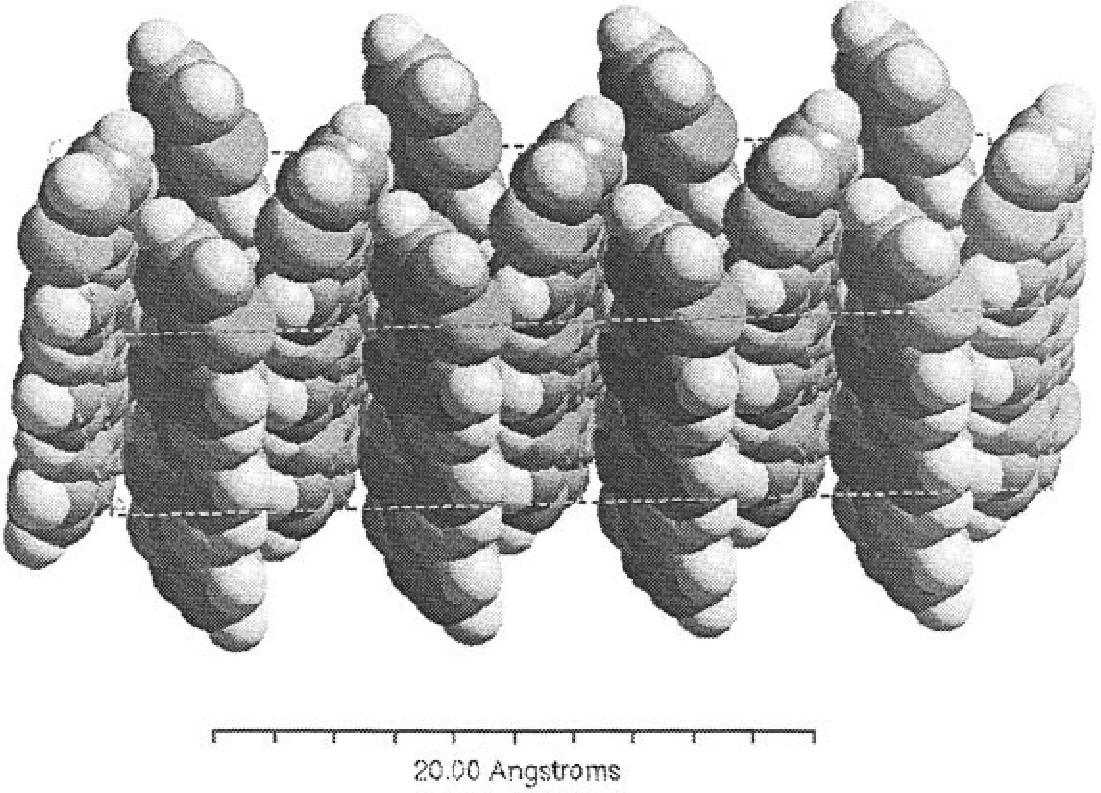

Figure 2. Lattice packing of these oligothiophenes as exemplified by α-6T and demonstrating the herringbone pattern of crystallization adopted by these materials.

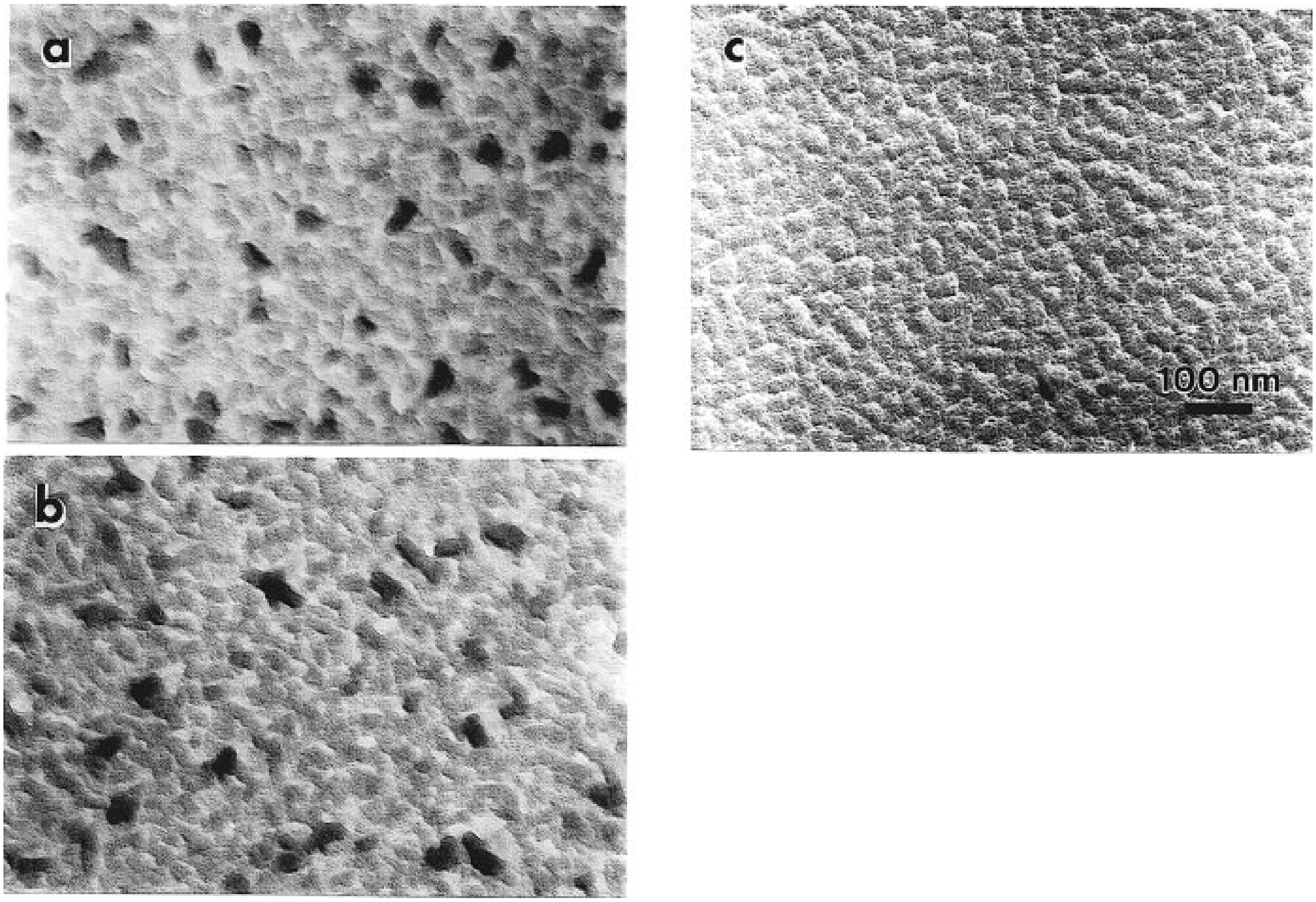

Figure 3. Bright-field transmission electron micrographs of (a) α-4T, (b) α-6T, and (c) α-8T thin films (ca. 50 nm thickness) that had been deposited by vacuum evaporation. The samples were shadowed obliquely with Pt/C to increase electron contrast.

same underlying chain conformation, and we have labeled these numerically in this manner. In each case, the first order corresponds to the full extended-chain packing of α-nT molecules end-to-end, as we found by

Table 1. Major Intermolecular Spacings in Oligothiophenes

	interplanar spacings (Å)		
reflection	α-4T	α-6T	α-8T
$41\bar{1}$	4.40	4.46	4.46
020	3.93	3.92	3.94
$42\bar{1}$	3.16	3.20	3.19

molecular modeling and by comparison with the very detailed analyses for α-6T.[6−8] It is interesting to note that the fourth order for α-4T, the sixth for α-6T, and the eighth for α-8T *do coincide* at a reciprocal-lattice spacing that corresponds to the monomeric repeat for thiophene (see again Figure 1). These results confirm the essentially all-trans conformation for α-4T and extend it now also to the octamer, which had not been studied before.

Figure 1 also displays a great similarity in the peaks of all three oligothiophenes that lie in the 19−23° 2θ region. This is better seen in Table 1, which identifies the corresponding reflections and *d* spacings (the identification follows the single-crystal-based assignments by Horowitz et al.[7]). Taking into account the fact that the molecules are inclined to all three unit-cell axes, these spacings correspond to the closest *side-to-side* packing of these molecules (which would be the *interchain* packing in macromolecules). These results therefore indicate that not only the conformation but also the arrangement of the molecules on a lattice is the same among all three oligomers. The arrangement is seen through space-filling molecular models in Figure 2 and is characterized by the herringbone packing of the chains which may play a major role in the exceptional charge-transport properties of these oligomers. A similar packing was also demonstrated for α-5T.[6] In α-3T the herringbone pattern is preserved, but the chains are now parallel to one axis of the unit cell which (cell) is doubled and contains eight molecules.[12]

In addition, we have also confirmed in thin films of α-4T and α-8T evaporated unto Si substrates that the orientation is as we had found earlier for α-6T, i.e., with the molecular chains close to normal to the substrate.[13−15] The corresponding diffractograms are dominated by the lowest-angle peak (and subsequent orders) similarly to Figure 5 of ref 14. As far as the morphologies of the tetramer and octamer are concerned, we found through transmission electron microscopy that they are totally analogous to that of α-6T,[13] consisting of very small, irregular grains <100 nm in average diameter (see Figure 3). Therefore, from all of the above we conclude that the structure, morphology, and substrate orientation of similarly processed α-4T, α-6T, and α-8T are the same, pointing to uniform molecular processes involved in the crystallization of these oligomers irrespective of chain length. This is an important result in understanding (and possibly extrapolating) their properties, and one that should not necessarily be assumed a priori: Of course, chain-length effects are more pronounced in the case of *side-chain* substituents. For example, in alkyl-substituted polysilanes the molecular conformation is all-trans for dimethyl[16] and dipropyl,[17] 7/3-helical for dibutyl[18] and dipentyl,[19] reverting once again to all-trans for dihexyl[20,21] and dioctyl.[21]

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