Structural Order in Conjugated Organic Films Prepared by Catalytic Deprotection of Self-Assembled Polymers

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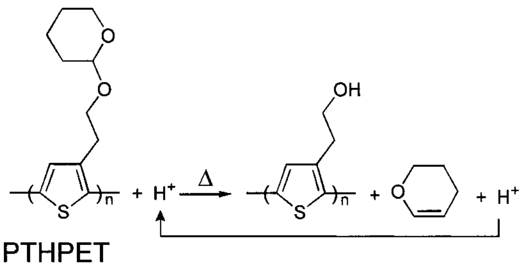
Persistent lamellar ordering, consistent with coplanar stacking of polymer chains, is found for films of poly(3-(2-hydroxylethyl)thiophene) (PHET) obtained by catalytic removal of tetrahydropyran from films of poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (PTHPET). Structural ordering appears to be due to H-bonding interactions between terminal hydroxy groups. This morphology is unique for films comprising of short side chain poly(alkylthiophenes), which are usually characterized as being amorphous. The resultant films possess void spaces due to loss of the bulky group and retention of the initial morphology. The formation of additional free volume may explain why this reaction is facile in these materials even though they are semicrystalline. Catalytic removal of tetrahydropyran from copolymer films of PTHPET and 3-hexylthiophene also leads to persistent ordering, but the lamellar framework partially relaxes in some cases so that the interlamellar spacing is reduced. These are metastable structures that become amorphous upon heating to elevated temperatures.

Introduction

Poly(3-(2-(2-tetrahydropyranyloxy)alkyl)thiophenes) are useful polymers from which functionalized polythiophenes can be prepared because the tetrahydropyran group (THP) can be cleaved by acid to render a terminal hydroxy group.[1] Recent studies on the solid-state reaction of poly(3-(2-(2-tetrahydropyranyloxy)-ethyl)thiophene) (PTHPET) indicates this polymer is stable up to 220 °C.[2] Above this temperature, dihydropyran (DHP) is eliminated, and the polymer is converted to poly(3-(2-hydroxylethyl)thiophene) (PHET). Films of PTHPET containing strong acids are relatively stable at room temperature, but elimination of DHP proceeds at 130 °C, i.e., much lower than in the absence of acid. The process is catalytic as illustrated in Scheme 1, therefore requiring only trace acid. Upon removal of THP, the resultant polymer is rendered insoluble and possesses an increased degree of conjugation compared to the parent polymer due to loss of the bulky side group. Insoluble films of regioregular, short side chain polythiophenes can thus be prepared on various surfaces where previously such films could only be obtained on conductive surfaces by electrochemical polymerization of the appropriate monomer.[3] In conjunction with the incorporation of photochemical acid generators and photolysis through a photomask, the solid-state deprotection reaction can be spatially controlled so that conjugated polythiophenes can be patterned with micron resolution with virtually no photolytic destruction of the π-conjugated system.[2a]

Scheme 1



A surprising feature of the catalytic reaction is that it occurs with striking efficiency even though the films are semicrystalline. To gain more insight into this, we investigated the morphology of the films by X-ray diffraction (XRD). To put the work in context, it is noted that XRD spectra of regioregular poly(3-alkylthiophenes) are characterized by a series of sharp and weak reflections indicative of short range order in the form of a comb-shaped/lamellar morphology in which adjacent thienyl units along the chain lie coplanar, and wherein the chains stack on top of each other.[4] The interlamellar

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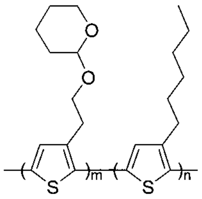
Table 1. *d* Spacings and UV−vis Absorption Data for PTHPET and P(THPET-*co*-3HT) Copolymer Films

	d-spacing (Å)		λ_{max} (nm)[a]		
polymer comp. (PTHPET/HT)	parent polymer	after catalytic removal of THP[b]	parent polymer	after catalytic removal of THP[c]	after noncatalytic removal of THP[d]
100/0	17.5	17.2	467	505	449
75/25	17.5	16.5	476	478	460
50/50	17.3	15.6/17.3	508	498	470
35/65	17.2	15.9/17.0	513	508	476
20/80	16.7	16.7	518	513	498
0/100	16.4		520		

[a] At 20 °C. [b] 130 °C for 30 min in the presence of 5% camphorsulfonic acid. [c] 140 °C for 20 min in the presence of 5% camphorsulfonic acid. [d] Acid-free polymer, 245 °C for 20 min.

separation varies with length of the side chain. For example, these spacings are 16.8, 21.0, 28.0, and 35.3 Å for hexyl, octyl, dodecyl, and hexadecyl derivatives, respectively.[5] These experimental values are smaller than calculated simply from the extended length of the side chain. Some authors attribute the difference to partial intercalation of the side chains, and others, to tilting of the side chains with respect to the polymer backbone.[4]

In this paper, details of structural order in films of PTHPET are presented. Also reported are XRD studies on related copolymers of (3-(2-(2-tetrahydropyranyloxy)-ethyl)thiophene) (THPET) and 3-hexylthiophene (**I**) prior to and following solid-state reaction.



I

Experimental Section

The synthesis of THPET, its homopolymerization, and copolymerization with 3-hexylthiophene were achieved by employing Grignard cross-coupling chemistry. Detailed procedures have been previously reported.[2b] The polymers used in this work include the homopolymer (PTHPET); copolymers possessing THPET/HT ratios of approximately 75/25, 50/50, 35/65, and 20/80, and the homopolymer P3HT.[2b] All the polymers were prepared in their regioregular configuration. NMR spectroscopy indicated the head-to-tail content to be >98%. Values of λ_{max} for polymer and copolymer films are reported in Table 1. Molecular weights, measured by gel permeation chromatography, ranged from 7400 to 11 500 g/mol. Molecular scale calculations were performed using Hyperchem software (Hypercube Inc.). Interlamellar spacings were estimated from the geometry of the polymer backbone, based on 2,2′−5′2″-terthiophene,[6] and the contour lengths of the side chains. Polymer films 600−800 nm thick for XRD studies and 100−150 nm thick for UV−vis absorption studies were prepared by casting polymers on to glass substrates from chloroform/THF solutions in the absence or presence of 5 mol % camphorsulfonic acid (mol % based on the thienyl unit). Acid-free samples were annealed at 115 °C for 10 min. Acid-catalyzed removal of tetrahydropyran was achieved by heating the sample at 130 °C for several minutes. XRD spectra of thin films on glass were obtained at room temperature using a Siemens D5000 diffractometer with a Cu X-ray tube. Samples were mounted horizontally in a Bragg−Brentano geometry, and the data were collected in $\theta-\theta$ mode from 2 to 35 in 0.1 intervals with a 3.6 s/point dwell time.

Results and Discussion

PTHPET Homopolymer. XRD spectra of PTHPET show a sharp peak at $2\theta = 5.05°$, which is equivalent to an interlamellar separation along the *a* axis (*d* spacing) of 17.5 Å (see Figure 1a and Table 1). Calculations of the dimensions of a coplanar regioregular PTHPET homopolymer indicate that the expected interlamellar separation for fully extended (2-tetrahydropyranyloxy)ethyl side chains, lying perpendicular to the *c* axis, is 18.5 Å. This value is larger than the measured *d* spacing. Interdigitation of the side chains is an unlikely cause since simple molecular modeling shows the THP is too bulky, and leads to the conclusion that the side chains are most likely tilted with respect to the direction of π-stacking. The XRD patterns shown in Figure 1a do not exhibit a peak due to the interstack spacing (*b* axis). However, a broad peak corresponding to the interstack spacing of 3.6 Å was observed for powdered samples (not shown). This indicates that the polymer film is anisotropic with the *b* axis parallel to the substrate surface, as is observed for regioregular poly(3-alkylthiophenes).[7]

The presence of 5 mol % camphorsulfonic acid in the polymer film at room temperature has no significant effect on the XRD spectra. Upon acid-catalyzed removal of THP at 130 °C, the XRD peak persists as shown by the dashed line in Figure 1a. The new *d* spacing, 17.2 Å, is only slightly smaller than that for the parent polymer, indicating that chains only marginally relax along the *a* axis to fill the void left by the THP groups. The interlamellar separations are depicted schematically in Figure 2. The persistence of such a large interlamellar spacing is surprising because calculation of a coplanar configuration of the resultant polymer, poly(3-(2-hydroxylethyl)thiophene) (PHET), indicates that the *d* spacing should be very much smaller (~11.8 Å). The discrepancy, ~5.4 Å, represents the dimension of the interlamellar voids that remains as a result of loss of THP. The self-creation of these voids may explain why the elimination of THP can be achieved with completeness. Even more surprising is the persistence of the lamellar structure since it is generally recognized

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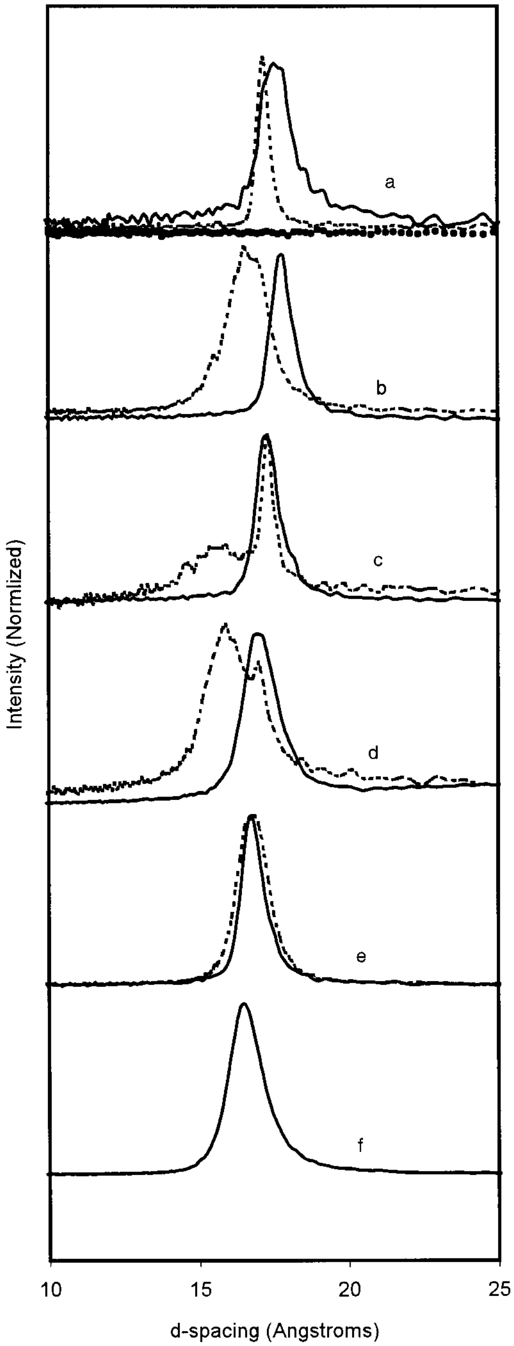

Figure 1. X-ray diffraction (XRD) spectra expressed as *d* spacings: (a) PTHPET; THPET/HT copolymers possessing molar ratios (b) 75/25, (c) 50/50, (d) 35/65, (e) 20/80; and (f) P3HT. Solid lines: parent polymer. Dashed lines: after catalytic removal of THP at 130 °C. Dotted lines: after noncatalytic removal of THP at 245 °C. Spectra were taken at 25 °C.

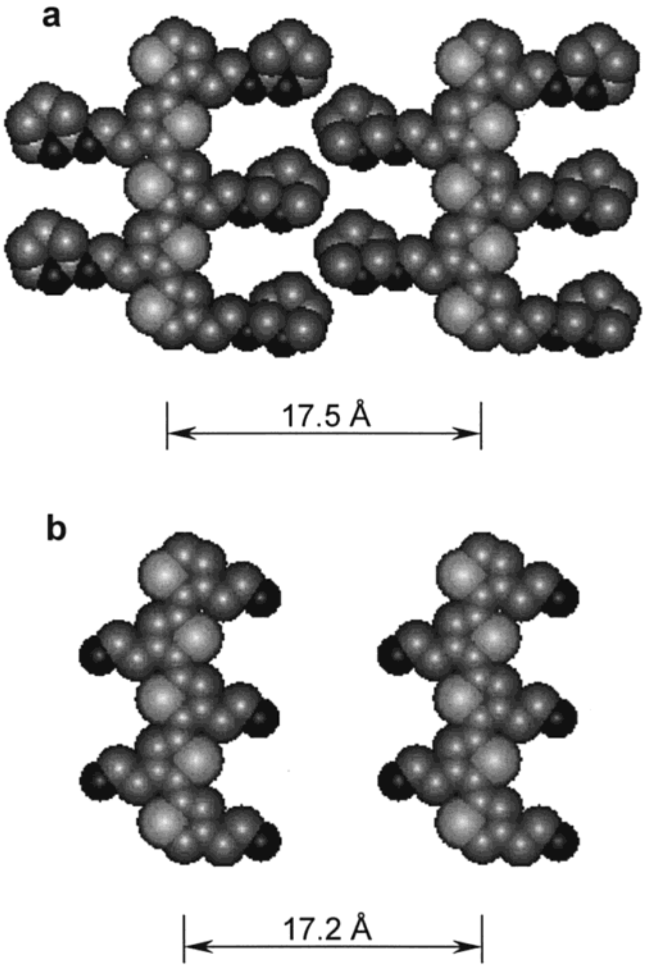

Figure 2. Structural dimensions of (a) PTHPET and (b) after catalytic removal of THP.

that such lamellar-type ordering in P3ATs requires side chains possessing at least four contiguous atoms (excluding H-atoms). P3ATs possessing side chains shorter than butyl, for example, are disordered and amorphous.[4a,e] Lamellar ordering in these systems is unexpected also because Barbarella et al have shown that polyhydroxyoligothiophenes such as 3,3′-bis(2-hydroxyethyl)-2,2′-bithiophene exhibit a noncoplanar, anticonformation, and an interannular twist angle of 67.5°.[8] Quaterthiophene and sexithiophene prepared from this dimer are reported to exhibit absorption maxima of 334 and 352 nm, respectively, which is much shorter than the parent oligothiophenes that possess no hydroxy groups. The highly twisted interannular structure is shown to result from intramolecular H-bonding. However, unlike the polyhydroxyoligothiophenes, which contain head-to-head linkages, the distance between terminal hydroxy groups on adjacent thienyls on PTHPET prepared in the present work is much too large for intramolecular H-bonding to occur since thienyl groups are linked head-to-tail. The persistence of the lamellar structure in deprotected PTHPET therefore most likely results from close juxtaposition of terminal hydroxyls on adjacent stacks of polymer layers. Evidence for H-bonding is qualitatively confirmed by the broadness of the absorption peak due to hydroxyl groups at~3400 cm^{-1} in the FTIR spectra of the deprotected polymer.[2b]

PTHPET Copolymers. XRD spectra of PTHPET-3HT copolymers are shown in Figure 1b−e. The *d* spacings possess values between those of PTHPET and P3HT homopolymers (17.5−16.4 Å) (listed in Table 1) and decrease in value with increasing 3HT content. Upon acid-catalyzed removal of THP, the dimensions of the structural ordering change depending on composition, but the lamellar network is retained. XRD spectra of the 75 mol % THPET copolymer exhibits a broad XRD peak after reaction that transposes to a *d* spacing that is narrower (16.5 Å) than that observed

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[8] Barbarella, G.; Zamianchi, M.; Bongini, A.; Antolini, L. *J. Org. Chem.* **1996**, *61*, 4708.

for the parent polymer (17.5 Å). By use of the same argument as for the parent homopolymer, voids several angstroms wide must exist.

For the copolymer possessing a THPET/HT ratio of 50/50, an interlamellar separation of 17.3 Å persists after reaction (Figure 1c), indicating that the morphology of a portion of the film does not change upon loss of THP. However, a broad peak at $2\theta = 5.65$ degrees appears which indicates that some diffracting domains possess an interlamellar spacing of ~15.6 Å. This value is even less than that observed for P3HT (see Figure 1f) and can be explained on the basis of slippage of the polymer chains in the direction of the *a* axis facilitated by the presence of the much shorter hydroxyethyl side chains. The fact that these much narrower *d* spacings were observed in the copolymer, and not in the PTHPET homopolymer, implies that the hexyl chains possess a plasticizing action on the polymer chains. The narrowing in *d* spacing upon removal of THP is even more pronounced in the sample containing 35 mol % THPET (see Figure 1d). Here, a peak possessing an interlamellar spacing of 15.9 Å is the dominant feature, and only a weak signal associated with the original interlamellar spacing is observed (17.0 Å). Hence, relaxation of the structural order upon loss of THP increases with 3HT content. However, XRD data for the deprotected 20 mol % THPET copolymer shows only a single peak indicating at *d* spacing 16.7 Å (Figure 1e), which is unchanged from its parent copolymer. This value is similar to that of poly(3-hexylthiophene) homopolymer. It is inferred that a narrowing of the *d* spacing does not occur upon reaction since the mole fraction of hydroxy ethyl side chains is relatively low compared to those of the other copolymers, and the structural is dominated by the hexyl side chains.

Absorption Spectra. The absorption spectra of PTHPET homopolymer and copolymers after removal of THP are indicative of a coplanar structure. For example, λ_{max} for the homopolymer is 505 nm after catalytic reaction at 130 °C (See Table 1), i.e., 38 nm longer than the parent polymer, due to a release in steric strain and a reduction in ring torsion between adjacent thienyl units. However, noncatalytic removal of THP at higher temperatures (245 °C), and even catalytic reaction at much higher temperatures, cause λ_{max} to be significantly lower (449 nm), when cooled to room temperature. The corresponding XRD spectra for polymers deprotected at these elevated temperatures show a complete absence of structural order, as shown in Figure 1a. This occurs because these higher temperatures are close to the melting point of the polymer.[2b] The disordered structure induced by melting is retained upon cooling presumably because of strong H-bonding between terminal hydroxyls.

The increase in λ_{max} upon catalytic reaction at lower temperature becomes less significant as the THPET content of the polymer in reduced, even though λ_{max} of the parent polymer increases (see Table 1), because the higher hexyl chain content favors coplanarity of adjacent thienyl units. In all cases, when THP is removed noncatalytically at higher temperatures, λ_{max} is much lower than those observed for the catalytically deprotected copolymer films, for reasons explained above, and the XRD spectra is featureless (not shown). However, the decrease in λ_{max} gets progressively smaller with decreasing THPET content because the resultant 3-HT content increases at the expense of the H-bonding hydroxy content.

Conclusions

The homopolymer of THPET and its copolymers with 3HT exhibit short-range order in the form of a π-stacked, comblike structure. Upon catalytic removal of THP, the interlamellar spacing, determined by the length and bulkiness of the side chain, is completely retained in some cases and partially retained in others. This persistent order may arise because of the existence of strong π-stacking forces or hydrogen bonding between highly organized hydroxy-terminated side chains. For copolymers possessing intermediate compositions of both monomers, evidence is presented which suggests that the lamellar framework relaxes so that the interlamellar spacing (*a* axis) is significantly reduced. Such lamellar-type structures are unique in polyalkylthiophenes possessing relatively short side chains. No such structures have been reported for polythiophene or poly(3-methyl thiophene). Catalytic removal of THP leads to voids, the creation of which facilitate elimination of THP, and may explain why the reaction is very efficient in these semicrystalline materials. The fact that structural order is lost upon heating the films at elevated temperature indicates that these are metastable structures that appear to exist because of H-bonding between terminal hydroxyl groups.

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