Macromolecules **2000,** *33,* 5073−5079

Solid-State Thermolytic and Catalytic Reactions in Functionalized Regioregular Polythiophenes

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Received November 2, 1999; Revised Manuscript Received April 21, 2000

ABSTRACT: (3-(2-(2-Tetrahydropyranyloxy)ethyl)thiophene) (THPET) was homopolymerized (PTHPET) and copolymerized with 3-hexylthiophene (PTHPET-*co*-3HT) to obtain functionalized regioregular π-conjugated polymers. Thermolytic and catalytic removal of the bulky tetrahydropyran (THP) group from thin solid films of the polymers was studied. Thermolytic cleavage of the THP group occurs with a remarkably high yield in the solid state. Deprotection can be achieved catalytically in the presence of acids, at a significantly lower temperature. For PTHPET homopolymer, an increased degree of conjugation persists upon removal of the THP group. Copolymer films, however, exhibit a melting transition and a subsequent decrease in coplanarity at high temperatures. This disorder prevails upon cooling due to either strong interchain H-bonding or the absence of crystallizable side chains. When deprotection is carried out at lower temperatures, a high degree of π-delocalization can be retained. The influence of composition on the reactivity of the polymers is described.

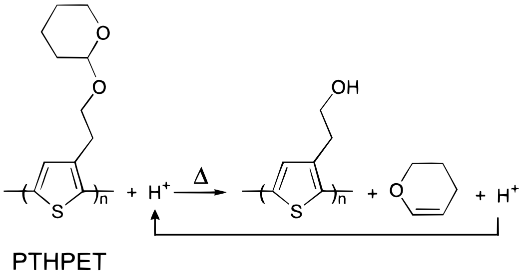
Introduction

Chemically amplified photolithography of a π-conjugated polymer film was recently reported.[1] In conjunction with a photoacid generator, poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) (PTHPET), irradiated with low incident doses through a photomask, was imaged with micron resolution. Both thermolytic and catalytic removal of the bulky pendant group tetrahydropyran (THP) from thin solid polymer films was demonstrated (Scheme 1).

Studies of solid-state deprotection/elimination reactions in polymers are studied in detail in the field of photoresist chemistry.[2] However, photoresist materials are usually based on polymers that are not π-conjugated and that are designed to yield amorphous films upon solution casting. In contrast, π-conjugated polymer films are often designed to possess long-range order and, in many cases, semicrystallinity. In the case of regioregular poly(3-alkylthiophenes) (P3ATs), for example, extensive interdigitation of side chains yields a lamellar-type structure in the solid state.[3] Although there have been several reports of synthetic procedures using elimination of protecting groups from the side chains of P3ATs in order to prepare functionalized polymers, these all describe reactions in solution.[4] Other than the preliminary report on chemically amplified photolithography of a π-conjugated polymer film,[1] similar reactions in the solid state have received no attention. It is not obvious whether deprotection and elimination reactions should occur with high efficiency in thin films because of the strong interchain interactions induced by lamellar formation and π-stacking. There is a clear need to investigate these reaction systems.

Regioregular PTHPET is a useful polymer to probe reaction processes in functional materials because they are soluble and characterizable, they show long-range order as evidenced by X-ray diffraction, and they can be copolymerized to afford a wide variety of diverse structures. Furthermore, detailed studies of these films will aid the understanding of chemically amplified photolithographic processes for which these polymers have been employed. This paper describes thermal and catalytic removal of THP from PTHPET in significantly more detail than previously reported.[1] To develop structure−property relationships in these systems, copolymers of (3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) and 3-hexylthiophene (PTHPET-*co*-3HT) have been prepared and studied. The incorporation of 3HT groups into the chain was intended to modify the free volume, structural ordering, and thermal properties of the polymer. The composition of the copolymers was indeed found to influence reactivity of the corresponding films.

Scheme 1. Acid-Catalyzed Elimination of Dihydropyran from PTHPET



Experimental Section

Syntheses of Poly(3-(2-(2-tetrahydropyranyl-2-oxy)-ethyl)thiophene (PTHPET). PTHPET was synthesized by the following procedure (Scheme 2). 2-(3-Thienyl)ethanol was brominated selectively with 1 equiv of NBS in DMF and protected by reacting with 5 equiv of dihydropyran to afford 2-bromo-3-(2-tetrahydropyranyloxy)ethyl)thiophene.[1,4a,b] The regioregular polymer, PTHPET, was prepared by cross-coupling of the corresponding 5-Grignard reagent.[5]

2-Bromo-3-(2-hydroxy)ethylthiophene. In the absence of light, a solution of NBS (3.56 g, 20 mmol) in DMF (20 mL) was added dropwise to a solution of 3-(2-hydroxyethyl)-thiophene (2.56 g, 20 mmol) (Aldrich) in DMF (20 mL). After stirring for 3 h, the reaction mixture was quenched with ice−water and extracted with dichloromethane. Combined organic

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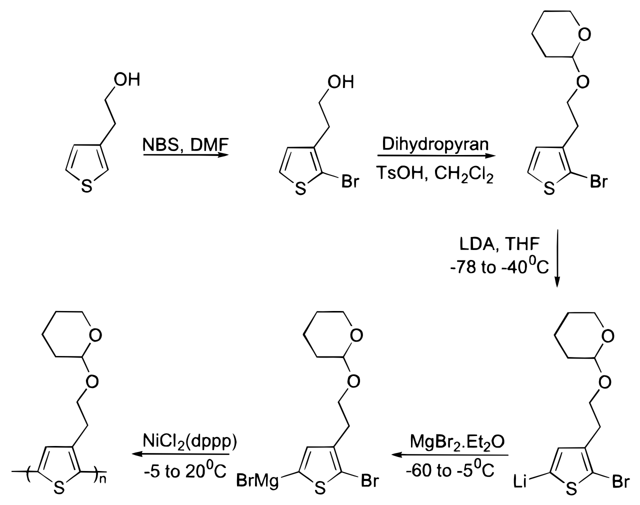
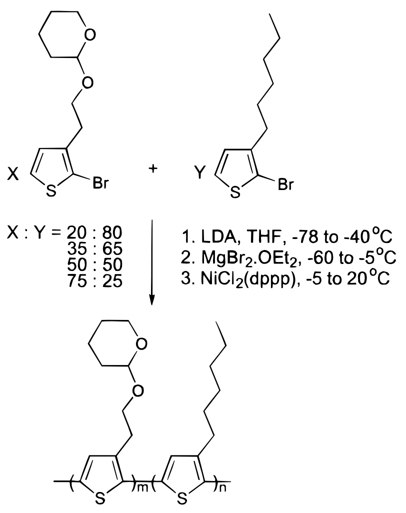
Scheme 2. Synthesis of PTHPET Homopolymer



Scheme 3. Syntheses of PTHPET-*co*-3HT Copolymers



phases were washed with water, dried over magnesium sulfate, and concentrated under vacuum. Distillation of the crude product gave 3.52 g (98%) of desired product. ^{1}H NMR: 7.23 (d, $J = 5.6$ Hz, 1H), 6.87 (d, $J = 5.6$ Hz, 1H), 3.84 (t, $J = 6.6$ Hz, 2H), 2.87 (t, $J = 6.6$ Hz, 2H), 1.53 (s, 1H). MS *m/z* (based on ^{79}Br). 206 M^{+}; 207 (M + 1)$^{+}$; 208 (M + 2)$^{+}$. Elemental analysis: Calcd: C, 34.80%; H, 3.41%. Found: C, 35.01%; H, 3.45%;

2-Bromo-3-(2-(2-tetrahydropyranyl-2-oxy)ethyl)thiophene (BTHPET). To a solution of 2-bromo-3-(2-hydroxy)-ethylthiophene (3.11 g, 15 mmol) and freshly distilled dihydropyran (6.31 g, 7 mmol) in 80 mL of dry dichloromethane, cooled to 0 °C, was added 29 mg (0.15 mmol) of *p*-toluenesulfonic acid monohydrate under N$_2$. After stirring for 10 min at 0 °C, by 2 h at room temperature, the mixture was poured into ice−water and extracted with dichloromethane. The organic phase was combined, washed with saturated sodium hydrogen carbonate solution and water, and dried over magnesium sulfate. The crude product obtained following removal of solvent was chromatographed on silica gel (Silica Gel 60, EM Science) with dichloromethane to afford 2.99 g (97%) of the desired monomer. ^{1}H NMR: 7.18 (d, $J = 5.6$ Hz, 1H), 6.88 (d, $J = 5.6$ Hz, 1H), 4.60 (m, 1H), 3.91−3.48 (m, 4H,), 2.88 (t, $J = 6.9$ Hz, 2H), 1.82−1.49 (m, 6H). MS *m/z* (based on ^{79}Br): 290 M^{+}, 291 (M + 1)$^{+}$, (M + 2)$^{+}$ 292. Elemental analysis: Calcd: C, 45.37%; H, 5.60%. Found: C, 45.75%; H, 5.38%.

Polymerization of 3-(2-(2-Tetrahydropyranyl-2-oxy)-ethyl)thiophene. At room temperature, 4.00 mL of *n*-butyllithium (10 mmol, 2.5 M in hexane) was syringed slowly into a solution of 1.40 mL of dry diisopropylamine (10 mmol) in freshly distilled THF (60 mL). The mixture was cooled to −40 °C and stirred for 40 min. The LDA solution was cooled to −78 °C, whereupon 2.91 g (10 mol) of BTHPET was added. After stirring for 40 min at −40 °C, the reaction mixture was cooled to −60 °C, and 2.58 g of magnesium bromide diethyl etherate (10 mmol, Aldrich) was added. The reaction was stirred for 20 min and allowed to warm slowly to −5 °C, at which time 38 mg of NiCl$_2$(dppp) was added. Finally the reaction mixture was warmed to room temperature and stirred for 24 h. The reaction was quenched with MeOH, and polymer was precipitated in MeOH. Soxhlet extraction with methanol and hexane yielded 0.79 g of polymer (38% based on BTHPET). ^{1}H NMR: 7.13 (s,1H), 4.66(t, 1H), 4.07−3.48 (m, 4H), 3.11 (t, 2H), 1.81−1.53 (m, 6H). ^{13}C NMR: 136.5, 133.7, 132.0, 129.5 (4C, thienyl ring), 98.8, 62.1, 30.7, 25.6, 19.5(5C, THP), 30.0 (1C, α-methylene), 67.1(1C, β-methylene).

Syntheses of Poly[3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene-*co*-3-hexylthiophene] (PTHPET-*co*-3HT). Using the same coupling reaction as described above (Scheme 3), 2-bromo-3-(2-(2-tertrahydropyranyl-2-oxy)ethyl)thiophene (BTHPET) and 2-bromo-3-hexylthiophene (B3HT) were copolymerized using different feed ratios to yield a series of copolymers with different compositions (see Table 1). Copolymers were purified by Soxhlet extraction using first methanol and then hexane. The yield was 18−35% based on the monomers. ^{1}H NMR: 7.13, 7.08, 7.04, and 6.98 (s, aromatic region); 4.67 (s), 4.08−3.49 (m), and 3.12 (t) (THPET); 2.80 (t) and 0.91 (t) (HT), 1.83−1.32 (m) (THPET and HT). ^{13}C NMR: 140.3−128.6 (m, aromatic region); 31.7, 30.5, 29.5, 29.2, 22.6, and 14.1 (HT); 98.7, 67.1, 62.1, 30.7, 29.9, 25.5, and 19.4 (THPET).

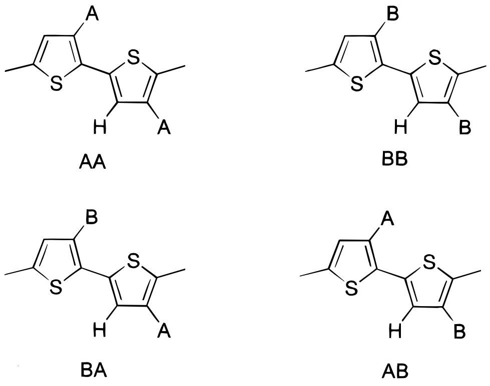
Table 1. Characteristics of Homopolymer and Copolymers of THPET

polymer composition (THPET/HT)					λ_{max} (nm)	
feed ratio	found	M_w	M_n	D	CHCl$_3$	film
100/0	100/0	19 900	10 700	1.85	439	467
75/25	77/23	12 500	8 000	1.56	440	476
50/50	49/51	12 300	8 200	1.49	442	508
35/65	34/66	18 300	10 800	1.68	446	513
20/80	19/81	10 100	7 400	1.39	447	518
0/100	0/100	16 300	11 300	1.44	449	520

Measurements. Molecular weights were measured by gel permeation chromatography (GPC) (Waters model 510) equipped with μ-Styrgel columns. Polymers were eluted with tetrahydrofuran using a flow rate of 1 mL/min and detected with a UV−vis spectrophotometer (Waters model 486) at 440 nm. Molecular weights were calibrated against poly(3-hexylthiophene).[6] UV−vis absorption spectra were recorded on a Cary 3E (Varian) spectrophotometer equipped with a custom-built temperature control cell (accuracy ±2 °C). Thin polymer films for UV−vis measurements were cast on glass plates from THF/chloroform solutions. Temperature-dependent UV−vis absorption were recorded using a scan rate of <2 °C/min and performed under a N$_2$ atmosphere.

^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AMX400 in CDCl$_3$. The compositions of copolymers were determined by the ratio of the integral of the α-methylene resonance peaks corresponding to THPET and HT units. FTIR spectra were recorded on a Bomen Michelson MB series. Polymer samples were cast on sodium chloride disks as thin films. Differential scanning calorimetry (DSC) measurements were carried out on 5−10 mg polymer using a Perkin-Elmer DSC-7 calorimeter. The scan rate was typically 10 °C/min under a N$_2$ atmosphere. Thermogravimetric analysis (TGA) was performed on Shimadzu TGA-50 thermogravimetric analyzer. Measurements were carried out at 5 °C/min on 3−5 mg polymer under ambient atmosphere unless specified. The onset temperature was estimated from the point of intersection of two lines: one extrapolated from the slope of the curve just prior to loss of the THP group and the second from the steepest part of the curve. The solubility of polymers before and after deprotection was determined by UV−vis absorbance of their solutions in different solvents.

Scheme 4. Possible Diads Resulting from Head−Tail Coupling between Two Monomers



Thermal deprotection of polymers was achieved by heating the polymers to 245−265 °C temperature for 10 min. Acid-catalyzed deprotection was carried out by heating the polymers in the presence of 5 mol % acid to 130−145 °C for 30 min.

Results and Discussion

Polymer Structure. The structure of the polymers was confirmed by NMR spectroscopy. PTHPET homopolymer gave ^{1}H NMR resonance peaks at 7.13, 4.66, and 3.11 ppm assigned to the thienyl ring, the methine of the THP moiety, and the α-methylene, respectively.[4a] Eleven resonance peaks were observed in the ^{13}C NMR spectra. Four peaks at 129.5, 132.0, 133.7, and 136.5 ppm were assigned to thienyl ring carbons.[5] The observed peaks at 19.5, 25.6, 30.7, 62.1, and 98.8 ppm are characteristic of the THP group.[7] Peaks at 30.0 and 67.1 ppm were assigned to α- and β-methylene carbons, respectively. The regioregularity of the polymer is evidenced by the fact that only four aromatic carbon signals and only one α-methylene carbon signal were observed.

^{1}H NMR analysis of PTHPET-*co*-3HT copolymers gave one methine resonance peak at 4.67 ppm assigned to the methine of the THP moiety, two α-methylene resonance peaks at 3.12 and 2.80 ppm corresponding to THPET and HT units, respectively, and peaks at 7.13, 7.08, 7.04, and 6.98 ppm assigned to aromatic protons. The four aromatic resonance peaks are consistent with the four possible diads resulting from head−tail coupling between two different monomers (Scheme 4). This is evidence for the high regioregularity of the copolymers. The composition of each copolymer was determined from the ratio of integrals of the two α-methylene peaks. The results (see Table 1) show that the feed ratios are conserved in final copolymers, presumably because the polymerization was allowed to go to completion. ^{13}C NMR of these copolymers exhibited 13 well-defined resonance peaks at 14.1, 22.6, 29.2, 29.5, 30.5, and 31.7 ppm, assigned to the six carbons on the hexyl chain, and at 19.4, 25.5, 29.9, 30.7, 62.1, 67.1, and 98.7 ppm, attributed to the seven carbons on the THPET unit. In the aromatic region >12 peaks (128.6−140.3 ppm) were observed, indicating that the copolymers possess a random subsequence structure.

The molecular weight, polydispersity index, and wavelength of maximum absorption for homopolymers and copolymers are shown in Table 1. The molecular weights and the polydispersities are typical of thienyl-based polymers prepared by this route.

UV−vis Absorption. Homopolymer and copolymers of THPET were found to exhibit broad absorption bands. Unlike P3HT homopolymer,[5] they did not show typical vibronic structure in the solid state. Absorption maxima ranged from 467 to 520 nm in the solid state and from 439 to 449 nm in solution. The change of λ_{max} with composition is shown in Figure 1, which illustrates how the inclusion of an increasing fraction of the bulky THP group decreases λ_{max}, particularly when the mole fractions is >50%. This effect is much more dramatic in the solid state because of the group's role in affecting long-range structural ordering. Nevertheless, the THP group does not completely prevent long-range ordering of the polymer. X-ray diffraction studies indicate an interlamellar spacing of 17.5 Å.

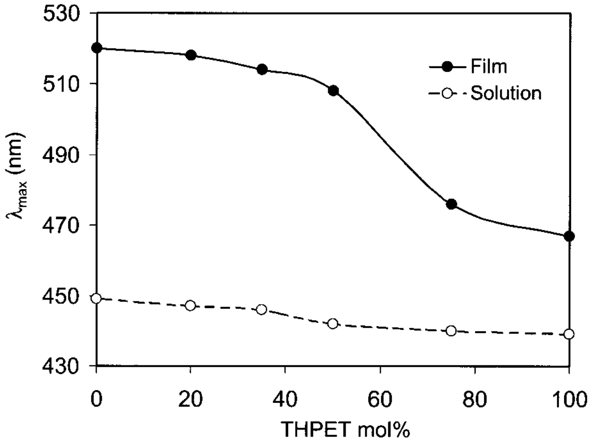


Figure 1. Effect of composition on λ_{max} of PTHPET-*co*-3HT copolymers.

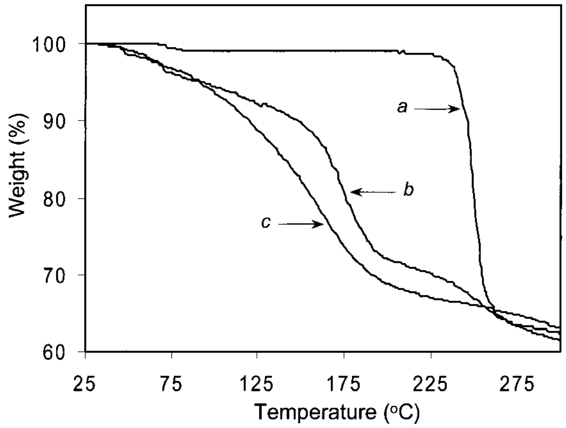


Figure 2. TGA thermograms of PTHPET in the absence of acid (a) and in the presence of 5 mol % triflic acid (b) and 5 mol % camphorsulfonic acid (c).

Thermal Properties/Acid Catalysis. Tetrahydropyranyloxy is generally regarded to be thermally stable protecting group for alcohols. Films of PTHPET homopolymer are indeed stable up to 220−230 °C. Above this temperature, a significant loss in mass is observed by TGA, as shown in Figure 2. The THP functionality represent 40 wt % of the polymer. The observed weight loss of 38 wt % is consistent with thermolytic cleavage of the tetrahydropyranyl group and elimination of dihydropyran. Dihydropyran is reported to vaporize at 90 °C,[8] so that at elevated temperature it is released from the film. FTIR analysis shows the emergence of a broad signal at ~3400 cm^{-1} upon thermolysis, due to the formation of the hydroxyl group (Figure 3). FTIR signals assigned to the THP group, originally at 1130, 1120, 1070, and 2940 cm^{-1}, diminish upon thermolysis.

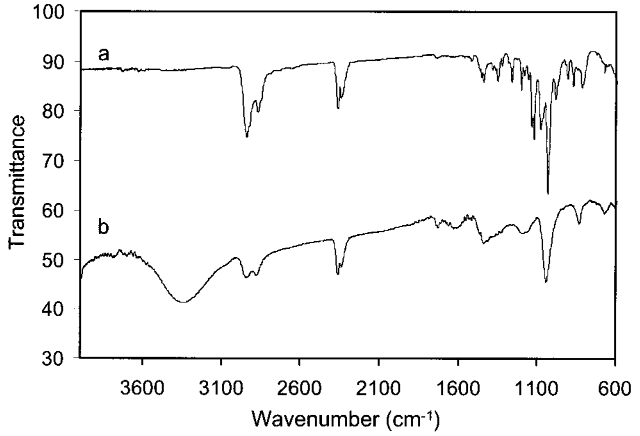


Figure 3. FTIR of PTHPET before (a) and after (b) thermal deprotection.

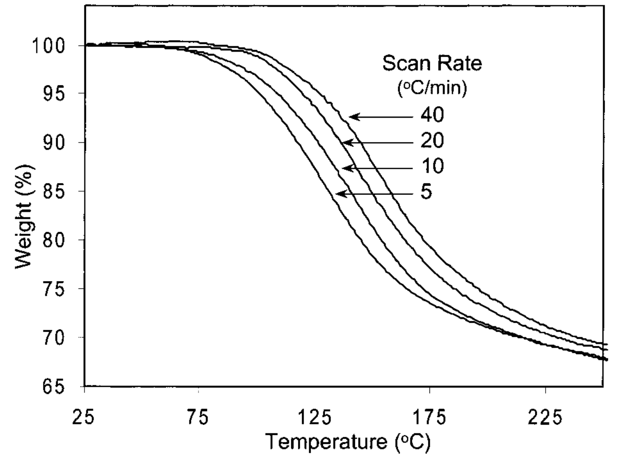


Figure 4. Scan rate dependence of TGA thermograms of PTHPET in the presence of 5 mol % camphorsulfonic acid.

The presence of acids such as triflic acid (TFA) or camphorsulfonic acid (CSA) has a pronounced effect on the thermolytic temperature of PTHPET films. Solutions of the polymer in the presence of TFA or CSA are chemically stable for several hours, and films cast from these solutions considerably more stable under ambient conditions. TGA curves shown in Figure 2 show that the presence of 5 mol % (mol % based on the thienyl unit) of either TFA or CSA causes the THP groups to cleave at a significantly lower temperature. Decreasing the temperature scan rate results in a decrease in deprotection temperature, as shown in Figure 4, indicating that the deprotection process is kinetically controlled on the time scale of the TGA experiment. In fact, almost complete deprotection of the polymer is achieved at 140 °C, in the presence of 5 mol % acid, if this temperature is maintained at for several minutes. This provides evidence that the acid reacting catalytically.

The role of acid concentration in the film on the rate and efficiency of the reaction was examined by TGA. Figure 5 shows TGA curves for films containing 2, 5, 20, and 40 mol % CSA. At a scan rate of 10 °C/min, the onset of deprotection occurs at a similar temperature. However, the rate of deprotection increases with increasing acid concentration. This is likely due to the rate of reaction being determined by the rate of acid diffusion in polymer above 70−80 °C.[9] CSA volatilizes at elevated temperature, resulting in a further decrease in mass of the film above 200 °C. This is more evident for the 20 and 40 mol % CSA containing samples.

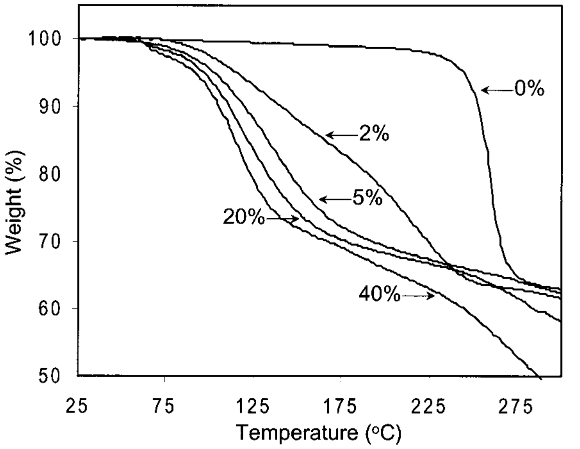


Figure 5. Effect of camphorsulfonic acid concentration on the TGA thermograms of PTHPET.

To disqualify the possible explanation that the decrease in reaction temperature is due to additional free volume being incorporated into the polymer by the presence of acid, camphor and sodium camphorsulfonate were employed in place of CSA. The presence of these nonacidic compounds did not lower the reaction temperature, and TGA curves were similar to those in the absence of acid. Thus, the lower reaction temperature in the presence of acids is the result of an acid-catalyzed reaction.

TGA curves for the copolymers, in the absence and presence of acid, are shown in Figure 6, a and b, respectively. Theoretical values for weight loss corresponding to complete removal of the THP groups are listed in Table 2. The experimentally determined values for acid-free copolymers are ≥95% of that predicted. In the absence of acid, copolymers possessing 35, 50, and 75 mol % THPET exhibit a similar onset temperature of ~200 °C. This value is ~35 deg lower than the homopolymer, PTHPET. This is attributed to the plasticizing effect of the linear hexyl side chains. The apparent higher onset temperature observed for the 20 mol % THPET copolymer appears anomalous, but it is reproducible. It is believed due to the high molar fraction of 3-hexylthiophene which leads to a denser morphology caused by interdigitation of the hexyl side chains. This is confirmed by XRD studies which indicate that the interlamellar spacing of the 20 mol % THPET copolymer is 16.8 Å compared to 17.50 Å for the PTHPET homopolymer.

The onset temperature required to remove the THP group from the copolymers (85−100 °C) is much lower in the presence of acid, with the exception of the 20 mol % THPET copolymer, which possesses a much higher onset temperature (~165 °C) for reasons previously explained. Unlike in the acid-free case, reaction of the PTHPET homopolymer does not require a higher temperature than the copolymers. This may be due to the fact that the temperatures involved in the acid-catalyzed reaction are generally lower than the intrinsic thermal transitions of the polymers. This is in contrast to the reaction in the absence of acid, which proceeds a melting transition of the polymer—a fact that is demonstrated by thermochromism (see later). The theoretical weight loss corresponding to loss of the THP groups for the following copolymers is listed in Table 2. The experimental values are ≥85% of that predicted, demonstrating the remarkable completeness of this catalytic solid-state reaction.

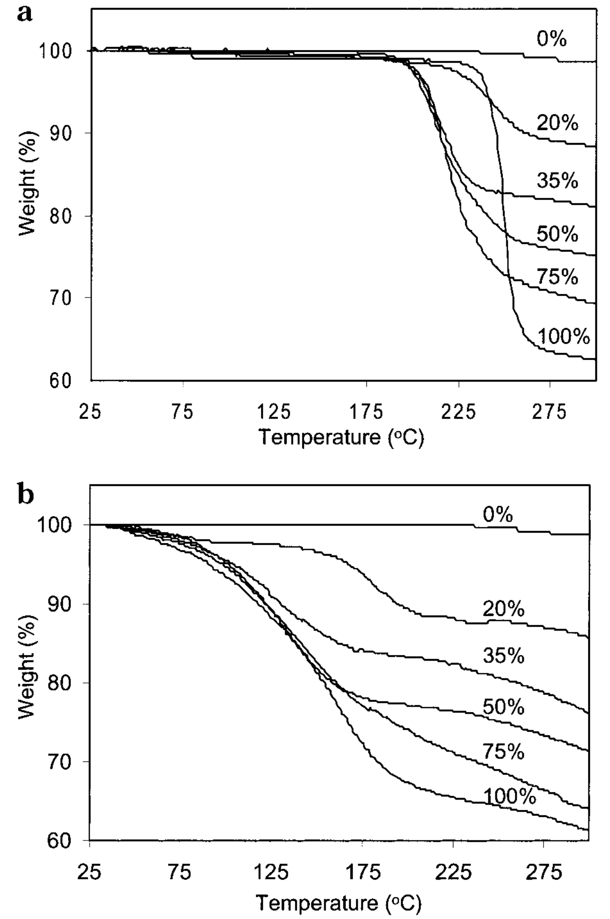


Figure 6. TGA thermograms of PTHPET-*co*-3HT copolymers in the absence of acid (a) and in the presence of 5 mol % camphorsulfonic acid (b).

Table 2. Weight Loss of Polymers in the Absence and Presence of Catalytic Acid

polymer composition (THPET/HT)	weight loss (%) theoret	 exptl (acid free)	 exptl (5% acid[a])
100/0	40	38	33
75/25	32	30	27
50/50	22	23	23
35/65	16	16	16
20/80	10	10	11
0/100	0	0	0

[a] Camphorsulfonic acid.

DSC data for the homopolymers and copolymers in the absence of acid are shown in Figure 7. All polymers exhibit an endothermic peak associated with cleavage of the THP group and subsequent volatilization of DHP.[7,8,10] The temperature of the transitions are consistent with the corresponding TGA data. They show that the PTHPET homopolymer requires the highest temperature for reaction. Incorporation of 25 mol % of 3-hexylthiophene (3HT) causes a 40 deg reduction in the required reaction temperature. Increasing the 3HT content further caused the reaction temperature to incrementally increase due to stronger side chain interdigitation and side chain crystallization.

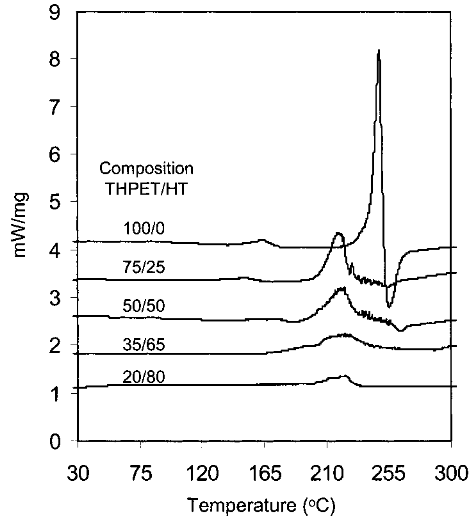


Figure 7. DSC curves of homopolymer and copolymers of THPET in the absence of acid.

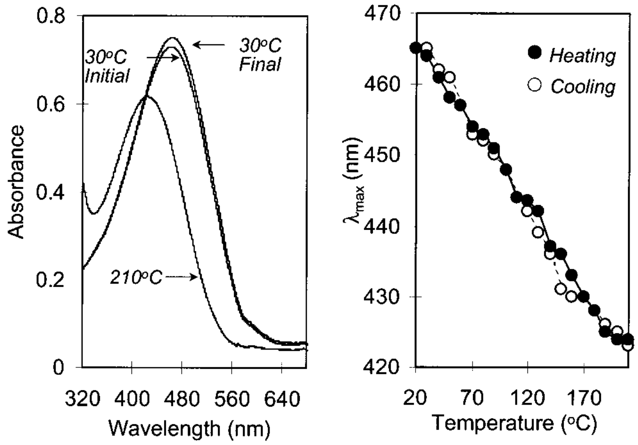


Figure 8. Temperature dependence of UV–vis absorption of PTHPET in the absence of acid.

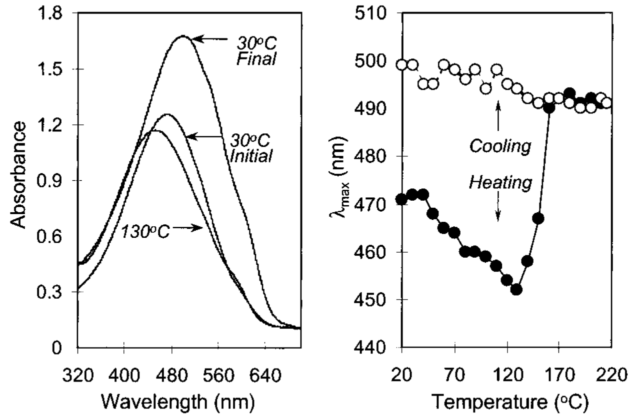


Figure 9. Temperature dependence of UV–vis absorption of PTHPET in the presence of 5 mol % camphorsulfonic acid.

Thermochromism. Removal of the THP group from PTHPET was expected to result in a considerable relief of steric interactions between adjacent thienyl units. This is clearly observed in the temperature dependence of the UV–vis absorption spectra shown in Figures 8 and 9. In the absence of catalytic acid, typical reversible thermochromism is observed for PTHPET, so long as the temperature is not allowed to exceed that required to deprotect the polymer (230 °C). λ_{max} decreases from 465 to 423 nm as the temperature is raised from 20 to 200 °C. No isosbestic point is observed, indicating that the polymer does not melt within this temperature range.[11] In the presence of 5 mol % CSA or TFA, the polymer exhibits reversible thermochromism between

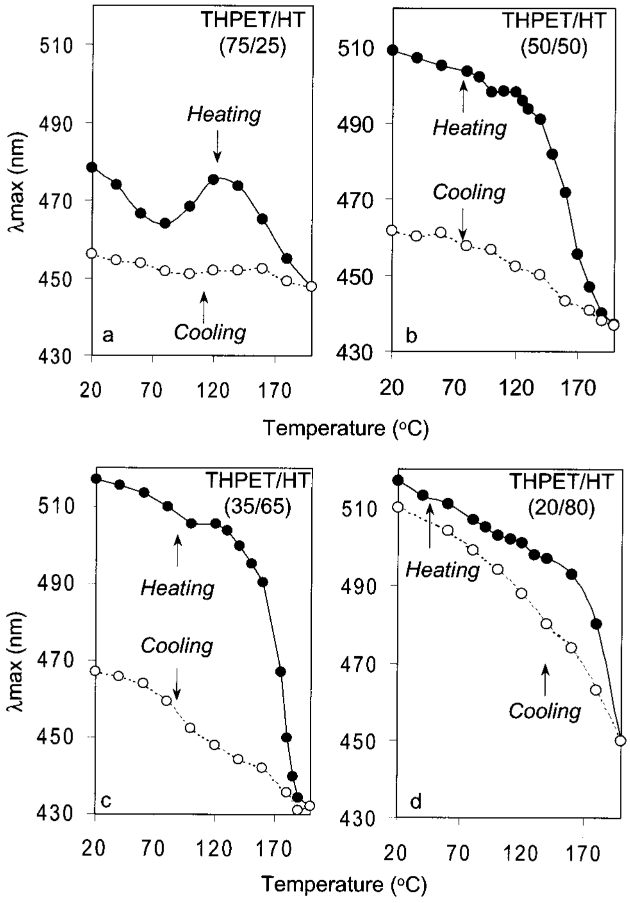


Figure 10. Temperature dependence of λ_{max} for PTHPET-*co*-3HT copolymers.

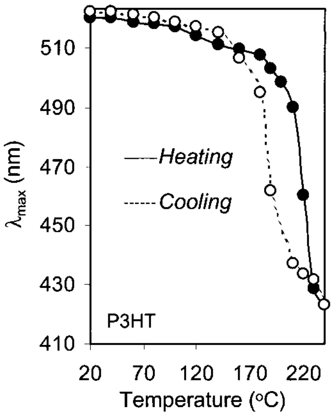


Figure 11. Temperature dependence of λ_{max} for poly(3-hexylthiophene) (P3HT).

20 and 110 °C, but λ_{max} increases dramatically when the temperature exceeds 125 °C (Figure 9). Following this, λ_{max} varies little with further increases in temperature. λ_{max} is observed to be relatively independent of temperature (±3 nm) upon cooling and subsequent heating and cooling cycles. The absence of thermochromism indicates that the conformation of the polymer film is rigidly locked. Furthermore, the resultant polymer is rendered insoluble in common solvents. The rigidity and insolubility of the polymer are attributed to both the relatively short side chain length and H-bonding between hydroxy functionality.

Thermochromism of the copolymers in the presence of acid varies with THPET content (Figure 10). Reversible thermochromism is observed between 20 and 80 °C for the 75 mol % THPET polymer. Between 80 and 120 °C λ_{max} increases concurrently with loss of the THP group (Figure 10a). However, in contrast to PTHPET homopolymer, λ_{max} decreases as the temperature is raised above 120 °C, and a clear isosbestic point is observed in the temperature-dependent UV−vis absorption spectra. This is clear evidence of melting of the polymer and a subsequent decrease in coplanarity of adjacent thienyl units along the main chain.[11] A decreased value for λ_{max} is evidence of increased morphological disorder and loss of the lamellar-type structure. This disorder prevails upon cooling, as evidenced by the relatively constant (±3 nm) λ_{max}. Either strong H-bonding or the absence of crystallizable side chains prevents the thienyl chains from achieving a higher degree of coplanarity upon cooling. A difference between THPET-containing copolymers and its homopolymer is now evident: In the former, the polymer melts upon a further heating beyond the reaction temperature; in the latter it does not. This results in a considerable difference in λ_{max} (45 nm) for the resultant polymers if heated to 200 °C.

For the 50 and 35 mol % THPET copolymers the change in λ_{max}, concurrent with loss of THP, is more subtle (Figure 10b,c) and is only evident as a flattening of the λ_{max} versus *T* curve between 90 and 110 °C and 100−120 °C, respectively. Both polymers exhibit a large drop in λ_{max} which onsets at 145 and 165 °C, respectively, due to melting. An isosbestic point is observed in the temperature-dependent absorption spectra. In both cases the polymers are disordered at 200 °C. This amorphous state is partially retained upon cooling as observed from the thermochromic data which shows that λ_{max} does not return to its original value. However, the 35 mol % THPET copolymer shows a slightly higher degree of recovery in λ_{max}, and hence coplanarity, after removal of THP due to it containing fewer H-bonding hydroxyls and a greater number of crystallizable hexyl side chains. The trend in the thermochromic data is maintained for the 20 mol % THPET copolymer (Figure 10d). The change in λ_{max} with loss of THP is difficult to observe because of its relatively low concentration. Melting of the polymer is still observed, and recovery of λ_{max} and long-range order is more substantial due to an even lower concentration of hydroxyls and a larger fraction of hexyl side chains.

P3HT homopolymer does not exhibit the same large decrease in λ_{max}, due to melting, within the temperature range 20−200 °C. This is due to extensive interdigitation of the side chains. Melting occurs at a higher temperature, between 200 and 230 °C, as shown in Figure 11, which is consistent with its melting point of ~227 °C obtained by DSC (not shown). The onset temperature for steep decrease in λ_{max} is observed for the acid-containing polymers at 140, 150, 160, and 170 °C for copolymers containing 75, 50, 35, and 20 mol % THPET, respectively. Similar onset temperatures are observed for copolymers in the absence of acid (not shown). The onset temperature for P3HT occurs at 210 °C. The presence of the THP group in the copolymer, therefore, lowers the melting transition of the polymers, presumably by disrupting interdigitation.

Since melting of the copolymer is still observed to occur at elevated temperatures following acid-catalyzed thermal elimination of THP, the hydroxy groups must not be participating strongly in interchain H-bonding. One explanation for this is that they may not initially be in close proximity to each other because of the dilution and shielding effect of the hexyl chains. Upon melting, however, the polymer chains find a preferred conformation that maximizes H-bonding between hydroxyls, as evidenced by the relatively low values for λ_{max} upon cooling.

Films of polymers containing 100, 75, 50, 35, and 20 mol % THPET possess values of λ_{max} of 505, 478, 498, 511, and 513 nm, respectively, at room temperature when deprotected at 140 °C. That is, when the temperature of the deprotected polymers and copolymers is not raised above that required to induce melting, the high degree of π-delocalization is retained. The decreasing λ_{max} with increasing THPET content reflects the THP group's influence on lowering the melting temperature as previously explained. Even deprotecting at 140 °C results in a certain degree of conformational disorganization in the copolymers that cannot be reversed upon cooling. The exception to this trend in λ_{max} is the homopolymer which, as explained previously, does not appear to undergo a melting transition below 200 °C because of the absence of hexyl side chains.

Conclusions

The bulky side groups on poly(3-(2-(2-tetrahydropyranyloxy)ethyl)thiophene) impart solubility, on an otherwise insoluble material, and impose a degree of steric hindrance which moderately affects the extent of π-delocalization along the chain. Spectroscopic and thermal data confirm the solid-state elimination of dihydropyran from PTHPET and related copolymers. Upon reaction, the soluble polymers are rendered insoluble and, in some cases, possess an increased degree of conjugation as evidenced by the increase in the maximum wavelength of absorption. Copolymer films melt at a much lower temperature than either PTHPET or P3HT homopolymers because the former possesses large bulky groups, and the latter posseses side chains that intergitate, both of which limit molecular motion of the main chain. Thermal or acid-catalyzed elimination of THP enables the deposition of dense, insoluble films. Insolubility is result of the polymers possessing short side chains and/or due to H-bonding via terminal hydroxyl groups. Previously films possessing short alkyl side chains could only be obtained on electrically conducting surfaces via electrochemical polymerization of the appropriate monomer. The processes described in this work enable deposition of dense films on a variety of nonconductive or conductive surfaces. Removal of the solubilizing group is efficient and can be achieved catalytically at moderate temperature. The extent of π-conjugation in the film depends on the composition and conditions employed.

Acknowledgment. This work was supported by Natural Sciences and Engineering Research Council of Canada

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MA991853I