

Sensitive Thermal-Undoping Characteristics of the Self-Acid-Doped Conjugated Conducting Polymer Poly[2-(3'-thienyl)ethanesulfonic acid]

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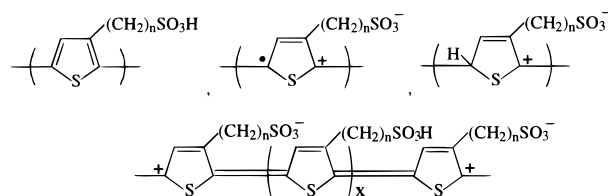
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The structure and properties of the poly[2-(3'-thienyl)ethanesulfonic acid] (P3TESH) treated at temperatures from 20 to 70 °C were investigated by thermal analysis, ultraviolet–visible–near-infrared and infrared spectroscopies, electron spin resonance, solid-state ¹³C nuclear magnetic resonance spectroscopy, X-ray photoelectron spectroscopy, and conductivity measurements. P3TESH is susceptible to thermal undoping at low temperatures (40 °C for thin solid film). Upon undoping, the color of P3TESH changes from the original brownish green to brownish orange. The thermal undoping is irreversible due to a permanent structure change resulting from the nucleophilic attack of the $-\text{CH}_2\text{CH}_2\text{SO}_3^-$ side chain at carbocations to yield C–O bonding and a coupling of the unpaired electrons in polarons on the main chains. As the solid film is subjected to undoping, its conductivity changes drastically from 10^{-2} to 10^{-7} S/cm. The sensitivity of P3TESH's color and conductivity changes are high compared to those of other conjugated polymers. Such characteristics allow P3TESH to be useful for the permanent recording of a temperature increase in the low-temperature range.

Introduction

Conjugated polymers can be doped chemically or electrochemically by oxidation or reduction accompanied by insertion of dopant ions, which can be either located externally or bound to polymer chains. Doping in the latter manner is termed "self-doping"^{1–4} or, when the dopant is an acid, as "self-acid-doping"^{5–12} such as is found in poly[*n*-(3'-thienyl)alkanesulfonic acid]s (P3TASH),^{5–7} sulfonic acid ring-substituted polyaniline (SPAN),^{8–10} and poly(aniline-*co-N*-propanesulfonic acid–aniline) (PAPSAH).^{11,12} Self-acid-doped conducting polymers are different from self-doped conducting polymers prepared by electrochemical methods, which produces "ejection" of π -electrons on the main chains and protons (or cations) on the side chains. The detailed structure of P3TASH involves four basic units:⁷ an undissociated unit, a ring with an electron/hole pair and $-(\text{CH}_2)_n\text{SO}_3^-$ side chain, a ring with a hole and addition of proton

from a side chain on the α -carbon and a bipolaron structure as shown below:



The latter three units are responsible for the conductivity. P3TASH has been found to have potential applications in display technologies owing to its fast electrochromic response¹³ and in electron beam lithography as a charge dissipation layer owing to its conductivity and water solubility.¹⁴ Apparently, P3TASH is quite temperature sensitive.¹⁴

This paper reports the sensitive irreversible thermal-undoping characteristics and accompanying structure changes of poly[2-(3'-thienyl)ethanesulfonic acid] (P3TESH). Its thin films change color from brownish green to brownish orange as a result of undoping when the sample is heated to or above 40 °C. The conductivity drops drastically by a factor of 10^5 from the original to the undoped state. Such characteristics allow P3TESH to be useful for the permanent recording of temperature increase in the low-temperature range. The identification of the structural changes during undoping could be useful in understanding the undoping behavior of polythiophenes doped by protonic acids.

Experimental Section

The preparation and characterization of P3TESH were previously reported.^{7,15} To avoid thermal-undoping, P3TESH in its aqueous solution was cast to form thin solid films at

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about 15 °C and 10^{-3} Torr, which was then stored at -4 °C. Films for ultraviolet–visible–near-IR measurements (1 μm thick) were prepared by coating aqueous solution of P3TESH on a piece of quartz. The spectra were recorded using an UV–vis–near-IR spectrometer (Perkin-Elmer UV–vis–near-IR spectrometer, Lambda 19). Variations of the spectra with temperature were recorded under vacuum at the temperature range 25–70 °C. The temperature was raised at 5 °C/min between levels and maintained at a specific temperature for 5 min for a spectral measurement (scan rate 480 nm/min).

The four-point method was used to measure the conductivity. During the measurement, an appropriate constant current in the range 0.5–30 μA was maintained on the two outer probes and the voltage across the two inner probes, was measured. Dimensions of the films used were about 10 mm \times 10 mm \times 0.1 mm. Conductivity variation was measured with changing temperature under vacuum in the temperature range 20–70 °C.

Electron spin resonance (ESR) measurements from 20–70 °C were performed in the X-band (9.5 GHz) using an IBM Bruker 200D 10/12 ESR spectrometer interfaced with an IBM computer for data acquisition and analysis. 1,1'-Diphenyl-2-picrylhydrazyl (DPPH) was used as a calibration standard. The microwave power was set below 1 mW in order to avoid saturation effects.

The solid-state ^{13}C NMR data of poly[sodium 2-(3'-thienyl)ethanesulfonate] (P3TESNa) and P3TESH were obtained using a Bruker MSL-200 using cross polarization and magic angle spinning techniques (pulse width 4 μs (90 pulse), spin-locking time 1 ms, waiting period 1 s).

Infrared spectra (IR) of the polymers at -30 to 70 °C under nitrogen stream were recorded using a Perkin-Elmer Model 983 infrared spectrophotometer at a resolution of 3 cm^{-1} and were reported in wavenumbers (ν , cm^{-1}). The samples were prepared by grinding the polymers with KBr powder and then compressing into pellets.

X-ray photoelectron spectroscopy (XPS) measurements were made on a Perkin-Elmer model 1905 XPS spectrometer with a twin-anode X-ray gun (Mg K α and Al K α lines at 1253.6 and 1486.6 eV photons, respectively). High-resolution scans were obtained with the magnesium source operating at 12 kV and 250 W. All measurements were made using a takeoff angle of 60° and a pass energy of 25 eV. The pressure in the analysis chamber was maintained at 10^{-8} Torr or lower during the measurements. The binding energies were referenced to the hydrocarbon component in the C(1s) envelope, defined to be 284.6 eV to compensate for surface charging.^{16,17} In spectral deconvolution, the line widths (full width at half-maximum) of Gaussian peaks were maintained constant (at the value for P3TESNa at the neutral state) for all components in a particular spectrum.

Results and Discussion

1. Ultraviolet–Visible–Near-Infrared Spectroscopy (UV–Vis–Near-IR) and Conductivity Measurements. The UV–vis–near-IR absorption spectra of P3TESH thin films measured at 25–70 °C in Figure 1a show that the intensities of the absorption peaks at about 800 and 1900 nm^7 (due to the presence of polaron/bipolaron) and at about 440 nm (due to π – π^* transition) decrease and increase with temperature, respectively, indicating an increase in the degree of undoping with temperature. At the same time, the color of the film changes from brownish green to brownish orange at 45 °C and to yellowish orange at 70 °C. At 70 °C, the polaron/bipolaron absorption peaks disappear completely. As samples are cooled from 70 to 25 °C, the

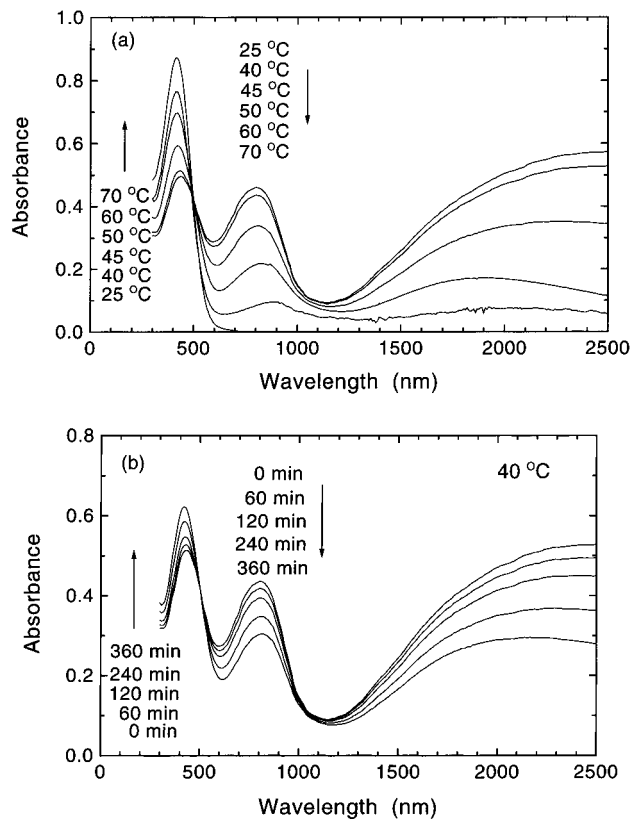


Figure 1. (a) UV–vis–near-IR spectra of P3TESH thin film measured under vacuum at different temperatures; (b) variations of UV–vis–near-IR spectra of P3TESH thin film with time measured under vacuum and 40 °C.

color remains yellowish orange and the absorption peaks due to the polaron/bipolaron do not recover. This undoping is solely due to a thermal effect, since P3TESH solid films stored at -4 °C for two months show no changes in their spectrum. Thus, the thermochromism of P3TESH is an irreversible process. The isosbestic point at 496 nm indicates the conversion of the doped phase into the undoped state, similar to that observed for FeCl_3 -doped poly(3-alkylthiophene). When the P3TESH film is heated at 5 °C/min from room temperature to 40 °C and then maintained at 40 °C for 360 min, the spectral variations with time (Figure 1b) show that even at such low temperatures, the undoping is significant and the color change is obvious after 240 min, from brownish green to brownish orange. The heat-treated P3TESH film was partially cross-linked, since it is only partially soluble in water.

Figure 2a shows the conductivity variation of P3TESH films from 20 to 70 °C at 5 °C/min under vacuum. The conductivity is 10^{-2} S/cm at temperatures lower than 38 °C, above which the conductivity decreases rapidly and then levels off at 10^{-7} S/cm at about 60 °C. After the heat-treated sample is cooled to 20 °C in vacuum, the conductivity remains unchanged. As the temperature is increased again from 20 to 70 °C, the conductivity is almost constant (Figure 2a, second scan). This means that the conductivity change is irreversible, which is in good agreement with the UV–vis–near-IR results above. As the P3TESH film was heated at 5 °C/min from room temperature to a specific temperature in the range 30–60 °C, and then maintained at that temperature, the conductivity decay with time increases sharply with temperature (Figure 2b). Even at 30 and 40 °C, the

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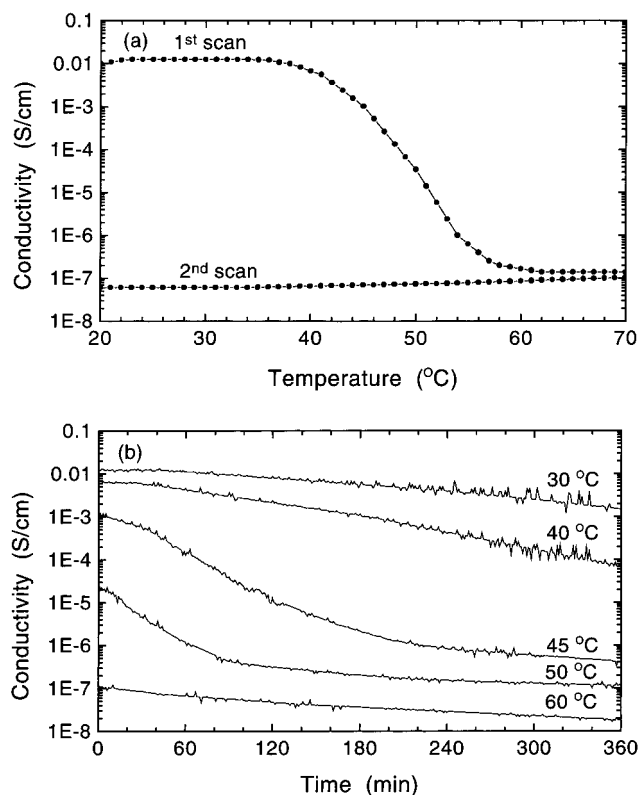


Figure 2. (a) Conductivity of P3TESH film versus temperature scanning from 20 to 70 °C under vacuum; (b) variations of conductivity of P3TESH films with time at different temperatures under vacuum.

conductivity decrease is significant, about 1–2 orders of magnitude after 360 min. At 60 °C, the conductivity drops very rapidly from 10^{-2} to 10^{-7} S/cm during the heating period from room temperature within 7 min, and the conductivity variation with time is not large. The thermal-undoping temperature of P3TESH is much lower than those of polythiophene and poly(3-hexylthiophene) doped by FeCl_3 ^{18,19} and the self-acid-doped polyanilines: sulfonic acid ring-substituted polyaniline²⁰ and poly(aniline-*co*-*N*-propanesulfonic acid-aniline),^{8,12} which have thermal-undoping temperatures higher than 100 °C. On the basis of this irreversible temperature sensing characteristic, P3TESH film can be considered for use as a temperature indicator for foods and drugs that need to be kept fresh at low temperature. When foods and drugs are exposed for a certain period of time (i.e., about 180 min) to temperatures of 40 °C, the P3TESH film would exhibit a permanent color change. Similar application has been reported on the color change in the conversion of diacetylene to polydiacetylene by Baughman et al.^{21–23}

2. Electron Spin Resonance (ESR). ESR analysis results for P3TESH powder at 20 to 70 °C including the peak-to-peak line width (ΔH_{pp}) and spin density (N_s),

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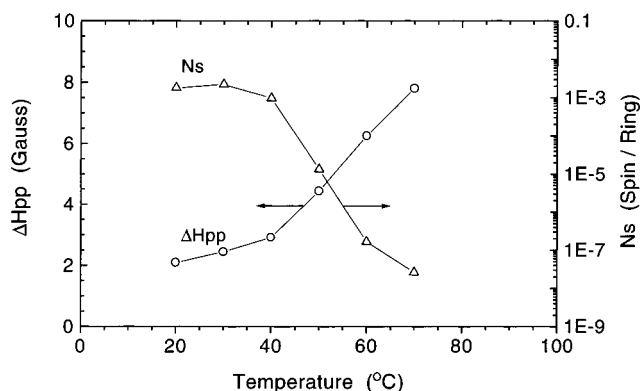


Figure 3. Peak-to-peak line width (ΔH_{pp}) and spin density (N_s) of P3TESH films at various temperatures.

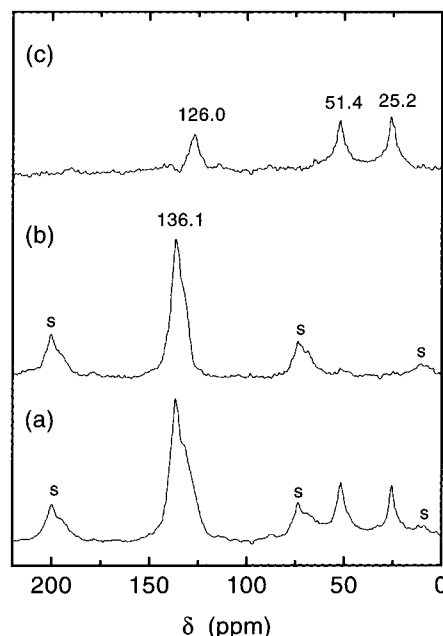


Figure 4. Solid-state ^{13}C NMR spectra of the neutral P3TESNa: (a) full spectrum, (b) quaternary carbon spectrum, and (c) subtraction of spectrum (b) from (a). "s" indicates sideband.

are shown in Figure 3. ΔH_{pp} increases slightly from 20 to 30 °C and pronouncedly above 40 °C, while N_s varies slightly from 20 to 40 °C and decreases sharply above 40 °C. As the temperature increases to 80 °C, no spin signal is detected even after the sample is cooled back to 25 °C. These results indicate that polarons of P3TESH are destroyed during the heating and cannot be recovered upon cooling and that the spins are more localized above 40 °C. These results are consistent with the UV-vis-near-IR (Figure 1a) and conductivity data (Figure 2a).

3. ^{13}C NMR. Solid-state ^{13}C NMR spectra of P3TESNa at 25 °C and P3TESH after heating at 70 °C for 30 min and then cooling to 25 °C are shown in Figures 4 and 5, respectively. P3TESH at 25 °C without heat treatment was not measured, since the presence of polarons would interfere with the spectrum. In both Figures 4 and 5, curve (a) is the original spectrum, curve (b) is the spectrum obtained by use of cross polarization and magic angle spinning techniques for nonprotonated carbons, and curve (c) is obtained by subtracting spectrum (b) from (a). For P3TESNa, Figure 4b shows that its structure has a quaternary carbon with an absorp-

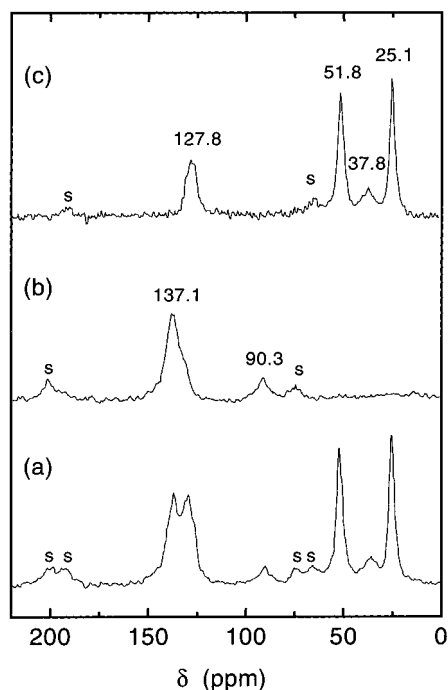
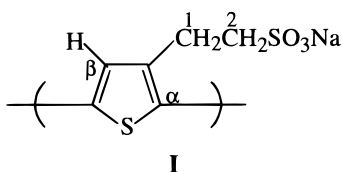


Figure 5. Solid-state ^{13}C NMR spectra of the P3TESH after heating at 70°C for 30 min: (a) full spectrum, (b) quaternary carbon spectrum, and (c) subtraction of spectrum (b) from (a). "s" indicates sideband.

tion peak at 136.1 ppm, α carbon, C_α , on the thiophene ring.^{24,25} Curve (c) shows absorption peaks at 126.0, 51.4, and 25.2 ppm, which correspond to the β carbon, C_β , on the thiophene ring,^{24,25} carbon 2 and carbon 1 on the side chain,²⁶ respectively (see structure I).



For the thermally treated P3TESH (Figure 5), curve (b) shows that its structure has two quaternary carbon absorption peaks at 137.1 and 90.3 ppm, which are assigned to C_α ^{24,25} and C_4 ²⁷ on the thiophene ring (see structure II). For C_4 , its absorption peak is shifted upfield by 46.8 ppm compared to C_α , indicating that this carbon must link with an oxygen,²⁷ which is generated by a reaction of the carbocation on the thiophene ring with the oxygen from the side chain $-\text{CH}_2\text{CH}_2\text{SO}_3^-$. This permanent structure change resulting from the nucleophilic attack²⁸ of the $-\text{CH}_2\text{CH}_2\text{SO}_3^-$ side chain at carbocations to yield C–O bonding and a coupling of the unpaired electrons in polarons on the main chains explains why the thermal undoping is irreversible. Curve (c) shows the presence of absorption peaks at 127.8, 51.8, 37.8, and 25.1 ppm, which can be assigned

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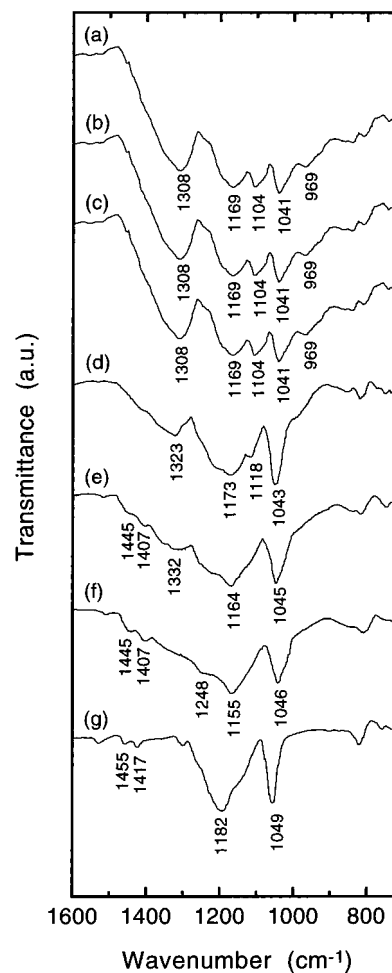
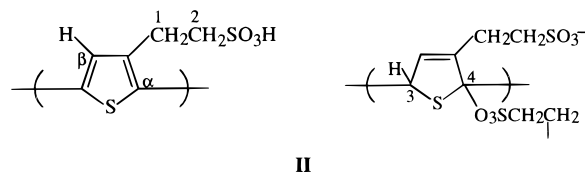


Figure 6. IR spectra of P3TESH films at various temperatures: (a) -30 , (b) 0 , (c) 25 , (d) 40 , (e) 50 , (f) 70°C , and (g) P3TESNa film.

to C_β on the thiophene ring,^{24,25} C_2 ,²⁶ C_3 ,²⁹ and C_1 ,²⁶ respectively (see structure II). C_3 originated from the addition of H^+ to the thiophene ring during self-acid-doping.⁷



4. Infrared Spectroscopy (IR). The IR spectra of P3TESH film from -30 to 70 and P3TESNa at 25°C are shown in Figure 6. In the temperature range -30 to 25°C , no spectral variation is observed for P3TESH. The characteristic absorption peaks^{7,30,31} are 1308 (T_4 mode, C=C stretching), 1169 and 1104 (including T_2 and T_3 (C–C stretching), C_β –H in-plane bending, asymmetric $\text{S}(=\text{O})_2$ stretching, and O–H bending), 1041 (symmetric $\text{S}(=\text{O})_2$ stretching), 969 (T_1 mode) and 804 cm^{-1} (C_β –H out-of-plane stretching). These T (transition) modes are related to the translational motion of intrinsic charge defects (polarons and/or bipolarons)

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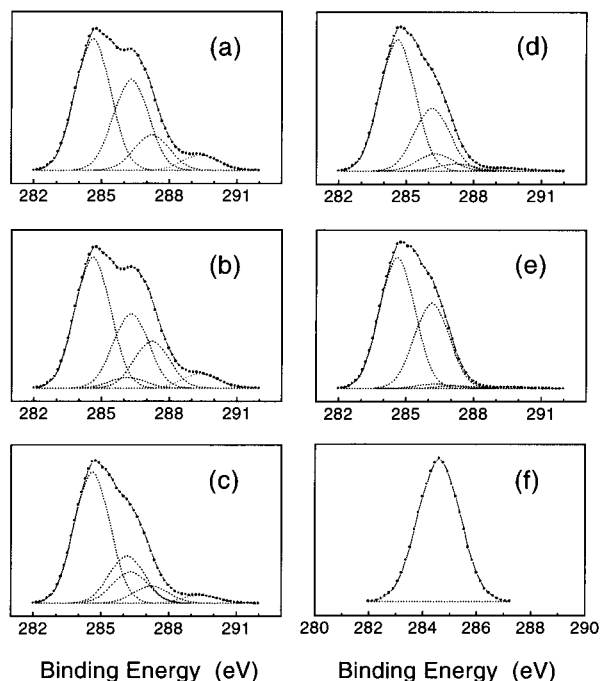


Figure 7. C(1s) XPS core level spectra of P3TESH films at various temperatures: (a) 25, (b) 40, (c) 50, (d) 60, (e) 70 °C, and (f) P3TESNa film. The circles are experimental results, dot lines represent deconvolution result, and solid line is the sum of all the curves with dashed lines.

arising from electron–phonon interactions,^{30,31} in which the peaks T_1 and T_4 do not overlap with other IR-active modes. With increasing temperature, the intensity of T_4 decreases and the peak position shifts from 1308 cm^{-1} at 25 °C to 1323 and 1332 cm^{-1} at 40 and 50 °C, respectively, and becomes a small shoulder at 70 °C. The T_1 peak varies similarly, becoming a shoulder at 40 °C and disappearing at 50 °C. These results indicate undoping. The intensities of the absorption peaks at 1445 and 1407 cm^{-1} (due to the thiophene ring stretching) increase with increasing temperature, indicating the formation of undoped thiophene rings of P3TESH during the undoping.

The pronounced thermal undoping of P3TESH film in the vicinity of 40 °C is probably due to segmental motion, since its glass transition temperature is 46.¹⁵ The segmental motion makes delocalizations of polarons and bipolarons more difficult and enhances the chance of contact between a carbocation on the main chain and a $-\text{SO}_3^-$ group of the side chain. As the carbocation in a polaron is attacked, the free spin becomes unstable and combines with another free spin in a nearby ring of the same chain.

5. X-ray Photoelectron Spectroscopy (XPS). The C(1s) core level spectra at room temperature for the heat-treated P3TESH at 25–70 °C and P3TESNa at 25 °C are shown in Figure 7 and the XPS data for P3TESH are listed in Table 1. For P3TESNa, the C(1s) binding energy is 284.6 eV (peak 1) as shown in Figure 7f. For P3TESH at 25 °C, the C(1s) core level binding energies

Table 1. XPS Binding Energy and Area Fractions for C(1s) of P3TESH

temp (°C)	area fraction					sum of peaks 2–4	286.1 (eV) peak 5
	284.6 (eV) peak 1	286.3 (eV) peak 2	287.2 (eV) peak 3	289.3 (eV) peak 4	286.1 (eV) peak 5		
25	0.422	0.291	0.198	0.089	0.578		
40	0.472	0.269	0.17	0.052	0.491	0.038	
50	0.559	0.134	0.073	0.034	0.241	0.201	
60	0.594	0.077	0.032	0.012	0.121	0.285	
70	0.586	0.015	0.012	0.006	0.033	0.381	

appear at 284.6, 286.3, 287.2, and 289.3 eV (Figure 7a), which are designated as peaks 1–4, respectively. Peak 1 can be assigned to subchains of undissociated P3TESH and peaks 2–4 to self-acid-doped P3TESH (with the formation of polarons/bipolarons^{17,32}) with the total area fraction (or doping level) 0.578, which is consistent with previous results⁷ obtained by titration, 0.522.

As temperature of the heat-treatment increases to and above 40 °C, the total area fraction of peaks 2–4 decreases with temperature (Table 1), indicating a partial undoping of P3TESH. At 70 °C, the doping level drops to only 0.033. After undoping, most of the thiophene units in the doped state change to the neutral state as indicated by the increase of the area fraction of peak 1. At 70 °C, it increases from 0.422 at 25 °C to 0.586. Note that a new peak at 286.1 eV (peak 5) starts to appear at 40 °C and its area fraction increases with temperature; at 70 °C, its area fraction is 0.381. This peak can be assigned to the carbon linked with oxygen on the main chain.^{17,33,34} The results at 70 °C show that as the undoping is nearly completed, the conjugated carbons in the doped state either change to the neutral state or react with $-\text{SO}_3^-$ in the side chain to produce C–O bonds.

Conclusion

P3TESH is susceptible to thermal undoping at low temperatures (40 °C for thin solid film). Upon undoping, the color of P3TESH changes from the original brownish green to brownish orange. The thermal undoping is irreversible due to a permanent structure change resulting from nucleophilic attack of the $-\text{CH}_2-\text{CH}_2\text{SO}_3^-$ side chain at carbocations to yield C–O bonding and coupling of the unpaired electrons in polarons on the main chains. As the solid film undopes, its conductivity changes drastically from 10^{-2} to 10^{-7} S/cm. The sensitivity of P3TESH's color and conductivity changes are high compared to those of other conjugated polymers. Such characteristics allow P3TESH to be useful for the permanent recording of a temperature increase in the low-temperature range.

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