Structure and Doping Level of the Self-Acid-Doped Conjugated Conducting Polymers: Poly[*n*-(3′-thienyl)alkanesulfonic acid]s

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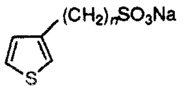
Received May 5, 1993
Revised Manuscript Received October 18, 1993

Conjugated polymers can be oxidized or reduced chemically or electrochemically accompanied by an insertion of counterions. During electrochemical doping and undoping, the rate is governed by diffusion of counterions. In order to improve the rates of doping/undoping, Heeger and co-workers[1] have prepared the self-dopable polymers poly[*n*-(3′-thienyl)alkanesulfonic acid]s (P3TASH) and their sodium salts with alkanes of carbon numbers 2 and 4, in which the dopants are covalently bonded to side chains. Upon electrochemical doping of these polymers in electrolyte solutions, a charge transfer accompanied by a generation of polaron/bipolaron occurs by ejection of protons or metal ions from the bonded dopant and simultaneously ejection of π-electrons from the conjugated main chains, as reflected by an increase of the proton or metal ion concentration in the electrolyte solution and the presence of free spins during the doping.[1] Reynolds et al.[2] and Havinga et al.[3] have extended this self-doping concept to polypyrrole systems.

Recently, Ikenoue et al.[4,5] found that poly[3-(3′-thienyl)propanesulfonic acid] (P3TPSH), which was obtained by exchanging the sodium ions in its sodium salt with protons using an H^+-type ion-exchange resin, was actually already self-doped, as evidenced by the presence of an additional optical absorption peak at 800 nm. Since no electrical potential was applied to the system, "ejection" of the protons should not occur. Thus, the structure and doping mechanism of P3TASH should be different from that obtained by the electrochemical doping of P3TASH or its sodium salt in the works of Heeger and co-workers.[1] However, in the work of Ikenoue et al.[4] the structure of self-doped P3TPSH and the mechanism of the doping have not been reported. In order to distinguish these two types of self-doping, the latter type is now designated as "self-acid-doping".

This paper reports the structure and effect of the side-chain length on the doping level of P3TASHs with alkanes of carbon numbers 2, 6, and 10. It is found that the doping level depends on the side-chain length and the doping also involves an oxidation of the π-system.

The three monomers, sodium 2-(3′-thienyl)ethanesulfonate (3TESNa), sodium 6-(3′-thienyl)hexanesulfonate (3THSNa), sodium 10-(3′-thienyl)decanesulfonate (3TDSNa), and their corresponding polymers were prepared and purified in accordance with the methods proposed by Baüerle et al.[6] and Heeger and co-workers[1] and were characterized by use of ^1H NMR to assure that the side chains were on the 3-position of the rings.



$n = 2, 6, 10$

The two polymers, P3TESNa and P3THSNa, from the former two monomers were converted to poly[2-(3′-thienyl)ethanesulfonic acid] (P3TESH) and poly[6-(3′-thienyl)hexanesulfonic acid] (P3THSH), respectively, by dissolving in deionized (DI) water and then exchanging Na^+ for H^+ using H^+-type ion-exchange resin (IR 120H resin from Rohm and Haas Co.). However, P3TDSNa could not be converted to P3TDSH, since this polymer is insoluble in water. The weight-average molecular weights and polydispersities relative to MW standards of poly(acrylic acid) and poly(vinyl alcohol) are 5×10^5 and 1.02, respectively, for both P3TESH and P3THSH, as were determined using gel permeation chromatography. Elemental analysis using an elementary analyzer and an inductively coupled plasma spectrometer (ICP) for P3TASHs and their sodium salts indicates that each thiophene ring in the polymers is linked with a side chain of alkanesulfonic acid and alkanesulfonic acid sodium salt, respectively, and that the ion exchanging of Na^+ to H^+ is complete (Table 1).

UV-vis-near-IR spectra of aqueous solutions of P3TESNa and P3THSNa and the aqueous dispersion of P3TDSNa (Figure 1a) exhibit only π-π^* transitions at 431, 402, and 299 nm, respectively. Ikenoue et al.[4] found that the UV-vis-near-IR spectrum of the aqueous solution of P3TPSH exhibits a π-π^* transition at 420 nm. The wavelength of the π-π^* transition or conjugation length decreases with increasing carbon number of the side chain. While the UV-vis-near-IR spectra of P3TESH and P3THSH exhibit additional peaks at 801 and 809 nm, respectively, for the former an extra peak is also present above 2000 nm. The absorption intensity ratio of the π-π^* transition to the peak at about 800 nm for P3TESH is significantly lower than that for P3THSH, indicating that the former has a higher self-acid-doping level than the latter[7,8] and that the lower doping level of the latter might generate mainly polarons with a minor amount of bipolarons. The lower doping level of P3THSH can be attributed to its higher oxidation potential due to a shorter conjugation length. The same trend is also observed for thin solid films (about 20 μm, after dynamic vacuum pumping for more than 1 week) of P3TESH and P3THSH (Figure 1b). For a solid film of P3TPSH, the UV-vis-near-IR spectrum of Ikenoue et al.[4] indicates a higher doping level than that of P3TESH. Thus, the self-acid-doping level of P3TASH exhibits a maximum with side-chain length.

Electron spin resonance (ESR) measurement on the aqueous solution of P3TESH gives a spin density of 2.2 $\times 10^{-3}$ spin/ring and $g = 2.0022$, while that on the aqueous solution of P3THSH gives a spin density of 1.1×10^{-2} spin/ring and $g = 2.0021$. These ESR results are comparable to that of poly(3-methylthiophene) doped by AsF_5 at the doping level 4.0% (spin density = 5.5×10^{-3} spin/monomer, $g = 2.0038$).[9] The presence of free spins indicates that the self-acid-doping is a redox process.

In order to explore the structure of the self-doped P3TASH, the system is simulated by the sulfuric acid-doped polythiophene (PT). IR spectra of PT before and after doping with sulfuric acid were examined as shown in Figure 2, in which no interference on absorptions from methylene linkages in the side chains needs to be considered. After doping with sulfuric acid, two new absorption peaks at 2919 and 2851 cm^{-1} are observed which can be assigned to the absorptions due to the stretching vibration of saturated CH[7] (Figure 2a). The generation of saturated CH in the ring was also found in the acid-doping of poly(dialkoxyphenylenevinylenes) by use of ^1H NMR.[10] This observation would indicate that the protons from the acid dopant do add to some of the thiophene rings on the α-position. In addition, four strong doping-

Table I. Elemental Compositions, Empirical Formulas, and Conductivities (at 25 °C) for P3TASNa and P3TASH

	elem composition (wt %)						formula		
sample	C	H	S	O	Na	total	theoretical	empirical	conductivity[f] (S/cm)
P3TESNa[a]	33.6	3.3	29.9	23.9	9.7	100.4	$C_6H_7S_2O_3Na$	$C_{6.0}H_{6.8}S_{2.0}O_{3.1}Na_{0.9}\cdot 0.1H_2O$	10^{-7}
P3TESH[b]	37.5	4.0	33.3	25.5		100.3	$C_6H_8S_2O_3$	$C_{6.0}H_{7.6}S_{2.0}O_{3.0}\cdot 0.06H_2O$	10^{-2}
P3THSNa[c]	44.4	5.5	24.9	18.4	7.7	100.9	$C_{10}H_{15}S_2O_3Na$	$C_{10.0}H_{14.8}S_{2.0}O_{3.0}Na_{0.9}\cdot 0.05H_2O$	10^{-8}
P3THSH[d]	48.4	6.5	24.5	19.5		98.9	$C_{10}H_{16}S_2O_3$	$C_{10.0}H_{16.0}S_{1.9}O_{3.0}\cdot 0.02H_2O$	10^{-4}
P3TDSNa[e]	51.5	7.0	18.7	14.8	7.8	99.8	$C_{14}H_{23}S_2O_3Na$	$C_{14.0}H_{22.7}S_{1.9}O_{3.0}Na_{1.1}\cdot 0.02H_2O$	

[a] P3TESNa: poly[sodium 2-(3′-thienyl)ethanesulfonate]. [b] P3TESH: poly[2-(3′-thienyl)ethanesulfonic acid]. [c] P3THSNa: poly[sodium 6-(3′-thienyl)hexanesulfonate]. [d] P3THSH: poly[6-(3′-thienyl)hexanesulfonic acid]. [e] P3TDSNa: poly[sodium 10-(3′-thienyl)decanesulfonate]. [f] Using four-probe method.

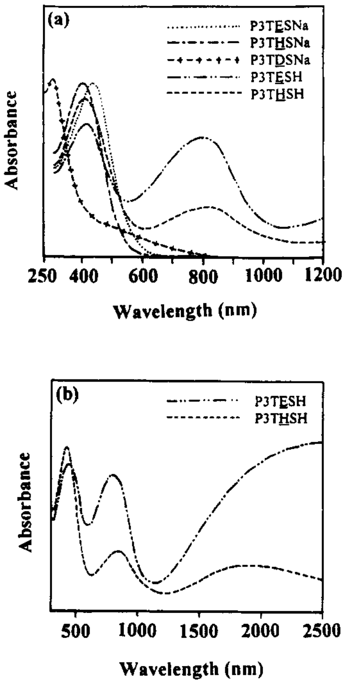


Figure 1. UV–vis–near-IR spectra of P3TASNa and P3TASH series at room temperature: (a) in H_2O; (b) thin film.

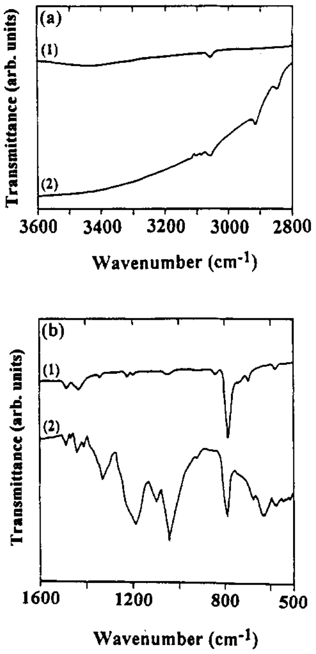


Figure 2. IR absorption spectra of a thin film of PT at room temperature: (a) from 3600 to 2800 cm^{-1}, (1) neutral form, (2) H_2SO_4-doped form; (b) from 1600 to 500 cm^{-1}, (1) neutral form, (2) H_2SO_4-doped form.

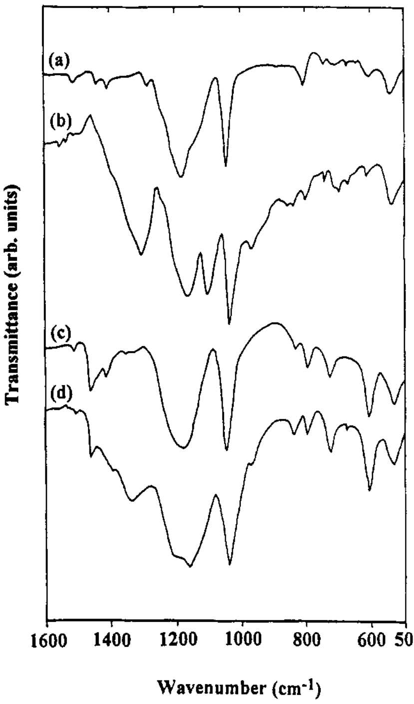


Figure 3. IR spectra of thin films at room temperature: (a) P3TESNa; (b) P3TESH; (c) P3THSNa; (d) P3THSH.

induced vibrational modes at 1329, 1186, 1095, and 1038 cm^{-1} are observed (Figure 2b). These respective modes can be ascribed to T_4, T_3, T_2, and T_1 infrared active vibrations, where T_4 and T_3 correspond to C═C and C–C stretching modes, respectively, as in the electrochemical doping of poly(3-methylthiophene).[7] These T (transition) modes are related to the translational motion of intrinsic charge defects (polarons or bipolarons) arising from electron–phonon interactions.[7,11]

Infrared spectra of P3TESH (Figure 3b) and its sodium salt (Figure 3a) and P3THSH (Figure 3d) and its sodium salt (Figure 3c) exhibit that the self-acid-doped P3TESH and P3THSH have characteristic peaks similar to those in the case of Lewis acid-doped P3ATs[7] and have polaron/bipolaron-induced absorption peaks due to C═C vibration at 1308 and 1327 cm^{-1} (T_4 mode), respectively.[7] The other three T modes (1250–950 cm^{-1}) are overlapped with the absorptions due to asymmetric and symmetric vibrations of O═S═O, which originally are located at 1182 and 1049 cm^{-1} for P3TESNa and 1196 and 1047 cm^{-1} for P3THSNa. The absorption peak at 1308 cm^{-1} for P3TESH is significantly smaller than that at 1327 cm^{-1} of P3THSH, which again confirms the result of UV–vis–near-IR that the self-acid-doping level of the former is higher than that of the latter.[12,13] Thus, it can be expected that the structure of P3TASH also involves polaron/bipolaron and proton addition on α-carbons as that of PT.

Titrations with 1.8×10^{-3} N aqueous NaOH on 1.5×10^{-2} equiv (7.5×10^{-4} N, 20 mL) and 1.15×10^{-2} equiv (5.75×10^{-4} N, 20 mL) of repeat units of aqueous P3TESH and P3THSH, respectively, at room temperature (Figure 4)

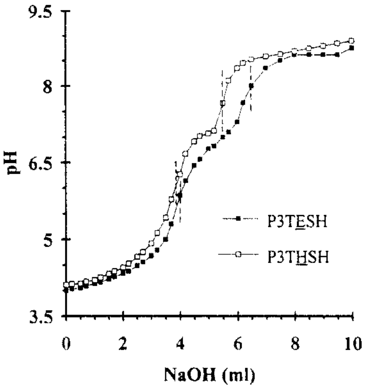
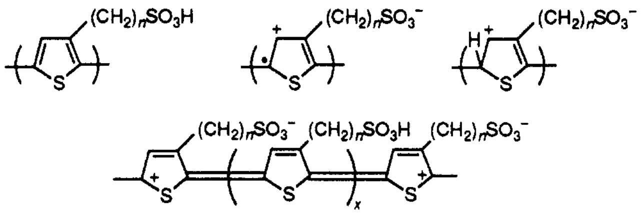


Figure 4. Titration curves of P3TESH and P3THSH with aqueous NaOH.

exhibit a two-stage variation in pH values for both polymers. The first stage involves a neutralization with free protons (H_f^+), while the second stage involves proton adding on α-carbons (H_α^+). The fractions of H_f^+ and H_α^+ calculated from the end points (at which the slopes are maximum) marked on the pH titration curves in Figure 4 are 48% and 30% for P3TESH and 61% and 25% for P3THSH, respectively. Suppose each repeat unit involves a H^+, the fractions of H^+ that were not observed from the titrations (or the fractions of missing H^+ (H_m^+)) are 22%, *i.e.*, (100 - 48 - 30)%, for P3TESH and 14% for P3THSH. Since the P3TASHs do possess free spins, a redox process evidently occurs. The protons could oxidize the π-system to yield hydrogen atoms, which then either add to α-carbons or recombine to yield hydrogen gas. The latter is generated from the H_m^+. In each reduction of a H^+, there is a corresponding loss of one π-electron. Thus, the doping levels of P3TESH and P3THSH in the aqueous solutions would be the sum of the fractions of H_α^+ and H_m^+ and are 52% (30% + 22%) and 39% (25% + 14%), respectively. These results are in agreement with the UV–vis–near-IR results above. The former is close to (or slightly lower than) that of the P3TESH thin solid film, 58%, as determined from X-ray photoelectron spectroscopy (XPS). Further details about XPS results of these polymers will be published elsewhere.

In conclusion, the self-acid-doping level of P3TASHs is dependent on the side-chain length and rather high, about 52% and 39% for P3TESH and P3THSH, respectively. The structure of self-acid-doped P3TASH involves polaron/bipolaron with addition of protons on some α-carbons of the rings resulting from a redox process and is composed of four basic units:



Acknowledgment. We thank the National Science Council of the Republic of China for financial aid through Projects NSC 81-0416-E007-04 and NSC 82-0416-E-007-156.

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