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# Poly($n$-(3-thienyl)alkanesulfonates): Synthesis, Regioregularity, Morphology, and Photochemistry

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ABSTRACT: Poly(n-(3-thienyl)alkanesulfonates) (P3TAS's) containing propanesulfonate, hexanesulfonate, and octanesulfonate substituents have been prepared by oxidative coupling using ferric chloride. The ratio of head-to-tail dyads to head-to-head dyads is 4:1. The extent of $\pi$-conjugation in the polymers, as determined by UV−vis spectroscopy, is relatively independent of whether the polymers are in solution or in the solid state. Polymer films of the sodium salt and sulfonic acid forms are amorphous in contrast to non-sulfonated analogs, i.e., the poly(3-alkylthiophenes), which self-organize into semicrystalline solids. Morphological differences between alkane and alkanesulfonate derivatives of polythiophenes are explained on the basis of ion aggregation which prevents polymer chains from achieving the coplanar conformation required for crystallization. Remarkably, the acid form of the polymers, termed "self-doped", exhibit electronic conductivities in the range $5 \times 10^{-2}$−$10^{-1}$ S/cm even though they too are amorphous and devoid of long range order. The photochemistry of P3TAS's, in both their sodium salt and "self-doped" form, was investigated. The primary photochemical process is photosensitization and reaction of singlet oxygen, which leads to photobleaching. In oxygenated solutions, P3TAS's are much more photostable than their non-sulfonated analogs due to quenching of photosensitized singlet oxygen by water. Films of P3TAS's take up atmospheric moisture in ambient air and, as a result, exhibit enhanced photostability compared to their non-sulfonated analogs exposed to ambient conditions. Anhydrous films, however, exhibit rates of photobleaching which are comparable to the poly(3-alkylthiophenes). The acid form of the polymers is found to be more photostable than their corresponding sodium salts. Unlike their non-sulfonated analogs, irradiated films of P3TAS's exposed to ambient atmosphere do not cross-link to form insoluble polymer upon irradiation due to the presence of residual moisture. However, photolithography can be performed on polymer films oxidized with ferric chloride. Anhydrous films of P3TAS's are rendered insoluble upon exposure to UV or visible irradiation, thus affording the deposition of negative polymer images.

## Introduction

A significant advance in the study of conducting polymers was made when the synthesis of "soluble" $\pi$-conjugated polymers was reported. The first of these soluble polymers were the poly(3-alkylthiophenes) which were obtained by derivatization of the $\beta$-position of the thiophene ring with alkane substituents.[1] It was shown that incorporation of the side groups on conjugated polymer chains increases their processability, but it was anticipated that derivatization of the polymer backbone would affect conductivity by modifying the planarity of the backbone, thus interfering with electron transport along, and between, polymer chains. This turned out not to be the case, and substituted polythiophenes, along with many other classes of conjugated polymer, continue to be widely studied. An extension of this field led to the synthesis of water soluble conjugated polymers including poly($n$-(3-thienyl)alkanesulfonates)[2,3] *N*-alkanesulfonate, and 3-alkanesulfonate poly(pyrroles),[4] and poly(anilines).[5]

The synthesis and study of poly(n-(3-thienyl)alkanesulfonates) (P3TAS's) also led to the introduction of the concept of "self-doped" conducting polymers.[6] Here, introduction of positive charges onto the polymer backbone by removal of electrons from the $\pi$-electron system is accompanied by ejection of cations ($H^+$ or $Na^+$). Since the anion is bound and cannot diffuse away from the polymer, it serves as the counterion. The result is a doped conducting polymer with a covalently-bonded counterion.

As part of a continuing study into the photochemistry and photolithiography of conducting and semiconducting $\pi$-conjugated polymers we have been investigating model systems in order to understand photochemical degradation, offer rationale strategies for enhancing photostability, and design conjugated materials which act as both photoresists and electronic conductors. We have previously shown that poly(3-alkylthiophenes) (P3AT's) undergo cross-linking, and thus become insoluble in organic solvents, when irradiated with UV−vis light.[7] These characteristics make poly(3-alkylthiophenes) interesting candidates for photoresist technology in applications of photolithiography since films of these polymers can be readily spin cast onto solid substrates and irradiated through a photomask and unexposed polymer can be removed by dissolution to provide a negative photoimage. Oxidation of the cross-linked polymer results in an electronically conducting pattern. In contrast to conventional photolithography, the soluble $\pi$-conjugated polymer acts as both the photoresist and the precursor to an electronically conducting pattern. In the neutral state the polymeric image is a semiconductor, and because these materials are known to electroluminesce,[8] photolithography offers a viable route for imaging these materials for display technology.[9]

Since a water-based photoresist would be more desirable to the microelectronics technology sector, we investigated the photochemistry and photolithography of water soluble poly(thiophenes), namely, poly(n-(3-thienyl)alkanesulfonates) (P3TAS's). We have synthesized P3TAS's containing propanesulfonate, hexanesulfonate, and octanesulfonate substituents (Chart 1) in order to examine the effect of the alkanesulfonate chain length

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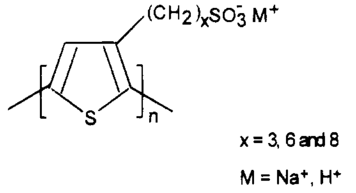
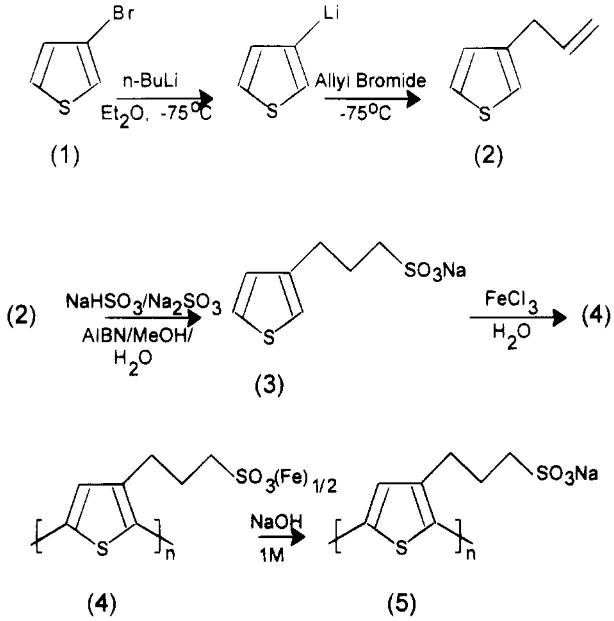
**Chart 1. Poly(n-(3-thienyl)alkanesulfonates) (P3TAS's) Prepared for This Study**



**Scheme 1. Synthesis of Poly(3-(3-thienyl)propanesulfonate) (P3TPSNa)**



on rates of dissolution of thin films and photolithographic contrast. Sodium ions associated with sulfonate groups were exchanged for protons to provide "self-doped" polymer systems. We utilized samples with different alkanesulfonate chain lengths containing either $Na^+$ or $H^+$ to provide information on the morphology, optical properties, and electronic properties of water soluble polythiophenes. Previous photochemical studies of poly(3-alkylthiophenes) revealed that the alkyl side chain and the photosensitization of singlet oxygen play a major role in their photochemistry, namely, photoinduced cross-linking and photobleaching.[10] The photochemistry of P3TAS's was investigated to determine whether similar mechanisms were operating, but as will become apparent, this is not necessarily the case. It was found that water soluble polymers can be cast onto solid substrates, oxidized, and irradiated through a photomask to form a relief image. The unexposed part of the polymer is soluble in aqueous solutions, whereas irradiated regions are not. The water soluble polymers are candidates for photoimaging of conducting organic networks since the disadvantages of using organic solvents are avoided. Finally, we describe studies of the electronic conductivities of both imaged and pristine polymers in both their sodium salt and acid forms.

## Experimental Section

**Instrumentation and Procedures.** Unless otherwise stated, all the reactions and manipulations of Grignard reagents were carried out under a nitrogen atmosphere. Diethyl ether and ethanol were distilled under nitrogen over sodium and calcium sulfate, respectively. Gas chromatographic analyses were performed on a Hewlett-Packard 5980 chromatograph. Electron impact (70 eV) mass spectra were obtained with a Hewlett-Packard 5985 GC–MS instrument; the peak of the ion of highest mass is reported. $^1H$ NMR spectra were recorded on a Bruker AMX-400 (400.16 MHz) spectrometer. Infrared spectra were recorded on a Bomem Michelson Model 120 FT-IR spectrometer. UV spectra were recorded on a Perkin-Elmer Lambda 3A spectrometer. The molecular weight of the synthesized polymers was measured by gel permeation chromatography (GPC) using 250, 500, and 1000 Å ultrahydrogel columns at 25 °C. Polymers were eluted with an aqueous solution of 0.4 M $NaNO_3$, and detected using a UV–vis spectrophotometer (Spectra Physics SP8400) and a differential refractometer (Waters R401). Photophysical studies were performed on polymers cast onto glass or sapphire substrates from aqueous solutions. Film thicknesses were ~300 nm. Steady state luminescence was measured on a LS-100 spectrofluorometer (Photon Technology International Inc.). Samples were irradiated at their maximum wavelength of absorption. X-ray experiments were performed with a Siemens D-5000 diffractometer with a Cu Kα source and graphite monochromator. The samples had a thickness of 0.5–1.0 μm and a geometry of 2 × 2 $cm^2$.

For electronic conductivity studies, polymer films were cast onto glass slides under vacuum from their corresponding aqueous solution (10 mg/mL). Chemical doping was performed by immersing the neutral polymer film into a nitromethane solution of the oxidizing agent. After saturation the polymer film was washed with nitromethane to remove excess oxidizing agent. Electronic conductivity measurements were performed using the four probe technique.[11] Thicknesses of polymer films were estimated from the optical density. A calibration of optical density against thickness was obtained using profilometry.

Photochemical studies were performed using a 150 W mercury lamp (Illumination Industries Ltd.). The light beam was focused to 4 cm diameter and passed through a water filter and a 300 nm cutoff filter to eliminate high energy radiation. For studies of rate of degradation, photolysis were carried out at 313 nm using an interference filter. The incident light intensity was 2.5 mW/$cm^2$. Photochemical studies were performed in ambient air. The solvent was $H_2O$ unless otherwise stated. Polymer solution (3 mL) was used for each photolytic experiment. The starting concentration was adjusted to provide an optical density of 1.0 at maximum absorption wavelength. Polymer solutions varied from $2.5 \times 10^{-4}$ to $4.0 \times 10^{-4}$ M in concentration. Polymer films were cast onto glass slides under vacuum from their corresponding aqueous solutions (10 mg/mL). Anhydrous films were prepared by subjecting the films to 120 °C for 48 h. Absorption spectra of the polymers in solution and in film were recorded during irradiation.

**Synthesis of poly(3-(3-thienyl)propanesulfonate) (P3TPSNa) (Scheme 1). 3-(3-Thienyl)propene (2).** Alkylthiophene monomers are commonly synthesized from 3-bromothiophene and alkyl Grignard reagents using [1,3-bis(diphenylphosphino)propane]nickel(II) chloride catalyst in high yields.[12] The nickel catalyst is effective for coupling alkyl and simple aryl Grignard reagents but is not effective in catalyzing the coupling of allyl Grignard reagents.[13] For the synthesis of 3-(3-thienyl)propene, the use of *n*-BuLi is necessary to achieve the alkylation of 3-bromothiophene.

3-Bromothiophene (**1**) (5.0 g, $3.1 \times 10^{-2}$ mol) (Aldrich Chemical Co.) in 20 mL of dry ether was added to 14.7 mL ($3.7 \times 10^{-2}$ mol) of 2.5 M *n*-butyllithium at −75 °C over a period of 20–30 min. The reaction mixture was stirred for 2 h and checked by GC for the presence of 3-bromothiophene. When the reaction was complete, 2.7 mL ($3.1 \times 10^{-2}$ mol) of allyl bromide was added slowly, and the reaction mixture was stirred for 2 h at −5 °C. The reaction was quenched by pouring the mixture into a separatory funnel containing 5% HCl. Following three other extractions, the combined organic layer was dried with $MgSO_4$. After evaporation of the solvent, a yellow oil was obtained which, upon passing through a silica gel (230–400 mesh) chromatographic column using hexane as eluent, gave a colorless oil (**2**) in 70% yield. NMR ($CDCl_3$, δ relative to TMS): 3.47 (2H, d, $J_{2,3}$ 6.7 Hz, $CH_2CH{=}CH_2$), 5.13 (2H, dd, $J_{1,1}$ 1.0 Hz, $J_{1,2cis}$ 4.0 Hz, $CH_2CH{=}CHH$), 5.18 (1H, dd, $J_{1,1}$ 1.0 Hz, $J_{1,2\mathrm{trans}}$ 8.5 Hz, $CH_2CH{=}CH\mathit{H}$), 6.07 (1H, m), 6.95 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{4,5}$ 5.0 Hz, $H_4$), 6.98 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{2,5}$ 3.0 Hz, $H_2$), 7.28 (1H, dd, $J_{2,5}$ 3.0 Hz, $J_{4,5}$ 5.0 Hz, $H_5$). GC−MS: *m/e* ($M^{\bullet+}$ 124). Number average molecular weight ($M_n$): 3100. Molecular weight dispersity (MWD): 1.3.

**Sodium 3-(3-Thienyl)propanesulfonate (3).**[14] A solution of 1.872 g ($1.8 \times 10^{-2}$ mol) of sodium bisulfite and 0.378 g ($3.0 \times 10^{-3}$ mol) of sodium sulfite in 24 mL of water was added to a solution of 1.5 g ($1.2 \times 10^{-2}$ mol) of **2** and 30 mg ($1.8 \times 10^{-4}$ mol) of AIBN in 24 mL of methanol. The resulting mixture was stirred overnight at 80 °C. The mixture was evaporated to dryness followed by washing with ether to remove the unreacted product (**2**) and organic products of AIBN thermal decomposition. The remaining solid was a mixture of the desired monomer (**3**) contaminated with excess sodium bisulfite and sodium sulfite. After extraction with dry ethanol, a white solid was obtained (**3**) in 50% yield. IR (KBr, $cm^{-1}$) 3588 (m), 3520 (m), 3099 (w), 2975 (m), 2938 (m), 1631 (m), 1211 (s), 1156 (s), 1059 (s). NMR ($D_2O$, δ relative to TMS): 2.02 (2H, tt, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 7.8 Hz, $CH_2\mathit{CH_2}CH_2SO_3Na$), 2.74 (2H, t, $J_{2,3}$ 7.8 Hz, $\mathit{CH_2}CH_2CH_2SO_3Na$), 2.84 (2H, t, $J_{1,2}$ 7.8 Hz, $CH_2CH_2\mathit{CH_2}SO_3Na$), 7.02 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{4,5}$ 5.0 Hz, $H_4$), 7.13 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{25}$ 3.0 Hz, $H_2$), 7.35 (1H, dd, $J_{2,5}$ 3.0 Hz, $J_{4,5}$ 5.0 Hz, $H_5$).

Autooxidation of bisulfite ions results in an increase in acidity which slows down the reaction. This was avoided by buffering the solution with $HSO_3^-/SO_3^{2-}$ in order to maintain an optimum pH of 5−6.

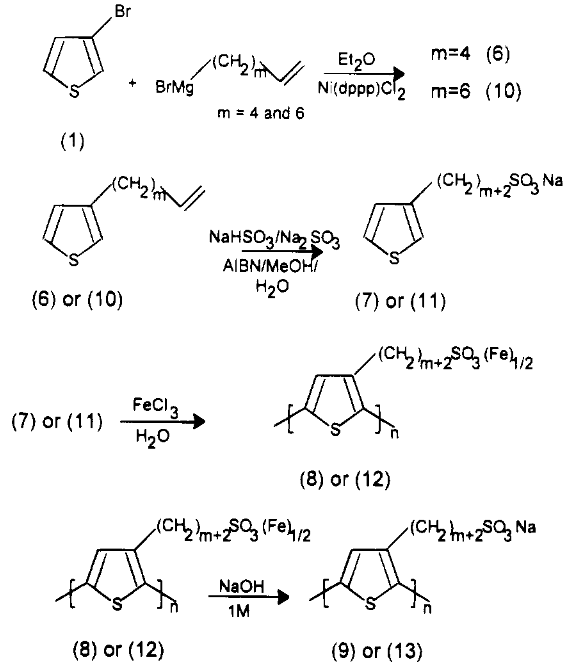
**Poly(3-(3-thienyl)propanesulfonate (P3TPSNa) (5).** The general method proposed by Ikenoue[14] was followed. Modifications to the procedure have been introduced to achieve higher yields. An 8.4 mL aliquot of an aqueous solution containing 0.85 g ($3.7 \times 10^{-3}$ mol) of sodium 3-(3-thienyl)propanesulfonate (**3**) was added to a heterogeneous mixture containing 2.4 g ($1.48 \times 10^{-2}$ mol) of ferric chloride. The reaction mixture was stirred for 12 h at room temperature. During the reaction, solid ferric chloride was maintained in the reaction vessel. The resulting mixture was washed several times with water. The intermediate polymer (**4**) was insoluble in water. When treated with 1.0 M NaOH, it formed a soluble polymer that was reprecipitated from methanol to yield 0.505 g (60%) of the desired orange-red polymer (**5**). IR (KBr, $cm^{-1}$) 3466 (w), 2938 (w), 2866 (w), 2486 (w), 2362, 1653 (m), 1451 (s), 1182 (s), 1051 (m).

The polymerization process requires solid ferric chloride as an oxidant since the active polymerization sites are iron(III) ions on the crystal surface. Soluble ferric chloride is inert.[15]

**Synthesis of Poly(6-(3-thienyl)hexanesulfonate) (P3THSNa) (Scheme 2). 1-Hexen-6-ylmagnesium bromide.** 6-Bromo-1-hexene (8.5 g, $5.2 \times 10^{-2}$ mol) was added to a stirred suspension of 1.5 g ($6.2 \times 10^{-2}$ mol) of magnesium turnings in 80 mL of dry ether. In order to initiate the reaction, 0.5 g of 6-bromo-1-hexene was added to the magnesium suspension. The remaining 6-bromo-1-hexene was added slowly over a period of 1 h. The reaction mixture was refluxed for 1 h and allowed to cool. The resultant solution, 0.65 M of 1-hexen-6-ylmagnesium bromide in ether was transferred via canula.

**6-(3-Thienyl)hexene (6).** The title compound (**6**) was synthesized by coupling 9.75 g ($5.2 \times 10^{-2}$ mol) of 1-hexen-6-ylmagnesium bromide 0.65 M with 8.5 g ($5.2 \times 10^{-2}$ mol) of 3-bromothiophene (**1**) (Aldrich reagent), using 90 mg ($1.7 \times 10^{-4}$ mol) of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride, in 50 mL of dry ether. The reaction was stirred overnight at 0 °C and checked by GC for the presence of 3-bromothiophene (**1**). The reaction was worked up by quenching the resulting mixture in a separatory funnel containing 5% HCl, followed by three ether extractions. The combined organic layer was dried with $MgSO_4$ and evaporated to give a yellow oil. Chromatographic purification on silica gel (similar conditions used for product (**2**)) afforded a colorless oil (**6**) in 65−70% yield. NMR ($CDCl_3$, δ relative to TMS): 1.44 (2H, tt, $J_{3,4}$ 7.8 Hz, $J_{4,5}$ 7.8 Hz, $CH_2CH_2\mathit{CH_2}CH_2CH{=}CH_2$), 1.65 (2H, tt, $J_{4,5}$ 7.8 Hz, $J_{5,6}$ 7.8 Hz, $CH_2\mathit{CH_2}CH_2CH_2CH{=}CH_2$), 2.08 (2H, m), 2.6 (2H, t, $J_{5,6}$ 7.8 Hz, $\mathit{CH_2}CH_2CH_2CH_2CH{=}CH_2$), 4.98 (1H, dd, $J_{1,1}$ 1.0 Hz, $J_{1,2\mathrm{cis}}$ 5.0 Hz, $CH_2CH_2CH_2CH_2CH{=}\mathit{CH}H$), 5.01 (1H, dd, $J_{1,1}$ 1.0 Hz, $J_{1,2\mathrm{trans}}$ 8.7 Hz, $CH_2CH_2CH_2CH_2CH{=}CH\mathit{H}$), 5.80 (1H, m), 6.91 (1H, dd, $J_{2,4}$ 1.0 Hz, $J_{2,5}$ 3.0 Hz, $H_2$), 6.95 (1H, dd, $J_{2,4}$ 1.0 Hz, $J_{4,5}$ 5.0 Hz, $H_4$), 7.25 (1H, dd, $J_{2,5}$ 3.0 Hz, $J_{4,5}$ 5.0 Hz, $H_5$). GC−MS: *m/e* ($M^{\bullet+}$ 166).

**Scheme 2. Synthesis of Poly(6-(3-thienyl)hexanesulfonate) (P3THSNa) and Poly(8-(3-thienyl)octanesulfonate) (P3TOSNa)**



**Sodium 6-(3-Thienyl)hexanesulfonate (7).** A similar procedure to that used for the synthesis of the propanesulfonate monomer was employed: 45−50% yield. IR (KBr, $cm^{-1}$): 3522 (m), 3483 (m), 3112 (w), 2917 (m), 2862 (m), 1659 (m), 1194 (s), 1180 (s), 1056 (s). NMR ($D_2O$, δ relative to TMS): 1.31 (2H, tt, $J_{3,4}$ 7.8 Hz, $J_{4,5}$ 7.8 Hz, $CH_2CH_2\mathit{CH_2}CH_2CH_2CH_2SO_3Na$), 1.40 (2H, tt, $J_{2,3}$ 7.8 Hz, $J_{3,4}$ 7.8 Hz, $CH_2CH_2CH_2\mathit{CH_2}CH_2CH_2SO_3Na$), 1.59 (2H, tt, $J_{4,5}$ 7.8 Hz, $J_{5,6}$ 7.8 Hz, $CH_2\mathit{CH_2}CH_2CH_2CH_2CH_2SO_3Na$), 1.68 (2H, tt, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 7.8 Hz, $CH_2CH_2CH_2CH_2\mathit{CH_2}CH_2SO_3Na$), 2.61 (2H, t, $J_{5,6}$ 7.8 Hz, $\mathit{CH_2}CH_2CH_2CH_2CH_2CH_2SO_3Na$), 2.84 (2H, t, $J_{1,2}$ 7.8 Hz, $CH_2CH_2CH_2CH_2CH_2\mathit{CH_2}SO_3Na$), 7.02 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{4,5}$ 5.2 Hz, H4), 7.06 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{2,5}$ 3.5 Hz, $H_2$), 7.35 (1H, dd, $J_{2,5}$ 3.5 Hz, $J_{4,5}$ 5.2 Hz, $H_4$).

**Poly(6-(3-thienyl)hexanesulfonate (P3THSNa) (9).** A polymerization procedure as described for **3** afforded a 55% yield of the desired red polymer (**9**) from 1 g ($3.7 \times 10^{-3}$ mol) of monomer **7**. IR (KBr, $cm^{-1}$): 3452 (w), 2934 (w), 2855 (w), 2494 (w), 2372 (w), 1653 (m), 1457 (s), 1186 (s), 1049 (m). Number average molecular weight ($M_n$): 6100. Molecular weight dispersity (MWD): 1.4.

**Synthesis of Poly(8-(3-thienyl)octanesulfonate) (P3TOSNa) (Scheme 2). 1-Octen-8-ylmagnesium bromide.** 1-Octen-8-ylmagnesium bromide was obtained by the method described for 1-hexen-6-ylmagnesium bromide: 4.8 g ($2.5 \times 10^{-2}$ mol) of 8-bromo-1-octene was added to 0.72 g ($3.0 \times 10^{-2}$ mol) of magnesium in 40 mL of dry ether. The resulting solution (0.63 M) was transferred via canula.

**8-(3-Thienyl)octene (10).** The compound (**10**) was obtained by the method described for **6** using 4.1 g ($2.5 \times 10^{-2}$ mol) of 3-bromothiophene, 5.4 g ($2.5 \times 10^{-2}$ mol) of 1-octen-8-ylmagnesium bromide (0.63 M), and 45 mg ($2.5 \times 10^{-4}$ mol) of [1,3-bis(diphenylphosphino)propane]nickel(II) chloride in 25 mL of ether. The crude product was obtained as a yellow oil that was purified by a chromatographic column (similar conditions used for product (**2**)), yielding 2.95 g (60%) of the pure compound (**10**). NMR ($CDCl_3$, δ relative to TMS): 1.35 (6H, m), 1.62 (2H, tt, $J_{6,7}$ 7.8 Hz, $J_{7,8}$ 7.8 Hz, $CH_2\mathit{CH_2}CH_2CH_2CH_2CH_2CH{=}CH_2$), 2.08 (2H, m), 2.62 (2H, t, $J_{7,8}$ 7.8 Hz, $\mathit{CH_2}CH_2CH_2CH_2CH_2CH_2CH{=}CH_2$), 4.95 (1H, dd, $J_{1,1}$ 1.0 Hz, $J_{1,2\mathrm{cis}}$ 5.0 Hz, $CH_2CH_2CH_2CH_2CH_2CH_2CH{=}\mathit{CH}H$), 5.08 (1H, dd,

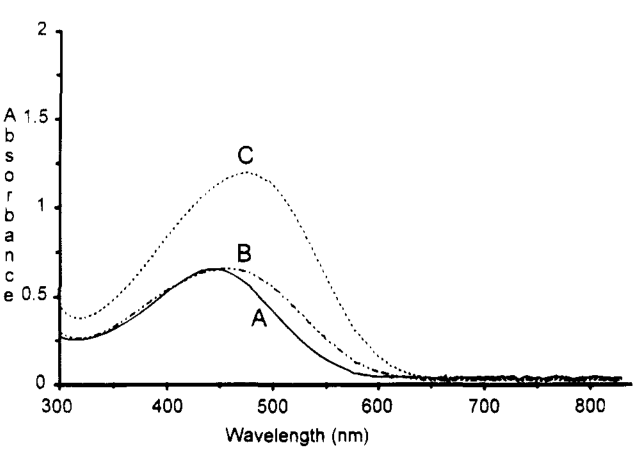
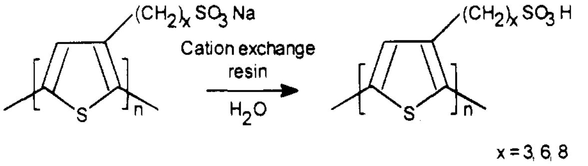


**Figure 1.** Absorption spectra of (A) sodium poly(3-(3-thienyl)-propanesulfonate) (P3TPSNa), (B) sodium poly(6-(3-thienyl)-hexanesulfonate) (P3THSNa), and (C) sodium poly(8-(3-thienyl)-octanesulfonate) (P3TOSNa) in aqueous solution.

### Scheme 3. Conversion of Sodium Salt (P3TASNa) to Acid Form (P3TASH)



$J_{1,1}$ 1.0 Hz, $J_{1,2\text{trans}}$ 8.75 Hz, $CH_2CH_2CH_2CH_2CH_2CH_2CH{=}CH\mathit{H}$), 5.82 (1H, m), 6.93 (1H, dd, $J_{2,4}$ 1.0 Hz, $J_{2,5}$ 3.0 Hz, $H_2$), 6.96 (1H, dd, $J_{2,4}$ 1.0 Hz, $J_{4,5}$ 5.25 Hz, $H_4$), 7.26 (1H, dd, $J_{2,5}$ 3.0 Hz, $J_{4,5}$ 5.25 Hz, $H_5$). GC−MS: *m/e* ($M^{\bullet+}$ 194).

**Sodium 8-(3-Thienyl)octanesulfonate (11).** A similar procedure to that used for the synthesis of the propanesulfonate monomer was employed to give a 56% yield of monomer **11**. IR (KBr, $cm^{-1}$): 3527 (m), 3476 (m), 3104 (w), 2925 (m), 2855 (m), 1649 (m), 1194 (s), 1167 (s), 1060 (s). NMR ($D_2O$, $\delta$ relative to TMS): 1.33 (8H, m), 1.58 (2H, tt, $J_{6,7}$ 7.8 Hz, $J_{7,8}$ 7.8 Hz, $CH_2\mathit{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2SO_3Na$), 1.67 (2H, tt, $J_{1,2}$ 7.8 Hz, $J_{2,3}$ 7.8 Hz, $CH_2CH_2CH_2CH_2CH_2CH_2\mathit{CH_2}CH_2SO_3Na$), 2.61 (2H, t, $J_{7,8}$ 7.8 Hz, $\mathit{CH_2}CH_2CH_2CH_2CH_2CH_2CH_2CH_2SO_3Na$), 2.85 (2H, t, $J_{1,2}$ 7.8 Hz, $CH_2CH_2CH_2CH_2CH_2CH_2CH_2\mathit{CH_2}SO_3Na$), 7.01 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{4,5}$ 5.25 Hz, $H_4$), 7.06 (1H, dd, $J_{2,4}$ 1.5 Hz, $J_{2,5}$ 3.0 Hz, $H_2$), 7.34 (1H, dd, $J_{2,5}$ 3.0 Hz, $J_{4,5}$ 5.25 Hz, $H_5$).

**Poly(8-(3-thienyl)octanesulfonate) (P3TOSNa) (13).** A chemical polymerization of 500 mg ($1.7 \times 10^{-3}$ mol) of monomer **11** with an excess of ferric chloride of 1.1 g ($6.7 \times 10^{-3}$ mol) in 4 mL of water was performed using the same method as described for **3**. This reaction yielded 280 mg (56%) of the polymer **13**. IR (KBr, $cm^{-1}$): 3445 (m), 2930 (m), 2861 (w), 2520 (w), 2382 (w), 1645 (m), 1458 (s), 1182 (s), 1051 (s). Number average molecular weight ($M_n$): 8200. Molecular weight dispersity (MWD): 1.6.

**Conversion of Sodium Salt to Acid Form of the Polymers.** All the synthesized polymers were soluble in $H_2O$. The sodium salt of the polymers were converted to the acid form (P3TPSH, P3THSH, and P3TOSH) by passing solutions of **5**, **9**, and **13**, through a cation exchange resin column (AG 50W-X8, Bio Rad) (Scheme 3).

## Results

**Spectroscopic and X-ray Diffraction Analysis.** The absorption spectra of polymers P3TPSNa, P3THSNa, and P3TOSNa in solution are shown in Figure 1. The wavelengths of maximum absorption are 436, 446, and 466 nm, respectively, and the extinction coefficients are 3000, 2480, and 3820 $M^{-1}\ cm^{-1}$. Longer wavelengths of absorption, indicating longer conjugation lengths, are observed when the length of the side chain is increased.

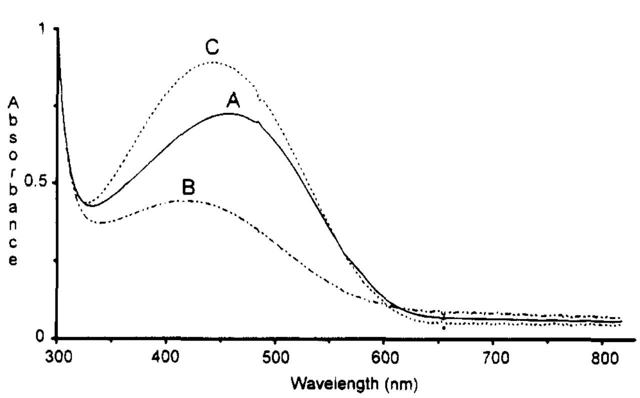


**Figure 2.** Absorption spectra of thin films of P3TPSNa, P3THSNa, and P3TOSNa.

This trend was observed consistently over the course of these studies for numerous batches of polymers with varying alkanesulfonate substituents. This observation suggests that longer alkanesulfonate substituents assume a more rod-like conformation in solution, whereas shorter substituents favor a helical conformation, as has been reported for poly(3-alkylthiophenes).[16] Notably, the wavelengths of absorption of these polymers are similar, if not red-shifted, compared to similar polymers reported in other studies.[6] This confirms that the molecular weights are sufficiently large so that the difference in molecular weights between samples does not influence the absorption spectra. Thus, the blue-shift observed in traversing the octane, hexane, propane series might be due to an increased steric interaction between the substituents and the sulfur lone pairs on adjacent rings. This leads to twisting of the adjacent thienyl rings and shorter conjugation lengths. For the propanesulfonate derivative, the sulfonate groups are held closer to the thienyl ring and thus the steric effects described above are expected to play a more dominant role.

Surprisingly, the absorption spectra of thin films of the sodium salt are not significantly red-shifted with respect to polymer solutions. $\lambda_{max}$ values are 458, 422, and 440 nm for films of propanesulfonate, hexanesulfonate, and octanesulfonate derivatives, respectively (Figure 2). In fact, the hexane and octane derivatives exhibit a blue-shift. These observations are in sharp contrast to the poly(3-alkylthiophenes) which exhibit red-shifts of >60 nm in going from solution to the solid state.[16-18]

The acid form of the polymers exhibit $\lambda_{max}$ values of 438, 422, and 464 nm for solutions of the propanesulfonate, hexanesulfonate, and octanesulfonate derivatives, respectively, and values of 452, 438, and 460 nm in the form of thin films. The absorption spectra of poly(3-(3-thienyl)propanesulfonic acid) (P3TPSH) in the solid state, and in solution, are shown in Figure 3. Similarly to the spectroscopy of the sodium salt, the acid form does not show significant red-shift between the solution and solid state. Broad electronic transitions in the near-IR region are observed ($\lambda_{max} \sim 800$ nm) for the sulfonic acid derivatives. These transitions are due to bipolaron bands which is consistent with the "self-doped" model.[3a]

Fluorescence spectra of films of P3TPSNa, P3THSNa, and P3TOSNa were broad and exhibited a maximum intensity at 627, 616, and 645 nm, respectively, and a width at half-height of ~100 nm. These represent a Stokes shift of approximately 200 nm. For poly(3-alkylthiophenes), a large Stokes shift indicates that the

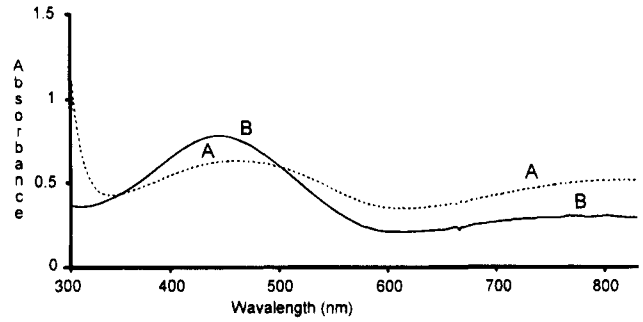


**Figure 3.** Absorption spectra of poly(3-(3-thienyl)propanesulfonic acid) (P3TPSH): (A) film; (B) in aqueous solution.

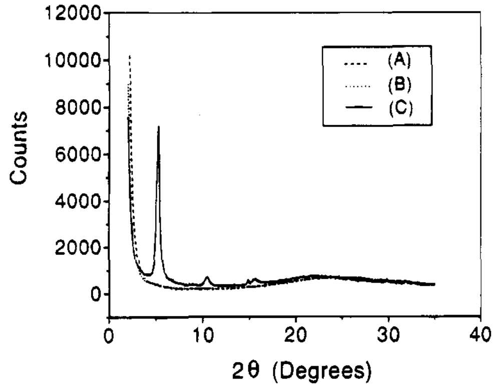


**Figure 4.** X-ray diffraction of thin films: (A) P3TPSNa, (B) P3TPSH, (C) poly(3-hexylthiophene) (P3HT).

backbone is considerably twisted in the ground state and that the conjugated segment experiences an increase in coplanarity in the excited state as a result of the increase in quinoid character.[18]

The morphology of thin polymer films (<1 μm) was probed by X-ray diffraction analysis. Diffraction spectra of P3TPSNa, P3THSNa, and P3TOSNa were featureless, indicating the absence of long range order. The broad reflection is due to the underlying glass substrate. Diffraction spectra of P3TPSH were also featureless, indicating that self-doping did not lead to a significant improvement in self-organization. Again this is in sharp contrast to non-sulfonated π-polymers where doping is usually accompanied by an increase in crystallinity. In contrast, thin films of the non-sulfonated analog, poly(3-hexylthiophene), exhibits strong diffraction peaks due to long range order arising from π-stacking (interchain spacing, 3.8 Å) and lamella packing (interchain distance, 16.4 Å) of copolanar polymer chains.[18] Figure 4 compares diffraction spectra of P3TPSNa, P3TPSH, and P3HT.

X-ray diffraction analysis shows that poly(n-(3-thienyl)alkanesulfonates (P3TAS's) are amorphous. Amorphology in poly(3-alkylthiophenes) can result from a large percentage of head-to-head (HH) dyads in the polymer (Figure 5), since HH linkages impose a limitation on the coplanarity of adjacent thienyl rings and prevents efficient chain packing and crystallization.[18]

In order to determine the HH dyad content in poly(n-(3-thienyl)alkanesulfonates) we investigated their configuration by $^1H$ NMR spectroscopy.[19] $^1H$ NMR spectra were obtained for the polymers in DMSO/$D_2O$ solvent. Four signals at 7.30, 7.26, 7.21, and 7.51 ppm could be clearly resolved for P3TPSNa and assigned to the β-protons on the thienyl rings which experience different fields due to the four triad configurations (HT-HT, HT-HH, TT-HT, and HH-TT).[20] The relative integrals associated with these triads were 13.6, 9.8, 4.3, and 1.0, respectively, from which, the ratio of HT to HH dyads was calculated to be 80:20. A similar analysis of P3THSNa yielded a HT:HH ratio of 79:21. Reliable data for P3TOSNa could not be obtained because of difficulties in dissolving the polymer in DMSO/$D_2O$. These data confirm that the regiospecificity of the polymerization of n-(3-thienyl)alkanesulfonates using ferric chloride is similar to that of non-sulfonated analogs and illustrate that lack of crystallinity in films of the sulfonated polymers does not arise because steric interactions prevent conjugated segments from achieving a coplanar state suitable for π-stacking. An alternative explanation is provided in the Discussion.

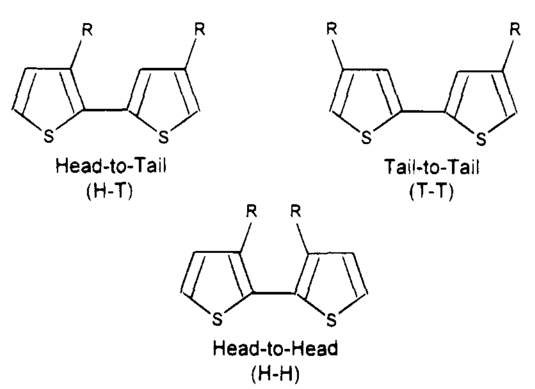


**Figure 5.** Regioisomers of poly(n-(3-thienyl)alkanesulfonate) dyads.

**Electronic Conductivity.** Electronic conductivity measurements were performed using the four-point probe technique. The undoped state of the sodium salt of the polymer films possessed conductivities of $<10^{-6}$ S/cm. After doping with nitromethane solutions of 0.1 M $FeCl_3$, conductivities increased to $10^{-3}$–$10^{-2}$ S/cm. When nitromethane solutions of 0.1 M $AuCl_3$ were used for doping, the conductivities increased to $10^{-1}$ S/cm. Enhanced conductivity of polythiophene films oxidized with $AuCl_3$ has been previously reported.[21] For both oxidants ($FeCl_3$ and $AuCl_3$), and for all three polymers, the oxidized polymer films were relatively unstable and returned to their original neutral state within a few days of exposure to the ambient atmosphere.

In the sulfonic acid form, poly(n-(3-thienyl)alkanesulfonates) were "self-doped". The doping process of "self-doped" polymers differs from other conjugated organic polymers in that the counterions ($SO_3^-$) are covalently bonded to the polymer chain. Ikenoue *et al.*[3a] have postulated that in the absence of water, protons associated with the sulfonic acid residues protonate the polythiophene backbone. It has also been shown that protonation leads to a redox process by which the number of charge carriers increases.[6g] As a consequence of the injected charge, the acid form of the polymers exhibits a substantially higher conductivity than the "undoped" sodium salt of the polymers. Films of "self-doped" polymers, P3TPSH, P3THSH, and P3TOSH, exhibited conductivities of $5 \times 10^{-2}$–$10^{-1}$ S/cm, consistent with previous studies. The relatively high conductivity is remarkable given that the polymers are virtually amorphous and devoid of long range order. The conductivities were invariant with the length of the alkanesulfonate substituents within experimental error and were found to be stable. As in the case of the sodium salt derivatives, the acid forms of the polymers were completely water soluble thus affording "water soluble" conducting polymers.

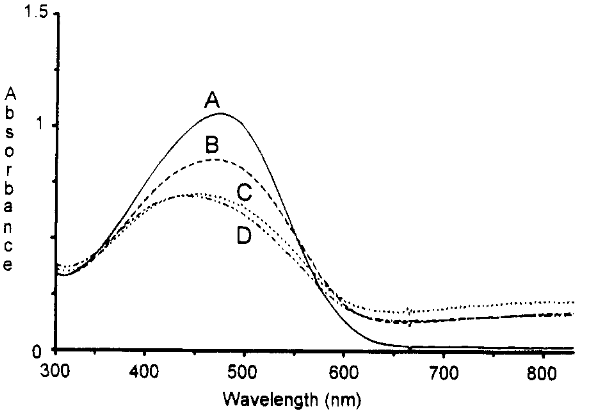


**Figure 6.** Photolysis of P3TOSNa in aqueous solution: (A) before irradiation ($t$ = 0 min); (B) $t$ = 2 min; (C) $t$ = 60 min; (D) $t$ = 120 min. Illumination source: 150 W Hg lamp; 300 nm cutoff filter.

**Photochemistry.** Potential applications of water soluble $\pi$-conjugated polymers in photolithography and electroluminescence make it worthwhile to investigate the chemical and physical changes that result from the interaction with UV–vis radiation. Solutions of sodium poly(n-(3-thienyl)alkanesulfonates) were found to undergo a small degree of photobleaching upon exposure to UV or visible light (Figure 6). It has been previously established that organic solutions of poly(3-alkylthiophenes) photobleach by a mechanism of singlet oxygen sensitization and its subsequent 1,4 Diels–Alder addition to thienyl units, wherein intermediate endoperoxide residues are unstable and rearrange with retention of sulfur to produce a sulfine, or elimination of sulfur to yield a *trans*-diketone.[10c] The blue-shift observed upon prolonged photolysis is consistent with endoperoxide formation and shortening of the $\pi$-conjugation length.

FTIR spectroscopy was used to probe chemical changes of poly(n-(3-thienyl)alkanesulfonates) during irradiation. Polymer solutions were irradiated, cast onto KBr disks, and subjected to vacuum for prolonged periods in order to remove trace moisture. The following features of FTIR spectra of photolyzed samples are noted: (1) the emergence of weak but characteristic absorption bands due to hydroxyl groups in the range 3300–3200 cm$^{-1}$; (II) evolution of characteristic keto and/or aldehyde group bands at 1716 (strong) and 1637 (weak) cm$^{-1}$; (III) a shift of the sulfonate band at 1187 cm$^{-1}$ to 1206 cm$^{-1}$, which is consistent with the formation of sulfine residues ($C{=}S^{+}{-}O^{-}$ or $C{=}S{=}O$). These observations are consistent with the proposed photochemical mechanism of degradation of P3AT's which have been studied in considerable detail.

Figure 7 compares the rates of photobleaching of an aqueous solution of P3THSNa with a chloroform solution of P3HT, as shown by the decrease in optical density at $\lambda_{max}$. In order to make direct comparisons between rates of photobleaching of polymer solutions and polymer films, and for various polymers, the incident light intensity was kept constant ($\lambda_{ex}$ = 313 nm) and the initial optical densities at 313 nm were adjusted to 1.0. Incident light of 313 nm was chosen because the optical density of the samples at this wavelength did not change significantly with irradiation dose, and thus the quantity of absorbed irradiation was constant. As can be observed, aqueous solutions of the sulfonated polymers are considerably more photostable than their nonaqueous analogs. Measurements of rates of photobleaching of the propanesulfonate and octanesulfonate derivatives gave similar results but the photostability of P3TASNa's was found to increase slightly with the length of the alkanesulfonate (not shown). An explanation of the origin of the enhanced photostability of aqueous solutions of these polymers is given in the Discussion.

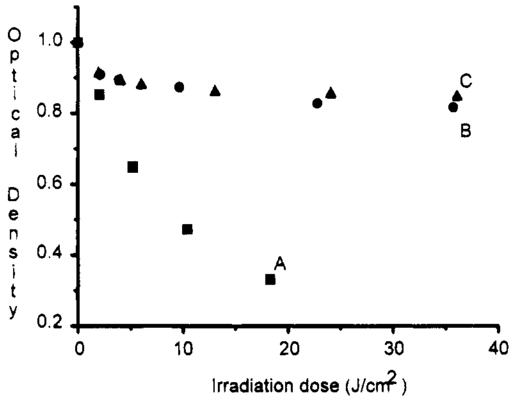


**Figure 7.** Change in optical density (at $\lambda_{max}$) of polymer solutions during photolysis: (A) poly(3-hexylthiophene) (P3HT) in chloroform; (B) P3THSNa in aqueous solution; (C) P3THSH in aqueous solution. Incident intensity = 2.5 mW/cm$^2$ at 313 nm. Initial optical density = 1.0 at 313 nm.

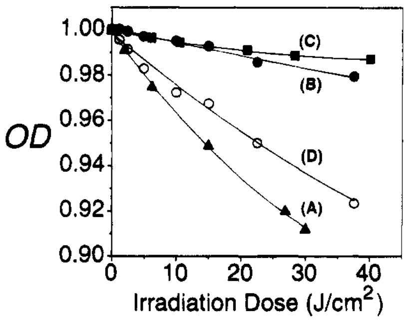


**Figure 8.** Change in optical density (at $\lambda_{max}$) of polymer films during photolysis in ambient air (unless stated): (A) P3HT; (B) P3THSNa; (C) P3THSH; (D) anhydrous P3THSNa in dry air. Incident intensity = 2.5 mW/cm$^2$ at 313 nm. Initial optical density = 1.0 at 313 nm.

Photobleaching of polymer films exposed to ambient atmosphere was very much slower compared to polymer solutions, and much slower than films of their nonsulfonated analogs, as shown in Figure 8. The rates of photobleaching can be directly compared to those obtained in solution, since films and solutions alike possessed the same initial optical density at the incident irradiation wavelength ($\lambda_{ex}$ = 313 nm). Comparison of Figures 7 and 8 show that films of P3THSNa were more stable than their solutions. Photolysis of films of P3TPSNa and P3TOSNa provided similar results. FTIR analyses on photolyzed films proved uninformative.

Films of P3TASNa's exhibited enhanced photostability over P3AT's when irradiated in ambient air (Figure 8). This can be explained on the basis of the hygroscopic nature of sulfonate-based polyelectrolytes. It was speculated that P3TASNa's might take up sufficient moisture from the atmosphere to quench photosensitized singlet oxygen and lead to lower rates of photobleaching. The presence of moisture was indeed confirmed by FTIR spectroscopy. Figure 9 compares FTIR spectra of two P3TASNa films, one exposed to ambient air and the other dried under vacuum at 120 °C for 48 h. The disappearance of the broad peak at 3000–3500 cm$^{-1}$ (due to $-OH$) upon drying at elevated temperatures indicates the anhydrous nature of the latter. It is

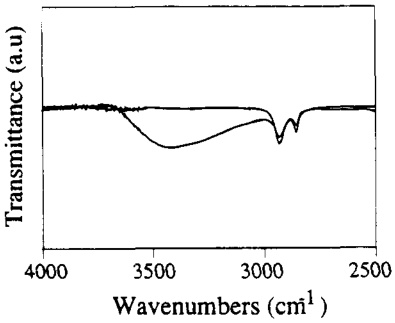


**Figure 9.** FTIR of P3THSNa films: (A) as-prepared in ambient air; (B) heated to 120 °C under vacuum for 48 h.

noteworthy, that application of vacuum alone at room temperature was insufficient to remove residual moisture. Photobleaching of an anhydrous film of P3TASNa is shown for comparison in Figure 8. The rate of photobleaching is comparable to P3HT which confirms that residual moisture in hygroscopic P3TASNa's is responsible for enhancing their photostability.

Films of the sulfonic acid form of these polymers exposed to ambient atmosphere are even more photostable than their sodium salt analogs. Figures 7 and 8 show the relative photostability of P3THSH in aqueous solution and in the form of thin films compared to their sodium salt and their non-sulfonated analogs. A remarkable feature is the photostability of the thin film of the acid form as indicated by the small change in optical density (~1%) upon irradiation for 2 h ($\lambda_{ex} = 313$ nm, 40 J/cm$^2$). Photolyses of P3TPSH and P3TOSH provided similar evidence of photostability. The issue of moisture content in P3TASH's and its role on photostability was not examined at this time.

An interesting characteristic of the sulfonated polymers in solution was an initial increase in absorption intensity at 800 nm upon irradiation. This can be clearly observed in Figure 6 for P3TOSNa. This observation suggests that polymers are photochemically oxidized, generating polarons and bipolarons. This is consistent with recent studies on the photochemical generation of radical cations from thiophene oligomers in nonaqueous solvent in which it is reported that excitation is followed by electron injection into the solvent. Upon prolonged irradiation of the sulfonated polymers, the absorption intensity at 800 nm decreases. This can be explained on the basis of disruption of the $\pi$-system, as evidenced by photobleaching of the $\pi-\pi^*$ band and its corresponding blue-shift, upon prolonged exposure.

The absorption intensity at 800 nm also increases with irradiation, for polymer solutions of the acid form (not shown) reaching a maximum optical density after 10 min irradiation time (~3 J/cm$^2$). Prolonged exposure to irradiation decreased the absorption intensity at 800 nm. After 2 h of exposure (40 J/cm$^2$), the optical density of the bipolaron transition was lower than that initially observed due to self-doping.

**Photoimaging.** P3TAS films exposed to ambient atmosphere remained water soluble even after 2 h of irradiation, in contrast to films of poly(3-hexylthiophene) which are rendered completely insoluble after a relatively short irradiation time.[7a] This is presumably due to the residual water in the sulfonated analogs which interferes with the cross-linking process. This was confirmed by the observation that anhydrous films were found to be rendered completely insoluble upon exposure to moderate doses of UV−vis irradiation. Negative images of these anhydrous polymers were produced in a manner previously described for the poly(3-hexylthiophene). P3TAS's, however, cannot be used directly as photoresists unless moisture is stringently excluded. Subsequently, it was discovered that photo-cross-linking and photoimaging of P3TAS's containing residual moisture could be achieved by introducing a photoinitiator into the polymeric matrix prior to irradiation. A suitable photoinitiator was found from a recent photochemical study of poly(3-alkylthiophenes) doped with the $FeCl_4^-$ counterion. In the reported study, it was shown that the counterion undergoes facile photochemistry leading to "dedoping" and insolubilization of the resultant polymer.[22]

To examine whether $FeCl_4^-$ would act as a photo-cross-linker in sulfonated poly(thiophenes), polymer films of P3TAS's were cast from their corresponding solution under vacuum, subsequently oxidized with a solution of 0.1 M $FeCl_3$ in nitromethane, air-dried, and irradiated for 15 s through a photomask. The photolysis conditions were identical to those employed in the photochemical studies. By control of the developing solution and choice of polymer, both negative and positive images of the polymer could be obtained. A positive image was obtained when films of P3TPSH oxidized with $FeCl_4^-$ were irradiated and developed with aqueous solution. In this case, photolysis converts oxidized polymer to its neutral form and since dissolution of the neutral polymer is faster than the oxidized material, the irradiated regions dissolved first. If the relief image is left in contact with the developing solution for longer periods, the unexposed polymer slowly dissolves. This may have use in "lift off" photolithographic techniques. In contrast, irradiation of P3TOSH oxidized with $FeCl_4^-$ provided a negative image when developed with an aqueous solution of acetic acid (50% v/v). We interpret the difference between the two cases as being due to the difference in solubility between the two polymers. The longer alkane chain associated with P3TOSH renders it less soluble than P3TPSH, and thus the former requires a lesser degree of cross-linking to confer insolubility. This statement does not indicate the absence of photo-cross-linking in P3TPSH, but simply implies that P3TPSH tolerates a larger degree of cross-linking and remains soluble. The photolithographic process for the formation of negative images is depicted in Figure 10. Examples of negative and positive photoimages produced by this procedure are shown in Figure 11. The negative image of the mask possessed a conductivity $<10^{-6}$ S/cm, indicating it had been converted to the neutral form in the process. When the polymeric image was chemically oxidized by immersing the substrate into a solution of 0.1 M of $FeCl_3$ in nitromethane, the resulting polymer pattern exhibited a conductivity of $10^{-1}-10^{-2}$ S/cm. The positive image possessed a conductivity similar to the self-doped polymers ($5 \times 10^{-2}-10^{-1}$ S/cm).

## Discussion

**Polymer Conformation.** The combination of UV−vis absorption, X-ray diffraction, and NMR data provides valuable insight into the microstructure of P3TAS's. UV−vis absorption spectra of P3TPSNa, P3THSNa, and P3TOSNa show little difference in the extent of $\pi$-conjugation for polymers dissolved in aqueous solution or polymers in the form of solid films. This leads to the interpretation that either $\pi$-conjugation has been maximized in both cases by achieving a rigid rod conforma-

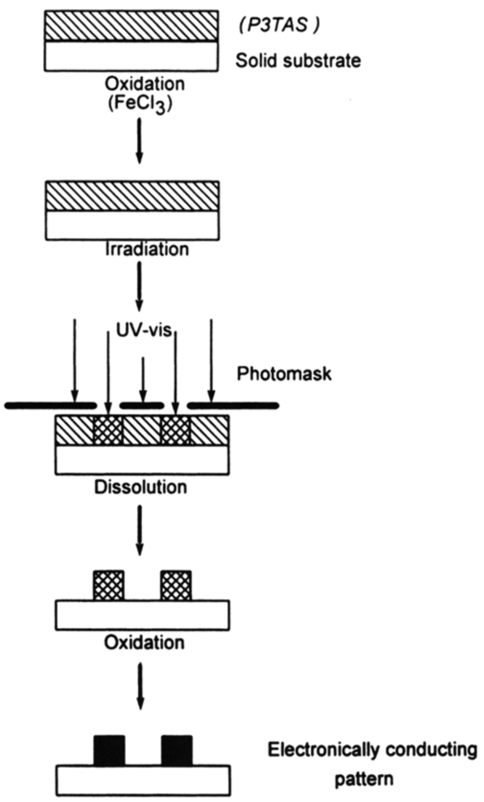


**Figure 10.** Photolithographic scheme for obtaining negative images for poly(n-(3-thienyl)alkanesulfonates) (P3TAS).

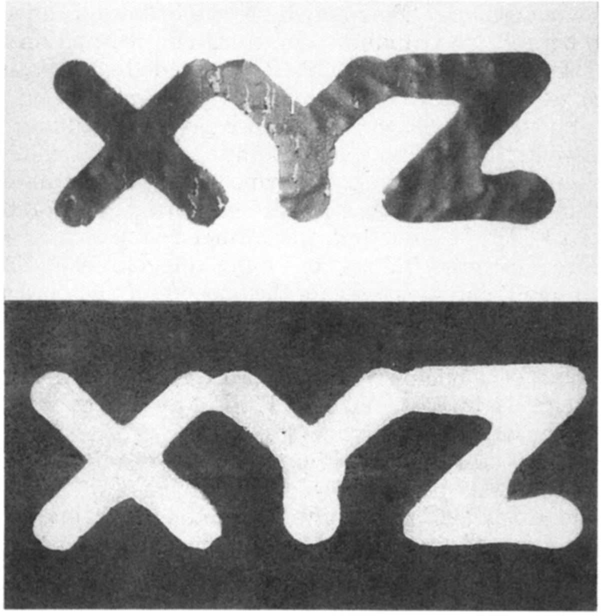


**Figure 11.** Photolithography of P3TAS's: (top) negative image of P3TOS; (bottom) positive image of P3TPS. Resolution of image = 0.5 mm. See text for a description of the imaging process.

tion or, in the other extreme, the polymer forms random coils in both the solution and solid state such that $\pi$-conjugation is substantially less than what would be predicted on the basis of a rigid rod structure. $\lambda_{max}$ values for the polymer solutions and polymer films are in the range 420–460 nm, which are much smaller than coplanar and fully conjugated polythienyl systems. The large Stokes shift observed for the luminescence of these materials is consistent with the fact that adjacent thienyl units experience a large degree of twist about the interannular bond in their ground state. All these data indicate that individual chains in the bulk polymer take on a more coiled conformation compared to their non-sulfonated poly(3-alkylthiophene) analogs. X-ray analysis provides direct evidence of this, since the data indicate the absence of crystallinity attributed to $\pi$-stacking and self-assemblage of coplanar conjugated segments. For P3ATs, amorphology has been observed for polymers which contain a high percentage of the sterically-strained head-to-head linkages. However, NMR analysis of the sulfonated polymers indicates a head-to-tail:head-to-head (HT:HH) ratio of 80:20. As a point of reference P3HT's prepared by oxidative coupling using ferric chloride also exhibit a HT:HH ratio of 80:20. In contrast to the alkanesulfonate polymers, however, $\lambda_{max}$ values for the non-sulfonated analogs increase from 440 to 505 nm for polymer solutions and polymer films, respectively, and the films possess a high degree of long molecular order, as determined by X-ray diffraction analysis.

Clearly, the presence of sulfonate groups attached to the terminus of the alkyl side chain on derivatized polythiophenes prevents the polymer chains from achieving a higher degree of coplanarity and $\pi$-conjugation in the solid state. This cannot be explained by invoking arguments based on increased steric interaction between adjacent thienyl rings. Nor can it be explained on the hygroscopic nature of the sulfonated polymers, which promotes takeup of water upon exposure to the atmosphere, since both completely anhydrous films and films containing residual moisture exhibited identical featureless X-ray diffraction spectra. A more satisfactory explanation can be found by considering ion aggregation. It is well documented that counterion condensation and ion pair formation takes place in low dielectric media.[23] Ion pairing creates a strong ionic dipole which can attract other ion pairs, thus resulting in aggregation of ionic species. The extent of aggregation depends on a number of factors but of relevance to the present study is the fact that ion aggregation is more pronounced for polymers containing large concentrations of covalently-bound ions. The dielectric constant of poly(3-alkylthiophenes) has been measured to be $\sim 12$,[24] which places it in the category of low dielectric media. Since P3TAS's are polyelectrolytes, containing one ionic species per repeating unit, ion aggregation is expected to occur in the solid state. This argument is based on the premise that the forces which drive ion aggregation are larger than those which drive the self-organization of $\pi$-conjugated segments.

For polymers dissolved in aqueous solution, the high dielectric medium screens the electrostatic interactions and no aggregation is anticipated. Thus a coiled conformation is adopted in solution. For this reason, $\lambda_{max}$ values of P3TAS's in aqueous solution are similar to P3HTs dissolved in nonaqueous solvents. However, as a result of ion aggregation in the solid state, adjacent thienyl rings in P3TAS's will be prevented from achieving a coplanar, rigid configuration, and since $\pi$-stacking and lamella-like formation is no longer possible, P3TAS's will be amorphous and devoid of long range order. Figure 12 illustrates this model wherein the polymer in solution is depicted as a random coil, albeit with a large persistence length. Upon removal of the solvent the polymers are prevented from self-organization (top right) by ion aggregation (bottom right).

As confirmation of this, films of P3TPSNa, P3THSNa, and P3TOSNa were cast from aqueous solutions con-

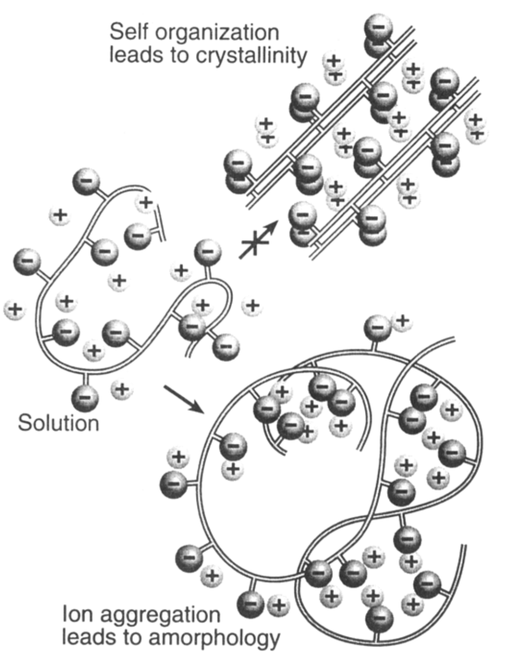


**Figure 12.** Diagram illustrating how ion aggregation prevents self-organization and crystallization of P3TAS's.

taining 1 v/v % ethylene glycol. Evaporation of the solvent provided homogeneous films containing ethylene glycol, thus increasing the dielectric constant of the medium. The wavelengths of maximum absorption were 476, 468, and 486 nm. These represent red shifts compared to films of the pure polymers where $\lambda_{max}$ values were 436, 446, and 466 nm, respectively, and is interpreted as being the result of a reduction in the extent of ion aggregation due to the increased dielectric constant of the medium.

**Photostability.** By comparison with previous studies of photodegradation of P3ATs, the major pathway leading to photobleaching of P3TAS's appears to be photosensitization and subsequent reaction of singlet oxygen. However, the lifetime of singlet oxygen is much shorter in aqueous solution (3 $\mu$s) than in chloroform (240 $\mu$s),[25] which suggests that photodegradation of poly(n-(3-thienyl)alkanesulfonates) in aqueous solution could be considerably slower than poly(3-alkylthiophenes) in oxygenated chloroforms, even though the solubility of oxygen in water is 1 order of magnitude smaller than in chloroform. The substantial increase in photostability of the sulfonate polymers in aqueous solution compared to nonaqueous solutions of P3HT (Figure 6) is consistent with this conclusion. The photostability was found to be slightly dependent on the length of the alkanesulfonate, but the origin of this result is unknown. Similarly, anhydrous films of the sulfonated polymers are substantially less stable to photodegradation than the films exposed to a moisture-containing environment.

The acid form of the sulfonated polymers exposed to ambient air exhibits an even greater photostability toward disruption of the $\pi$-conjugated backbone. This might be due to a combination of moisture uptake and the enhanced rigidity of the polymer backbone which leads to efficient internal quenching of excitation via lattice relaxation. It is well documented that the presence of polaronic and bipolaronic charges on the polymer backbone serve as quenching centers for deactivation of excitation.[26]

Finally, it is apparent that films of the alkanesulfonate derivatives are less susceptible to photo-cross-linking than non-sulfonate analogs when they are exposed to a moisture-containing atmosphere. It has been demonstrated that introduction of iron species and their subsequent photolysis do lead to cross-linking. The fact that the length of the alkanesulfonate side chain confers different solubilities to the polymer enables the fabrication of either negative or positive images of water soluble $\pi$-conjugated polymers. Alternatively, photolithography can be performed on P3TAS's if they are stringently dried.

## Conclusion

Poly(n-(3-thienyl)alkanesulfonates) prepared by oxidative coupling using ferric chloride yield water soluble polymers which possess a relatively large degree of regioregularity. In spite of this, polymer films are amorphous, possibly due to ion aggregation in the bulk which prevents individual chains from achieving a coplanar conformation. The substantial increase in photostability of the sulfonate polymers in aqueous solution is consistent with the conclusion that singlet oxygen is an intermediate leading to photobleaching and that the lifetime of singlet oxygen is reduced in aqueous solution. The role of $H_2O$ in enhancing photostability is confirmed by the photochemistry of thin films, where it is found that anhydrous films are much more susceptible to photodegradation. The acid forms of the polymers are even more photostable because of additional quenching of excitation which can take place by charge carriers originating from self-doping. Irradiated polymer films do not cross-link upon irradiation but can be induced to do so upon addition and irradiation of ferric salts. Both positive and negative photolithography can be performed on these systems depending on the length of the alkanesulfonate chain.

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