

ELECTRONIC EFFECTS OF POLYFLUORINATED SUBSTITUENTS ON THE POLYMERIZATION AND THE PROPERTIES OF POLYTHIOPHENES*

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ABSTRACT

Three series of polythiophenes containing fluoroalkoxy and fluoroether substituents were prepared by electrochemical polymerization. The effect of substituents with fluoroalkoxy or ether functional groups on the electrochemical polymerization of thiophene monomers and properties of the obtained polymers were analyzed. The introduction of a fluoroether functional group at the 3-position of the thiophene ring leads to an increase of the oxidation potential of the monomer and to a decrease of the conductivity of the resulting polymers, even with the use of a CH₂ group as spacer. Conversely, the presence of an oxygen atom directly at the 3-position of the thiophene ring, which offsets the negative withdrawing effect of fluoroalkyl groups, facilitates the synthesis of highly conducting polythiophenes.

INTRODUCTION

Electronically conducting polymers have received considerable attention because of their remarkable electronic, magnetic and optical properties and their wide range of potential applications in many areas. Among all the conducting polymers, polythiophenes are particularly interesting owing to their improved environmental stability as compared with polyacetylene and also because they can be easily prepared as films of controlled thickness by electrochemical synthesis. The incorporation of relatively long and flexible side chains in 3-position of thiophene monomer leads to the resulting materials either meltable or solution processable and highly conductive^[1]. Recently, several fluoroalkyl substituted polythiophenes have been prepared due to their promising trends to be conductive polymer films^[2]. It is anticipated that the

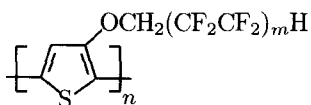
*This work was supported by the National Natural Science Foundation of China.

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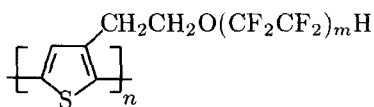
Received May 2, 1995

fluorinated polymers will possess improved chemical and thermal stability over the nonfluorinated analogs.

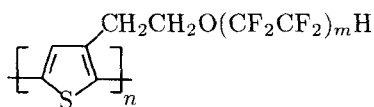
In our earlier paper, we reported synthesis and characterization of a novel series of fluoroalkoxy polythiophenes (Type A)^[3]. It is necessary to control the electronic effect of the side chain in order to provide both the polymerizability of the monomer and the electronic properties of polymer obtained. Here, the other two series of polythiophenes containing fluoroether substituents (Type B and C) have been investigated.



Type A, $m = 1, 2, 3$ which stand for polymers (1), (2) and (3), respectively.



Type B, $m = 1, 2, 3$ which stand for polymers (4), (5) and (6), respectively



Type C, $m = 1, 2, 3$ which stand for polymers (7), (8) and (9), respectively

The electronic effects of these fluoro-substituents on the process of electrochemical polymerization of thiophene monomers and the properties of the obtained polymers have been studied. Introduction of fluorine atom by using conventional fluoroalcohol causes little increase of expense. Actually we get fluoro-polymers with highly electronic, electrochemical and thermal-air stability, which can be applied in many practical areas such as rechargeable batteries, electrochromic devices and biosensors, etc.

EXPERIMENTAL

Monomer synthesis

3-Methylthiophene, 3-bromothiophene and 2-(3-thienyl) ethanol were obtained from Aldrich Chemical Co.. 3-fluoroalkoxythiophenes were prepared from 3-bromothiophene and sodium fluoroalkoxide in the presence of copper oxide and potassium

iodide. (3-thienyl) methyl fluoroxyalkyl ethers were prepared by side chain bromination of 3-methylthiophene and ether formation using the convenient alcoholates as nucleophiles. Synthesis of 2-(3-thienyl) ethyl fluoroxyalkyl ether was performed using 2-(3-thienyl) ethanol and convenient halo or oxyalkyl derivative. All these raw products were purified by adsorption chromatography on silica gel using petroleum ether and ethylacetate as eluent.

Monomer (1), yield, 22%. Anal. Calcd for $C_7H_6F_4OS$: C%, 39.25; H%, 2.80; S%, 14.95; F%, 35.51. Found: C%, 39.26; H%, 2.84; S%, 14.94; F%, 35.85. ^1H NMR ($CDCl_3$, ppm): 6.5–7.1 (3H, m); 6.3 t, 5.7 t, 5.1 t, 1H; 4.2 (2H,t). ^{19}F NMR (standard- $CFCl_3$, ppm); –138 (2F, d); –124 (2F, d). MS: m/e, 214.

Monomer (2), yield, 16%. Anal. Calcd for $C_9H_6F_8OS$: C%, 34.39; H%, 1.91; S%, 10.19; F%, 48.41. Found: C%, 34.91; H%, 2.12; S%, 10.72; F%, 48.58. ^1H NMR: 6.5–7.1 (3H, m); 6.4 t, 5.8 t, 5.2 t, 1H; 4.2 (2H,t). ^{19}F NMR –137 (2F, d); –130 (2F, d); –125 (3F, d); –119 (2F, d). MS: m/e, 314.

Monomer (3), yield, 8%. Anal. Calcd for $C_{11}H_6F_{12}OS$: C%, 31.88%; H%, 1.45; S%, 7.73; F%, 55.07. Found: C%, 31.54; H%, 2.21; S%, 7.82; F%, 54.76. ^1H NMR: 6.5–7.1 (3H, m); 6.4 t, 5.8 t, 5.2 t, 1H; 4.2 (2H,t). ^{19}F NMR –134 (2F, d); –127 (2F, s); –120 (6F, m); –116 (2F, s). MS: m/e, 414.

Monomer (4), yield, 51%. Anal. Calcd for $C_8H_8F_4OS$: C%, 42.11%; H%, 3.51; S%, 14.04; F%, 33.33. Found: C%, 42.41; H%, 3.65; S%, 14.08; F%, 33.55. ^1H NMR: 6.6–7.3 (3H, m); 6.3 t, 5.7 t, 5.1 t, 1H; 4.2 (2H,t). 3.6 (2H, s). ^{19}F NMR –138 (2F, d); –124 (2F, d). MS: m/e, 228.

Monomer (5), yield, 45%. Anal. Calcd for $C_{10}H_8F_8OS$: C%, 36.58%; H%, 2.44; S%, 9.75; F%, 46.34. Found: C%, 36.98; H%, 2.35; S%, 9.16; F%, 45.98. ^1H NMR: 6.6–7.3 (3H, m); 6.5 t, 5.5 t, 4.6 t, 1H; 4.2 (2H,t). 3.6 (2H, s). ^{19}F NMR –137 (2F, d); –130 (2F, d). –125 (2F, d); –119 (2F, d). MS: m/e, 328.

Monomer (6), yield, 41%. Anal. Calcd for $C_{12}H_8F_{12}OS$: C%, 33.64%; H%, 1.87; S%, 7.48; F%, 53.27. Found: C%, 33.48; H%, 1.70; S%, 7.28; F%, 53.85. ^1H NMR: 6.6–7.3 (3H, m); 6.5 t, 5.5 t, 4.6 t, 1H; 4.2 (2H,t). 3.6 (2H, s). ^{19}F NMR –134 (2F, d); –127 (2F, d). –120 (6F, m); –116 (2F, s). MS: m/e, 428.

Monomer (7), yield, 34%. Anal. Calcd for $C_9H_{10}F_4OS$: C%, 44.63%; H%, 4.13; S%, 13.22; F%, 31.40. Found: C%, 44.12; H%, 3.98; S%, 12.86; F%, 31.24. ^1H NMR: 6.6–7.3 (3H, m); 6.6 t, 6.0 t, 5.2 t, 1H; 4.2 (2H,t). 3.6 (2H, t); 2.9 (2H, t). ^{19}F NMR –138 (2F, d); –124 (2F, d). MS: m/e, 242.

Monomer (8), yield, 37%. Anal. Calcd for $C_{11}H_{10}F_8OS$: C%, 38.60%; H%, 2.92; S%, 9.36; F%, 44.44. Found: C%, 38.72; H%, 2.75; S%, 9.25; F%, 44.97. ^1H NMR:

6.6–7.3 (3H, m); 6.6 t, 6.0 t, 5.2 t, 1H; 4.2 (2H, t). 3.6 (2H, t); 2.9 (2H, t). ^{19}F NMR –137 (2F, d); –130 (2F, d). 125 (2F, d); –119 (2F, d). MS: m/e, 342.

Monomer (**9**), yield, 34%. Anal. Calcd for $\text{C}_{13}\text{H}_{10}\text{F}_{12}\text{OS}$: C%, 35.29%; H%, 2.26; S%, 7.24; F% 51.58. Found: C%, 35.25; H%, 2.30; S%, 7.22; F%, 51.90. ^1H NMR: 6.6–7.3 (3H, m); 6.6 t, 6.0 t, 5.2 t, 1H; 3.6 (2H, t). 2.9 (2H, t); ^{19}F NMR –134 (2F, d); –127 (2F, s). –120 (6F, m); –116 (2F, s). MS: m/e, 442.

Polymers

The electrolytes, tetrabutylammonium hexafluorophosphate (Bu_4NPF_6), tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) and anhydrous lithium perchlorate (LiClO_4) were obtained from Tokyo Kasai Chemical Industry Co. and used without further purification. Electrochemical synthesis of polymers was conducted under galvanostatic conditions (current density = 0.5–2.0 mA/cm²) on 2–3 cm² Pt in argon atmosphere at ambient temperature for 2–4 hours. The polymer film grown on the electrode was rinsed thoroughly in acetone and then electrochemically undoped by reversing the current flow (0.01 mA/cm²) until the potential of the working electrode indicated that the polymer has reached neutral state.

Physical measurements

Cyclic voltammetry was carried out in an one-compartment cell using an EG&G PAR (Model 273) potentiostat/galvanostat with a PARC M270 programmer and a X-Y recorder. Voltammograms of the reduced polymers were recorded on 0.1 cm² Pt in 0.1 mol/L $\text{LiClO}_4\text{-CH}_3\text{CN}$ at a scan rate of 20 mV/s versus saturated calomel electrode (SCE). The oxidation potentials of the various monomers have been measured by cyclic voltammetry in anhydrous acetonitrile containing 0.1 mol/L of LiClO_4 . Low monomer concentration (0.001 mol/L) and high scan rate 200 mV/s were used in order to prevent from polymerization. All potentials were referred to the SCE, UV-Visible spectra were performed by using polymer in DMF on a Perkin-Elmer Lambda 5 Spectrophotometer. Standard four-probe conductivity measurements were conducted on in-situ films of the doped polymers at room temperature in air.

RESULTS AND DISCUSSION

An investigation of polythiophene films with appropriate substituents shows that when the peak oxidation potential of some substituted monomers are plotted against their respective Hammett substituent constants, a linear correlation is obtained shown as in Fig. 1.

The Hammett substituent constant σ^{+1} for para substituents for the reaction type $R^0 \rightarrow R^+$ is used. Waltman et al. first noted this correlation, which clearly

shows that electronic effects drastically affect the electronic density of the thiophene ring and hence its reactivity^[4]. The straight-line fit shows that all of the thiophene monomers are oxidized by the same mechanism. The positive sign for the substituent constant in Hammett Equation indicates that the more electrophilic character the substituents take on, the higher tendency to be oxidized the corresponding thiophenes have. It is postulated that the stability (or reactivity) of thiophene monomers is affected by the substituents. The monomers substituted by strongly electron-withdrawing groups such as 3-thiophenecarboxylic acid and 3-cyanothiophene have overhigh oxidation potentials compared with unsubstituted thiophene, hence they cannot polymerize electrochemically. When 3-bromothiophene is used as monomer, it leads to poorly conducting polymers with high oxidation potentials. The effect of these strongly electro-withdrawing group is to destabilize the radical cation intermediate to the extent that radical cation coupling reactions become unfavorable as compared with other reaction pathways. In the other extreme case, the substitution of thiophene by strongly electron-donating groups such as 3-alkoxythiophene produces a great decrease of oxidation potential and hence an over-stabilization of the corresponding radical cation intermediates results. These intermediates have high tendency to be attacked by nucleophiles such as the solvent or other nucleophilic species in the vicinity of the electrode and thus diffuse away from the electrode surface to form soluble oligomers in solution. A typical example is 3-thioalkylthiophenes, which are difficult to become high molecular weight polymeric films with good conductivity and electrochemical stability. Similar effects result from the grafting of alkoxy groups on the thiophene ring. These facts suggest that there should be an optimum potential range standing for reactivity of the radical cation intermediate, which favors radical cation coupling in the follow-up reaction to yield polymeric films^[4,5].

Table 1 Cyclic voltammetric data for 10^{-3} — 10^{-4} mol/L thiophenes measured in 0.1 mol/L $\text{LiClO}_4/\text{CH}_3\text{CN}$ using Pt vs. the saturated calomel electrode (SCE)

Sample	Epa monomer (V vs. SCE) ^a	Epa polymer (V vs. SCE) ^b
thiophene	2.05	0.97
3-methylalkoxy thiophene	1.47	0.61
3-methyl thiophene	1.65	0.72
3-bromo thiophene	2.36	1.21
2, 2-bithiophene	1.30	0.61
3-thiophenecarboxylic acid	2.38	

a. Epa monomer stands for the potential for the peak of monomer oxidation

b. Epa polymer stands for the potential for the peak of polymer oxidation

Cyclic voltammetric data for some thiophene monomers and their corresponding polymers are given in Table 1. All of the monomers show irreversible oxidation peaks and give rise to colored solutions upon electro-oxidation.

Table 1 describes the property-structure correlation between thiophene monomers and their corresponding polymers. When the peak oxidation potentials of some thiophene monomers are plotted against those of their respective polymers, a straight-line is obtained (Fig. 2).

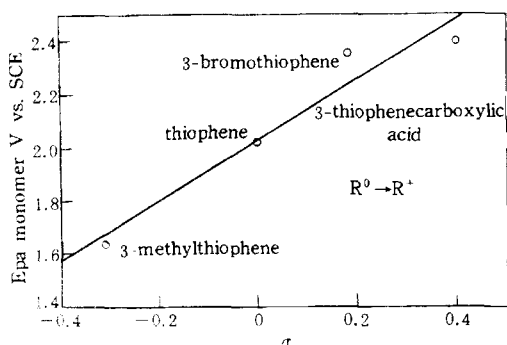


Fig. 1 Electrochemical peak oxidation potential of thiophene monomers vs. their respective Hammett substituent constants

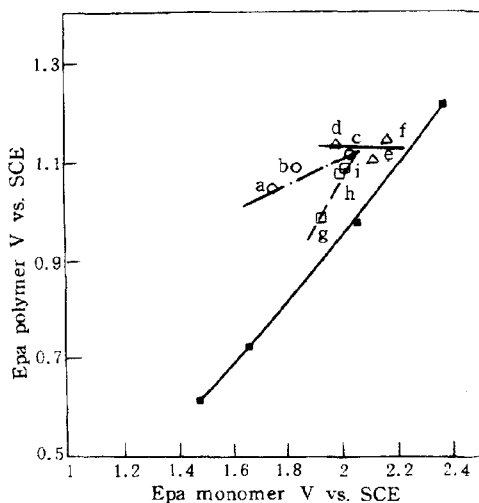


Fig. 2 Peak oxidation potential of thiophene monomers vs. their respective polymers in 0.1 mol/L LiClO₄/CH₃CN. [letters a-i denote the polymers (1)-(9)]

It suggests that 3-substituted monomers and their respective polymers are made up of a related system of electrons. This result is important because it is a key example of a property-structure correlation between a conducting polymer and its corresponding monomer produced by a systematic variation in the chemical structures^[5]. Because of the high expenses of synthesis, there is few reports related to the synthesis of fluorinated group substituted thiophene monomer. In the present work, three series of polythiophenes containing fluoroalkoxy and fluoroether groups synthesized by electrochemical polymerization are used to fit into the straight-line in Fig. 2. The electrochemical properties of the 3-fluoroalkoxyl and 3-fluoroether thiophene series have been characterized in terms of the potential for the peak of monomer oxidation, E_{pa} (mono), and redox properties of the resulting polymers, E_{pa} and E_{pc}. Table 2 shows the cyclic voltammetric data of these monomers and their corresponding polymers.

Table 2 Electrochemical properties and UV-VIS spectroscopic properties of the polythiophenes^a

Samp.	Epa monomer V vs. SCE	Epa polymer V vs. SCE	Epc polymer V vs. SCE	Neutral form ^b	Oxidized form ^c	Doping level %
(1)	1.75	1.04	0.94	red-violet	black	32.4
(2)	1.83	1.08	0.94	dark red	blue-violet	35.2
(3)	2.03	1.11	0.97	red	green	36.8
(4)	1.98	1.13	0.93	yellow	orange-red	28.7
(5)	2.11	1.10	0.98	pale yellow	orange	31.0
(6)	2.16	1.14	0.96	pale yellow	orange	35.8
(7)	1.92	0.98	0.92	brown-red	blue	27.9
(8)	1.99	1.07	0.92	brown	greenish blue	32.4
(9)	2.01	1.08	0.91	brown	greenish blue	37.8

Cyclic voltammetry in 0.1 mol/L Li ClO₄/CH₃CN at 20 mV/s on 0.1 cm² Pta. electrochemically synthesized polymer, deposition charge 100 mC/cm²

b. the species at 0.0 V vs. SCE; c. the species at nearly +1.0 V vs. SCE

Among these three series, series B presents the most high Epa (mono) and Epa (polymer). This is due to the strong electron-withdrawing of the fluoroalkyl groups together with the same effect of the oxygen atom in the ether group. It is noted that the monomers in the same series show the greater oxidation potentials as the lengths of the fluorinated chains in the monomers increase. For example, as in the same series, the Epa (mono), from low to high, is (1) < (2) < (3). Correspondingly, the same order of Epa of the resulting polymers is found, indicating the electronic structures of the monomers and their corresponding polymers must be alike. Bucher et al. reported that the preparation of poly [3-(polyfluoroalkyl) thiophenes] by electrochemical polymerization requires the existence of —CH₂— spacer groups between the thiophene ring and the fluorinated alkyl group^[6]. Two —CH₂— spacers between a perfluorohexyl group and the ring lead to a powder deposit on the electrode with inferior property, while three —CH₂— spacers yield a free-standing film. The need for the spacer groups is attributed to the inhibition of polymer formation by the presence of an electronegative fluorinated group linked with the aromatic heterocyclic ring. In our study, series C, which possesses two —CH₂— spacers between the conjugated system and fluoroalkoxy group still shows high Epa (mono) and Epa (polymer). This means that two —CH₂— spacers can not effectively offset the negative electron-withdrawing effect of the polyfluoroalkyl group. Surprisingly, we found that series A, especially (1) and (2), which have medium monomer potentials, can be recycled between the conducting (oxidized) and nonconducting (neutral) states

without significant decomposition of the material. The switching is also accompanied by a reversible color change, as for polymer (1), from brown (neutral) to black (oxidized).

Table 3 presents the conductivity and the $\lambda_{\max}$ value in UV-Visible spectra of these fluoro-polythiophenes. Among all these data, polymer (1) and polymer (2) show higher conductivity and $\lambda_{\max}$ values. All the other polymers possess lower conductivity (10^{-3} – 10^{-4} S/cm) and more hyperchromic shifted $\lambda_{\max}$ values. This result suggests that the method which uses only $-\text{CH}_2-$ spacers to inhibit the negative electron-withdrawing effect of polyfluoroalkyl groups is less effective than that of using oxygen directly at the 3-position to compensate the negative effect. The use of fluoroalkyl substituents will cause a rising of the positive oxidation potential of monomers beyond the desirable range for polymerization and lead to low conductivity of the prepared polymers. Thus it appears that electronic effects play a determining role on the reactivity of substituted polythiophenes and that the obtainment of extensively conjugated and highly conducting substituted polythiophenes requires that the monomer reactivity is kept within a defined limit.

Table 3 Conductivity and UV-VIS data of electrochemically synthesized polymers^a

Polymer	Dopants	Conductivity (S/cm)	λ (nm) ^b
(1)	Bu ₄ NPF ₆	0.1	529
	Bu ₄ NBF ₄	7.0×10^{-2}	
(2)	Bu ₄ NPF ₆	7.0×10^{-3}	472
	Bu ₄ NBF ₄	9.0×10^{-3}	
(3)	Bu ₄ NPF ₆	1.0×10^{-3}	428
	Bu ₄ NBF ₄	8.0×10^{-4}	
(4)	Bu ₄ NPF ₆	8.0×10^{-3}	328
(5)	Bu ₄ NPF ₆	8.0×10^{-3}	328
(6)	Bu ₄ NPF ₆	5.0×10^{-3}	324
(7)	Bu ₄ NPF ₆	2.0×10^{-2}	372
(8)	Bu ₄ NPF ₆	8.0×10^{-3}	372
(9)	Bu ₄ NPF ₆	8.0×10^{-3}	358

a. deposition charge 14.4 C/cm² on 3 cm² Pt; b. neutral polymers

CONCLUSION

Electronic effects drastically affect the electronic density of the thiophene ring and hence its reactivity. An optimum range for effective electrochemical polymerization is required for thiophene monomers to form conductive polymers with good

electric and electrochemical properties. Fluoroether thiophenes, even with $-\text{CH}_2-$ spacers' inhibition, lead to an increase of the oxidation potential of the monomer and to a decrease of the conductivity of the resulting polymers. However, fluoroalkoxy polythiophenes having more reasonable electronic effect and medium monomer oxidative potential possess higher conductivity and more extended λ_{max} value.

Keywords:

Electronic effect; Electrochemical polymerization; Polythiophene polyfluorinated substituent

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