

STRUCTURAL ANALYSIS AND ENVIRONMENTAL STABILITY OF POLYFLUORINATED GROUP SUBSTITUTED POLYTHIOPHENES*

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ABSTRACT

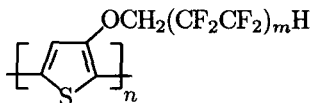
Electrochemical polymerization of 3-fluoroalkoxy and 3-fluoroether thiophenes gives polymers with relatively high molecular weights and good processability. Investigation of these polymers by means of GPC indicates that an increase in the number of fluorine atoms in the fluorinated group results in a decrease in degree of polymerization of the polymers in the same polythiophene series. As shown by NMR and FTIR, the polyfluorinated group substituted polythiophenes have regular 2, 5-coupling in their main chains. The SEM micrographs of the polymer films exhibit that polymer (1)-poly [3-2, 2, 3, 3-tetrafluoro-propoxy] thiophene] possesses more regular structure than the other polymers do. Substitution of polythiophenes by fluorinated groups leads to the polymers with high electric, electrochemical and thermal stability.

INTRODUCTION

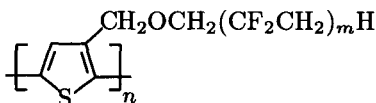
Electrically conducting polythiophenes have attracted great attention, owing to their various electronic properties such as electrochromism, energy storage and electrochemical sensors and modified electrodes. Many studies have shown that the properties of polythiophenes can be improved by the introduction of substituents in 3-position of the thiophene ring. These substituents include long alkyl, branched alkyl, aryl, ether and polyether chains, etc.^[1-5]. Synthesis and characterization of the fluorinated group substituted polythiophenes have recently become the subject of considerable interest because of the possibility for these polymers as a novel series of conducting polymers with improved chemical and thermal stability over their non-fluorinated analogs^[6-7]. In our recent work, we have described the preparation and properties of three novel series of polyfluorinated groups substituted polythiophenes.

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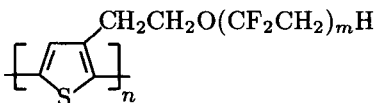
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Type A, $m = 1, 2, 3$ which stand for polymers (1), (2) and (3), respectively.



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

Scheme 1

In order to get a better knowledge of the structural versatility, electrochemical property and stability of the interesting substrates, the structural analysis and environmental stability of these fluoro-polymers were studied.

EXPERIMENTAL

Synthesis and characterization of the monomers were described in the early paper^[8]. The polymer films were prepared using the method reported previously^[9]. Molecular weights of the polymers were determined by gel permeation chromatography against polyacrylonitrile standards using a Waters 150-c ALC/GPC apparatus with N, N-dimethylformamide as the eluting solvent. NMR experiments were performed in deuterated DMSO on a 300 MHz Bruker pulsed Fourier transform instrument for ^1H and a 60 MHz Varian EM 360 spectrometer for ^{19}F . Fourier transform infrared spectra were recorded on a Perkin-Elmer 983 spectrometer. Scanning electron micrographs of the polymer films were obtained on Hitachi S-450 SEM instrument. Cyclic voltammetry was carried out in a one-compartment cell using an EG&G PAR (model 273) potentiostat/galvanostat. All potentials were referred to a saturated calomel electrode (SCE). Four-probe conductivity measurements were conducted on films or pressed pellets of the doped polymers at room temperature in air. Finally, thermogravimetric analysis was measured on a Shimadzu TGA-50 apparatus.

RESULTS AND DISCUSSION

1. *Structural analysis*

(1) Gel permeation chromatography

Table 1 Evaluation of the $\overline{M}_n$, $\overline{M}_w$, $\overline{M}_w/\overline{M}_n$ and $\overline{DP}_n$ from the soluble fraction of different fluoropolythiophenes^a

No.	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{DP}_n$
(1)	2.90×10^4	7.94×10^4	2.74	370
(1) ^b	4.43×10^4	7.65×10^4	1.71	360
(2)	3.12×10^4	7.56×10^4	2.42	240
(3)	2.68×10^4	6.67×10^4	2.49	160
(4)	3.08×10^4	8.68×10^4	2.81	380
(5)	2.68×10^4	7.58×10^4	2.82	230
(6)	2.97×10^4	7.40×10^4	2.49	170
(7)	2.64×10^4	7.18×10^4	2.71	310
(8)	4.18×10^4	7.26×10^4	1.73	210
(9)	3.12×10^4	7.67×10^4	2.46	180

GPC was performed with solutions of the undoped polymers in DMF using a low molecular weight polyacrylonitrile calibration. a. Electrochemically prepared polymer in 0.05 mol/L Bu₄NPF₆/PhNO₂ (J=0.05 mA/cm², time: 2h). b. Performed with solutions of the polymers in THF using a low molecular weight polystyrene calibration

The undoped fluoropolythiophenes can be partially dissolved in THF. While in strong protonic solvent DMF or DMSO, the polymers can be completely dissolved. The true molecular weight of fluoropolythiophenes can not be directly measured from the GPC curves because a calibration is lacking. In the present study, the GPC curves of these fluoropolymers are gained using DMF as solvent at 80°C and comparing the data based on a calibration curve of polyacronitrile standard. Molecular weights of various polymers are compiled in Table 1. In Table 1, the polymerization degrees of fluoropolythiophenes in the same series decrease as the fluorine atoms in the substituted group increase. Due to the bulk hindrance of the big substituent, the chain propagation during polymerization becomes difficult.

(2) IR pectroscopy

The spectra of 3-fluoroalkoxy and 3-fluoroether polythiophenes were shown in Fig. 1.

The spectra of the polymers in the same series are essentially identical with each other. In Fig. 1, polymer (1) has only one band at 3060 cm⁻¹ attributable to the aromatic C—H stretching vibration of (4) position —C—H bond and no band

attributable to the (2 or 5) —C—H bond. The spectrum of the polymer (1) film showed a band at 830 cm^{-1} that is assigned to the C—H deformation vibration of a 2, 3, 5-trisubstituted thiophene ring. These observations demonstrate that 2,5-linkage dominates in the main chain of the polymer. The same results are obtained among the other polymers. From Fig. 1, it can be seen that the fluoropolythiophene films possess a highly defined structure.

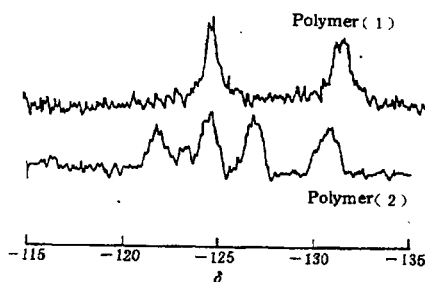
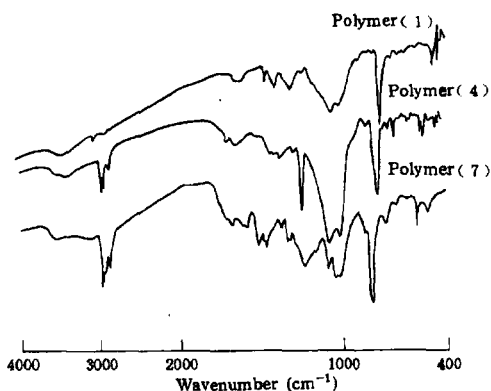


Fig. 1 FTIR spectra of undoped polymers (1), (4) and (7) Fig. 2 ^{19}F NMR spectra of polymer (1) and polymer (2)

(3) NMR spectroscopy

The chemical structures of these fluoropolymers are also analyzed by NMR, and some of these ^1H NMR spectra are tabulated in Table 2.

Table 2 ^1H NMR chemical shifts and assignments for polythiophenes (ppm)

Polymers	Aromatic	Methylene
	$\beta\text{-H}$	
(1)	8.3, 8.1, 7.8, 7.6	4.7
(2)	8.3, 8.1, 7.9, 7.6	4.9
(3)	8.5, 8.2, 7.5, 7.1	4.9
(4)	8.3—7.7	4.7, 2.1
(5)	8.3—7.7	4.7, 2.1
(6)	8.3—7.7	4.7, 2.1
(7)	8.3—7.1	4.1, 3.6, 2.3
(8)	8.3—7.1	4.1, 3.6, 2.3
(9)	8.3—7.1	4.1, 3.6, 2.3

For polymer (1), at least four peaks are found above 7.0 ppm, and these peaks can be assigned to hydrogen atoms in the β -position of polymer (1) having unequivalent chemical environments because of the different arrangement of the aromatic nucleus. Peaks for thienyl proton are not observed between 6.0—7.0 ppm (no $\alpha\text{-H}$). This

indicates that a linear and high molecular weight structure exists in the main chain of the polymer. Peak at 4.7 ppm is assigned to two hydrogen atom near fluorinated group. Investigation of polymer (4) and polymer (7) give the same results.

The spectra of the polymers are quite similar to those of their monomers. But the peaks of polymers are broader than those of their monomers, indicating the presence of different couplings (i.e., 2, 2', 2, 5' and 5, 5' couplings) and complicated chemical environment.

(4) Scanning electron micrographs

Fig. 3 shows the scanning electron micrographs of the surface of polymer films (1), (4) and (7). The surface in the micrograph is contacting with the electrolyte solution. The surface of the polymer (1) differs from that of polymer (4) and (7). The film of polymer (1) consists of a dense microfibril layer at the solution side. As for polymer (4) and (7), the surfaces on solution-side exhibit microporous structures. The film of polymer (7) possesses denser structure than the film of polymer (4), indicating the order of regularity and supermolecular structure of the three polymer films are (1) > (7) > (4). The reason may be due to the electronic effect of the substituted fluorinated groups. On the basis of these observations, one could expect polymer (1) to be more ordered and probably more conductive than polymer (4) and (7). In our previous paper,^[8] we found that polymer (1) possesses conductivity up to 0.1 S/cm, which is two orders of magnitude higher than that of polymer (4) and (7).

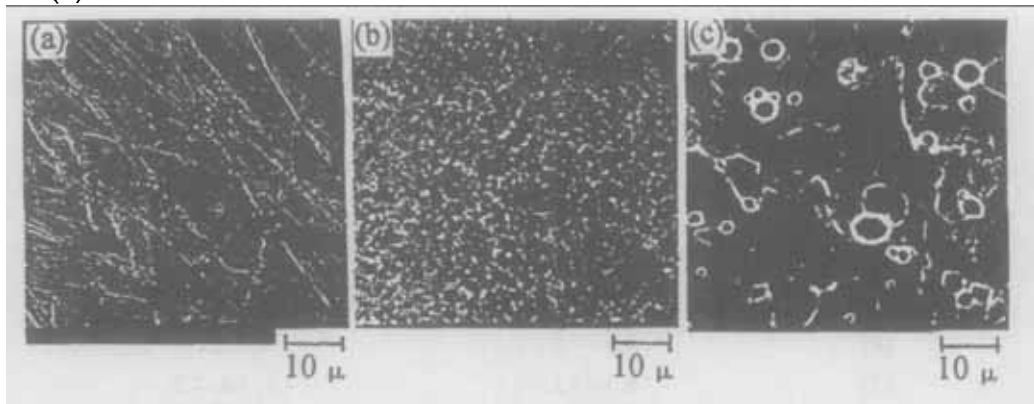


Fig. 3 Scanning electron micrographs of the surface of polymer films (1), (4) and (7)

2. Environmental stability

(1) Stability of the doped polymers

The conductivity of the doped polyfluoroalkoxy and polyfluoroether thiophenes decreases gradually in air as shown in Fig. 4. The conductivity of polymer (1) doped

with PF_6^- and BF_4^- is reduced to about 85% and 56% of the initial value respectively after 100 days. However, the conductivity of polymer (4) and (7) doped with PF_6^- or BF_4^- is reduced to about 1% of the initial value after 100 days. For polymers (1), (4) and (7) doped with the same dopants, their order of the stability are as follows: polymer (1) $\gg$ polymer (7)=polymer (4). The difference in the stability may be brought about by the partially electron-donative fluoroalkoxy group, which may stabilize the positively charged polymer chain.

Conductivities σ_0 and σ were examined shortly after preparation and also after storage respectively.

(2) Electroactive stability

Cyclovoltammetric measurements were performed between 0 and 1.4 V vs. the saturated calomel electrode (SCE) in order to obtain some data concerning the electroactivity of the fluoro-polymers. All fluoro-polymers show high stability of electroactivity. Fig. 5 shows the cyclic voltammograms of polymer (1). The electroactivity of the polymer still maintains after 400 cycles.

Compared with polymer (1), its hydrocarbon analog, poly(3-propoxy thiophene) loses its electroactivity noticeably, as expressed by the decrease of the peak area and the shift of the peaks to higher potentials. The shift of the peaks to higher potentials may be due to the partial oxidation of the side hydrocarbon chain and the nucleus. After only 50 cycles, the films were seriously destroyed.

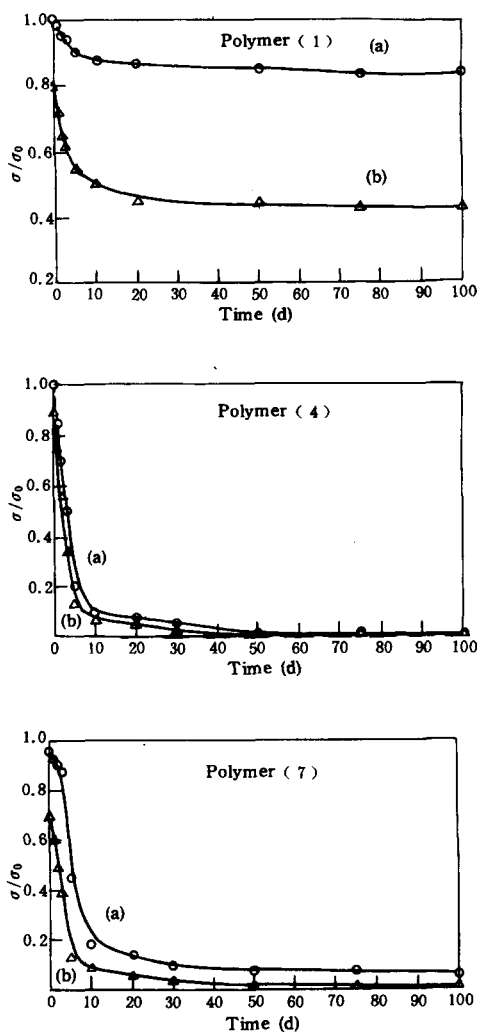


Fig. 4 Relative conductivity of doped polymers vs. time of exposure in air (a) PF_6^- doped polymer, (b) BF_4^- doped polymer

From the above comparison, a conclusion may be drawn that the introduction

of the fluorinated group to polythiophene will improve its electroactive stability.

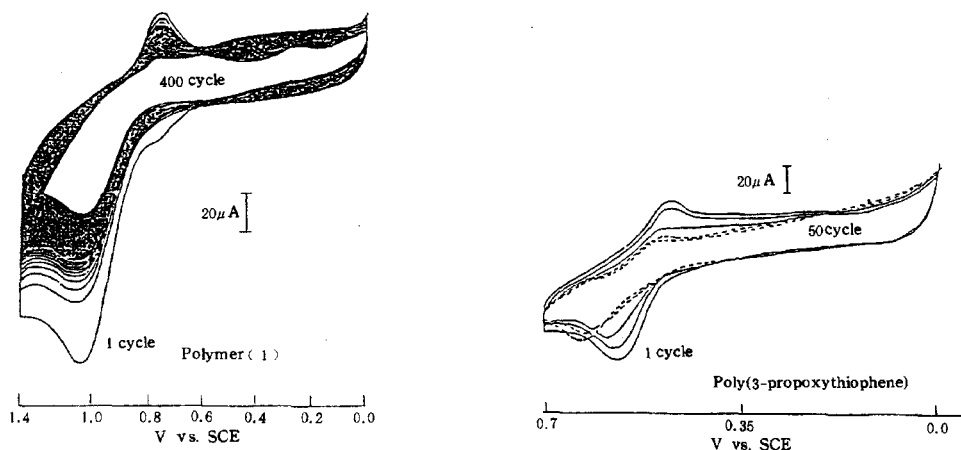


Fig. 5 Cyclic voltammograms of polymer (1) and its hydrocarbon analog-poly (3-propoxythiophene) measured at a scanning rate at 200mV/s vs. SCE on Pt.

(3) Thermal/air stability

The thermal/air stability of polythiophenes is of importance from the practical point of view. As shown in Table 3, TGA measurements on these fluoro-polymers were carried out.

Table 3 TGA data for different polythiophenes*

Polythiophene	$T_d(^{\circ}\text{C})^a$	$M_d/M_0(\%)^b$
(1)	310	40.6
(2)	315	38.2
(3)	312	37.4
(4)	306	56.3
(5)	312	53.7
(6)	302	52.1
(7)	308	53.0
(8)	312	48.1
(9)	302	45.4
(10) ^c	182	91.3

* Heating rate: 20°C/min

a. The temperature at which the polymer began to decompose;

b. M_d : the weight of the polymer lost at 500°C; M_0 : the original weight of the polymer; c. poly (3-propoxythiophene)

All these fluoro-polymers are stable under 300°C. They begin to lose their weights near 310°C. For example, above 300°C, the weight of polymer (1) decreases gradually when temperature increases. The weight at 500°C is 59.4% of the initial value.

However, poly(3-propoxy) thiophene begins to decompose at 168°C and its weight is reduced to only about 8.7% of the initial value. Hence, it is noted that introduction of fluorinated group to the 3-position of thiophene will greatly increase the thermal/air stability of the resulting polymers.

CONCLUSION

The present study indicated that the novel fluoroalkoxy and fluoroether group substituted polythiophenes are soluble and processable conducting polymers with high molecular weights. ^1H NMR and FTIR show that the polymers are 2, 5-coupled in their main chains. The micrographs of the polymer films exhibit that they have relatively ordered structure. Introduction of fluorinated groups in the 3-position of thiophene rings leads to the resulting polymers with high electric, electrochemical and thermal stability.

Keywords:

Structural analysis; Environmental stability; Polyfluorinated substituent; Polythiophene

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