# Synthesis of Fluoroalkoxy Substituted Polythiophene under Well-Controlled Electrosynthetic Conditions

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ABSTRACT: Poly[3-(2,2,3,3-tetrafluoropropoxy)thiophene] was prepared by electrochemical polymerization under various conditions. Analyses of conductivity, electrochemical and spectroscopic properties as functions of current density ($J$) in the electrosynthesis showed that mean conjugation of polymer chains was noticeably extended at low current density. The above properties of the polymer also varied with different solvents and working electrodes. The electrosynthetic conditions determine to a large extent the molecular structure and physicochemical properties of the resulting polymer.

KEY WORDS    Polythiophene / Fluoroalkoxy Substituted Polythiophene / Current Density / Mean Conjugation Length /
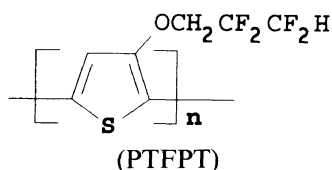
Achieving practical applications of conducting polythiophenes (PTs) in molecular electronic devices, solid-state batteries, chemically modified electrodes, and sensors requires solution to some serious problems such as inconvenient processability and environmentally instable conductivity.[1-4] Advances in film casting were made in the last few years through the manipulation of the monomer structure by covalent grafting of various side chains. Thus 3-substituted thiophenes with alkyl, alkoxy, alkylsulphonate, and polyether chains and their corresponding polymers have been described in recent literature aiming at improving the solution processibility.[5-8] More recently, polythiophenes 3-substituted by polyfluoroalkyl groups have also been reported with improved environmental stability.[9,10]

Furthermore, as a consequence of the diversity of the electropolymerization factors, which involves solvent, reagents, anode materials and applied electrical conditions, and complexity of the polymerization mechanism, electrosynthetic conditions affect to a large extent the structure and properties of the resulting polymers.[11,12] The optimization of

electrosynthetic conditions is generally known to be another strategy in the control of polymer properties.

PTs substituted by alkoxy groups have been investigated by several research groups because of their good solubility and low oxidation potential,[13,14] However, due to the negative electronic effects of alkoxy side chains attached to the thiophene ring, the conductivity and electrochemical stability of the resulting polymer are significantly lower than those of unsubstituted polythiophene. Hence, it is necessary to offset the electronic effect of oxygen atom linked to the thiophene nucleus in order to achieve both the polymerizability of the monomer and the electronic properties of the polymer obtained. It is anticipated that the introduction of fluorine atoms to the alkoxy chain on the 3-position of thiophene will lead to a new interesting material. In our previous communication,[15] we described a novel poly-(thiophene) containing polyfluoroalkoxy substituent, namely poly[3-(2,2,3,3-tetrafluoropropoxy)thiophene] (PTFPT), which incorporates the specifies of alkoxy and fluoroalkyl groups and possesses good stability and solu-

tion processability. We describe here the effects of the electrochemical factors of polymerization on the properties of PTFPT and optimization of preparation conditions.

$$\text{(PTFPT)}$$

with structure showing OCH$_2$CF$_2$CF$_2$H substituent on thiophene ring, S in ring, and n repeating unit.

## EXPERIMENTAL

### Materials

The solvents, nitrobenzene (PhNO$_2$), acetonitrile (CH$_3$CN), benzonitrile (PhCN), and nitromethane (CH$_3$NO$_2$) were purified according to the previously described procedures.[16] The electrolytes, tetrabutylammonium tetrafluoroborate (Bu$_4$NBF$_4$), tetrabutylammonium perchlorate (Bu$_4$NClO$_4$), and tetrabutylammonium trifluoromethanesulfonate (Bu$_4$-NCF$_3$SO$_3$) were prepared using the reaction of tetrabutylammonium hydroxide and corresponding acids. After synthesis, the products were recrystalized twice. Lithium Perchlorate (LiClO$_4$) and tetrabutyl ammonium hexafluorophosphate (Bu$_4$NPF$_6$) were used as received from Tokyo Kasai Chemical Industry Co., Ltd. All electrolytes were dried under vacuum before use.

### Monomer

3-(2,2,3,3-tetrafluoropropoxy)thiophene was prepared from 3-bromothiophene and sodium fluoro-propoxide in the presence of copper oxide and potassium iodide,[17] under the following conditions: 100 mmol 3-bromothiophene was added to a suspension of 150 mmol of sodium fluoro-propoxide, 4.0 g of copper oxide and 0.1 g of potassium iodide in 50 ml of toluene. The resulting mixture was then refluxed for 120 hours. After cooling the suspension was treated with 1 N HCl and ether. The organic phase was washed with water until neutral, dried and evaporated under vacuum. The crude products were purified by chromato-

graphy (SiO$_2$/petroleum benzine, ethyl acetate) and distillation. 3-(2,2,3,3-tetrafluoropropoxy)thiophene-yield: 35%. *Anal.* Calcd for: C, 39.25%; H, 2.80%; S, 14.05%; F, 35.51%. Found for: C, 39.26%; H, 2.84%; S, 14.94%; F, 35.85%. $^1$H NMR (200 MHz, CDCl$_3$, TMS, ppm): 4.30 (2H, t); 6.28 t, 6.02 t, 5.76 t, 1H, 6.34 (1H, dd, $J$ = 1.5, 2.0), 6.78 (1H, dd, $J$ = 1.5, 3.0), 7.20 (1H, dd, $J$ = 3.0, 5.0). $^{19}$F NMR (60 MHz, CDCl$_3$, CFCl$_3$, ppm): $-138$ (2F, d); $-124$ (2F, d). IR (cm$^{-1}$); 3100 w, 2900 m, 1500 s, 1100—1230 s, 950 s, 850 s. MS: $m/z$, 214; C$_5$H$_5$SO$^+$, 113; C$_4$H$_3$SO$^+$, 99; C$_4$H$_5$S$^+$, 85. UV-VIS: $\lambda_{max}$, 310 nm; log $\xi$, 2.57.

### Preparation of Polymer

The electrosynthesized polymer was prepared in a one-compartment cell containing 0.1 mol l$^{-1}$ monomer and 0.05 mol l$^{-1}$ Bu$_4$NPF$_6$ in various solvents. The solutions were degassed by argon bubbling prior to polymerization. Electropolymerization was performed at ambient temperature under argon atmosphere at constant current of 0.5—10 mA cm$^{-2}$. After polymerization, the film was rinsed with acetone or $n$-hexane, dried in a nitrogen flow and stored in the dark.

### Physical Measurement

Electrosynthesis and cyclic voltammetric (CV) experiments were conducted using an EG & G PAR (Model 273) potentiostat/galvanostat equipped with a PAR 270 universal programmer. UV-VIS spectroscopy was recorded with a Perkin-Elmer Lambda 5 spectrophotometer. FTIR spectroscopy was performed on a Perkin Elemer 983 spectrophotometer. Conductivities were determined by the standard four-probe technique.

The polymers for CV experiment were grown on platinum electrodes (surface area = 0.1 cm$^2$) using a deposition charge of 100 mC cm$^{-2}$. CV experiments were performed in a three-electrode cell containing 0.1 mol l$^{-1}$ LiClO$_4$ in dry CH$_3$CN. All potentials refer to a saturated calomel electrode (SCE). Films for conductivity measurement have been prepared on

platinum flag electrodes (surface area = 2—3 cm$^2$) using deposition charge of $7.2\,C\,cm^{-2}$. A platinum foil was used as cathode. All platinum electrodes were cleaned in a $H_2O_2$–$H_2SO_4$ (1:4, v/v) solution and treated with an oxidizing flame before use. The polymers for UV-VIS spectroscopy were prepared under the above conditions on platinum flag electrodes, rinsed with acetone, electrochemically undoped by reversing the direction of the current flow (0.01 mA cm$^{-2}$) until the potential of the working electrode was constant at about 1.1 V *vs*. SCE, indicating the polymer was no longer being reduced and then dried under nitrogen flow and dissolved in *N,N*-dimethylformamide (DMF).

## RESULTS AND DISCUSSION

### Effect of Electrosynthetic Current Density on the Properties of the Polymer

Previous studies on electrosynthesized PTs show that the current density ($J$) in polymerization exerts a strong effect on the properties of the polymers such as $E_{pa}$ (anodic peak potential for the oxidation reaction), absorption maximum value ($\lambda_{max}$) and conductivity.[18] But the relationships between electrosynthetic conditions and structure and properties of the polymer have been scarely considered.[19] The properties of the polymer PTFPT film prepared at various current densities have been examined at various current densities to get more detailed information on structure-property relations. Figure 1 shows the dependence of the conductivity on the current density ($J$). The highest conductivity (about 0.1 s cm$^{-1}$) was reached by using 0.5 mA cm$^{-2}$. Below 0.5 mA cm$^{-2}$, there were no polymers growing onto the electrodes. This suggests that the corresponding radicals of monomers generated on Pt surface can diffuse away from the electrode to form soluble oligmers in solution when the applied current density is quite low. It was also observed that higher current density led to more brittle film with lower conductivity. Beyond the optimal
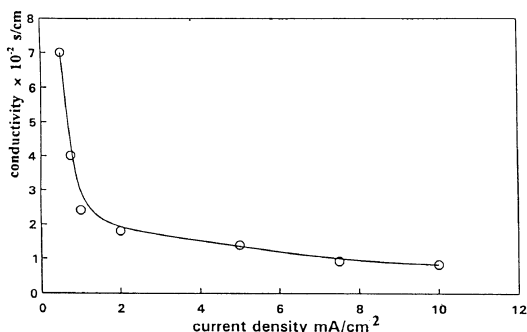


**Figure 1.** Dependence of conductivity on current density (deposition charge, $7.2\,C\,cm^{-2}$).

current density, linkage defects in the polymer chains greatly increased and could generate distortions in other chains.[20] Moreover, the early formed polymers on the electrode could be degraded at overhigh current density. The correlation between the current density and the conductivity of PTFPT films implies that an regular structure leading to highly conjugated planar conformation of the polymer chains is a critical factor for increased of conductivity observed in polymer films. Another possible cause for high conductivities may be modification of the intramolecular structure along polymer chains and particularly, longer mean conjugation in the polymer films at low current density of polymerization.

Table I shows the electrochemical properties of PTFPT films synthesized under various current densities. The data in Table I indicate that lowering the current density leads to less positive $E_{pa}$. Such a conclusion is consistent with previous observations reported for poly(3-methylthiophene).[21] Many authors show that the oxidation potential, the position of the absorption maximum ($\lambda_{max}$) and the electric conductivity are closely related to the extent of conjugation.[22] In Table I, the shift of $E_{pa}$ toward less positive values when reducing the current density appears corresponding to moving toward longer mean conjugations. Figure 2 depicts the FTIR spectrum of polymer PTFPT electrosynthesized under various current densities. The polymer synthesized under

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**Table I.** Electrochemical properties of PTFPT films synthesized in nitrobenzene at various current densities[a]

| Current density[b] mA cm$^{-2}$ | $E_{cell}$[c] (V *vs.* SCE) | $E_{pa}$ (V *vs.* SCE) | $E_{pc}$[d] (V *vs.* SCE) |
|---|---|---|---|
| 0.5 | 2.65 | 1.05 | 0.94 |
| 1.0 | 2.79 | 1.07 | 0.92 |
| 2.0 | 3.14 | 1.12 | 0.88 |
| 5.0 | 4.07 | 1.15 | 0.84 |
| 10.0 | 4.58 | 1.20 | 0.82 |

[a] Synthesized polymers using 0.1 mol l$^{-1}$ monomer and 0.05 mol l$^{-1}$ Bu$_4$NPF$_6$. [b] Cyclic voltammogram of PTFPT (deposition charge, 100 mC cm$^{-2}$ on 0.1 cm$^2$ Pt; electrolytic medium, 0.1 mol l$^{-1}$ LiClO$_4$/CH$_3$CN; scanning rate, 20 mV s$^{-1}$. [c] Cell potential measured by chronoamperometry. [d] Cathodic current peak.
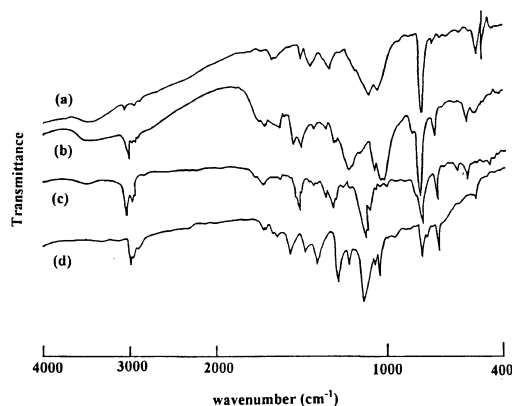


**Figure 2.** FTIR spectra of neutral PTFPT synthesized at various current densities (*J*). a, *J* = 0.5 mA cm$^{-2}$; b, *J* = 2.0 mA cm$^{-2}$; c, *J* = 5.0 mA cm$^{-2}$; d, *J* = 10.0 mA cm$^{-2}$.

0.5 mA cm$^{-2}$ [curve (a)] had one band at 3060 cm$^{-1}$ attributable to the $\beta$(4)-C–H bond in the region of the aromatic C–H stretching vibration and no band attributable to $\alpha$(2 or 5)-C–H bond at 3110 cm$^{-1}$. The spectrum also showed a band at 840 cm$^{-1}$ assigned to the C–H deformation vibration of a 2,3,5-trisubstituted thiophene ring. There did not appear to be any significant $\alpha$(2 or 5)-C–H out-of-plane bending absorptions in the spectrum. These results demonstrated that the polymer chain had a highly defined $\alpha$–$\alpha'$ structure. The average conjugation length along the polymer

chains was mainly determined by the regioregularity of the polymer, *i.e.* the ratio of $\alpha$–$\alpha'$/$\alpha$–$\beta$ linkages of thiophene units. It is well known that the reactivity of the $\alpha$ position in the thiophene monomer is much higher than that of the $\beta$ position. The overhigh current density, which decreases the difference of the reactivity between the $\alpha$ and $\beta$ positions, leads to a statistical increase of the number of $\alpha$–$\beta$ couplings and hence to a decrease of the regioregularity in the polymer. In curves (b), (c), and (d), when the current density used for synthesizing PFTPT was turned up, a band at 720 cm$^{-1}$ assigned to the $\alpha$-C–H out-of-plane bending absorptions appeared and grew stronger. In the meantime, the band at 840 cm$^{-1}$ grew weeker. All these data indicate that there were a few $\beta$–$\beta'$ or $\alpha$–$\beta$ defects in the polymer chain when the polymer was grown at relatively high current density. It is indicated that the presence of a larger number of the defects when applied overhigh current density could generate distortions both intramolecularly and intermolecularly.

The absorption spectra of the undoped PTFPT in *N,N*-dimethylformamide (DMF) as a function current density are given in Figure 3. These spectra and Table II show that the $\lambda_{max}$ shifted bathochromically from 367 nm to 529 nm when the current density decreases from 10 to 0.5 mA cm$^{-2}$. Such a displacement of the $\lambda_{max}$ indicates that the average length of conjugation on which the electron delocalization occurs is considerably extended in films at low current density. Furthermore, the color of the polymer in DMF changes from pale yellow to amethyst violet (Table II) when the current density is decreased. This indicates that various lengths of conjugated segments exist at different current densities.

*Effects of Solvents on the Properties of the Polymer*

The solvent of the electrolytic medium exerts a strong effect on the structure and properties of PTs films. The solvent must simultane-
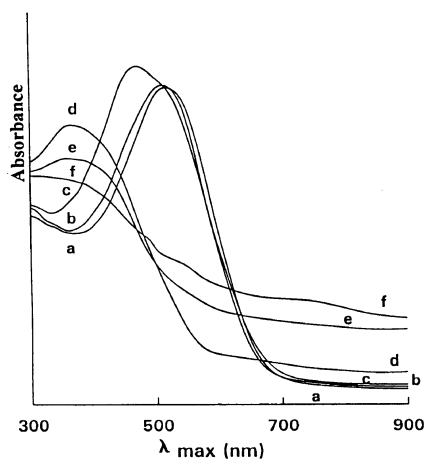
**Figure 3.** Effects of current density ($J$) on the UV-VIS spectra of undoped PTFPT in DMF under various current densities. a, $J=0.5\,\mathrm{mA\,cm^{-2}}$; b, $J=1.0\,\mathrm{mA\,cm^{-2}}$; c, $J=2.0\,\mathrm{mA\,cm^{-2}}$; d, $J=5.0\,\mathrm{mA\,cm^{-2}}$; e, $J=7.5\,\mathrm{mA\,cm^{-2}}$; f, $J=10.0\,\mathrm{mA\,cm^{-2}}$.

**Table II.** UV-VIS spectroscopic data of PTFPT in DMF synthesized in nitrobenzene under various current densities[a]

| Current density[b] | $\lambda_{max}$[c] | Color |
|---|---|---|
| mA cm$^{-2}$ | nm | (Neutral state) |
| 0.5 | 529 | Amethyst violet |
| 1.0 | 509 | Amethyst violet |
| 2.0 | 484 | Brick red |
| 5.0 | 378 | Mineral yellow |
| 7.5 | 369 | Pale yellow |
| 10.0 | 367 | Pale yellow |

[a] Electrochemical undoped by reversing the direction of current flow (0.01 mA cm$^{-2}$). [b] Deposition charge 7.2 C cm$^{-2}$ on 3 cm$^2$ Pt. [c] Polymers dissolved in DMF.

ously possesses a high dielectric constant to ensure the ionic conductivity of the electrolytic medium and an adequate stability to allow the electropolymerization of the monomer.[23] Some rigorously anhydrous solvents of high dielectric constant and low nucleophilicity such as acetonitrile, benzonitrile, nitrobenzene, nitromethane, and propylene carbonate, which offer highest current efficiency, are usually used in electropolymerization of thiophene monomer and derivatives. Table III lists elec-

**Table III.** Properties of PTFPT synthesized in various solvents

| Solvent | $E_{pa}$[a] (V vs. SCE) | $E_{pc}$ (V vs. SCE) | $\lambda_{max}$[b] nm | Conductivity s cm$^{-1}$ |
|---|---|---|---|---|
| PhNO$_2$ | 1.05 | 0.94 | 528 | $7.0 \times 10^{-2}$ |
| CH$_3$CN | 1.08 | 0.94 | 430 | $6.0 \times 10^{-4}$ |
| PhCN | 1.10 | 0.94 | 420 | —[d] |
| CH$_3$NO$_2$ | 1.14 | 0.92 | 398 | —[d] |
| PhNO$_2$ | 0.61 | 0.51 | 525 | $9.0 \times 10^{-4}$ |

[a] Cyclic voltammogram of PTFPT (deposition charge, 100 mC cm$^{-2}$ on 0.1 cm$^2$ Pt; electrolytic medium, 0.1 mol l$^{-1}$ LiClO$_4$/CH$_3$CN; scanning rate, 20 mVs$^{-1}$). [b] Polymer disolved in DMF. [c] Poly(3-propoxy)thiophene. [d] Film too brittle to be measured.

trochemical properties and UV-VIS spectroscopic data of PTFPT synthesized in various solutions. Nitrobenzene allowed the obtainment of compact and flexible films, with conductivity of about 0.1 s cm$^{-1}$. Acetonitrile led to powdery deposits with poor conductivity ($6 \times 10^{-4}$ s cm$^{-1}$). Nitromethane and benzonitrile afforded slack deposits. The conductivities of these deposits could not be measured by the four-probe method.

## Effects of Working Electrodes on the Properties of the Polymer

The physicochemical properties of the surface of the working electrode determine the nature and strength of the bond between the polymer and electrode, which can affect both the polymerization process and the properties of the resulting polymer. Platinum, on which PTs are effectively electrosynthesized, is studied in the literatures.[24] However, PTs have been also deposited on other surfaces such as titanium or iron. Glass carbon, usually used to synthesize some organic compounds not applied to synthesize PTs before. Another electrode, nickel is always used to synthesize fluoro-compounds. In the present study, we investigated the influence of the anodes on the structures of the polymers. Figure 4 compares the CV of PTFPT films synthesized on Pt and glass carbon in acetonitrile. These curves and
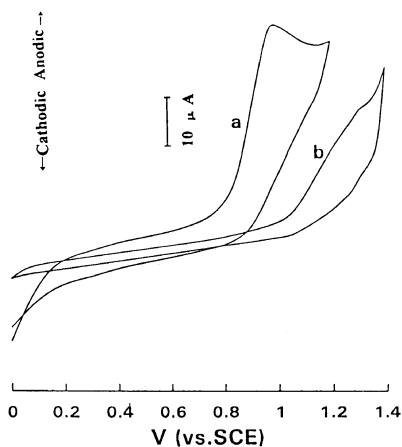
**Figure 4.** Cyclic voltammogram of PTFPT in $0.1 \, mol \, l^{-1}$ $LiClO_4/CH_3CN$ (deposition charge $100 \, mC \, cm^{-2}$; scan rate $20 \, mC \, cm^{-2}$). a, on platinum; b, on glass carbon.

**Table IV.** Properties of PTFPT synthesized in nitrobenzene with various working electrodes

| Working electrode | $E_{pa}^{a}$ (V vs. SCE) | $E_{pc}$ (V vs. SCE) | $\lambda_{max}^{b}$ nm | Conductivity $s \, cm^{-1}$ |
|---|---|---|---|---|
| Pt | 1.08 | 0.94 | 528 | $7.0 \times 10^{-2}$ |
| Glass carbon | 1.30 | 1.11 | —[c] | —[c] |
| Ni | —[d] | —[d] | 472 | $3.0 \times 10^{-4}$ |

[a] Synthesized polymer in $CH_3CN$ (deposition charge, $100 \, mC \, cm^{-2}$). [b] Synthesized polymer in $PhNO_2$ and then dissolved in DMF. [c] Film is too brittle. [d] Surface of Ni is complicated.

the data in Table IV show that Pt electrode yielded a sharpening of anodic wave, together with a 220 mV of shift the anodic current peak ($E_{pa}$) toward less positive potentials. It has been shown that the electropolymerization of thiophene is initiated by the adsorption of monomer onto the electrode surface.[25] The initial step in the electropolymerization consists of the formation of a monolayer of polymer growing two-dimensionally, parallel to the electrode surface. Thus, the differences found between glass carbon and platium anodes may reflect that thiophene adsorbed more strongly on Pt than on glass carbon because Platinum has a larger number of potentially active sites.[22]

The properties of the surfaces of the electrodes exerted different influence on the polymerization process. Platinum allowed instantaneous creation of initial nucleation sites, which contributed to the compactness and thus conductivity of the polymer. The formation of nucleation sites in the early steps of electropolymerization on the surface of the electrode has dramatic consequences for the overall stereoregularity and stacking order of the polymer chains. Platinum, which favors chain-growth process of electropolymerization, allowed more ordered and longer conjugated polymer chains. Compared with the polymer synthesized on the glass carbon, the polymer synthesized on the platinum decreased the oxidation potential of the polymer and a bathochromic shift of the $\lambda_{max}$ and increased conductivity. This appears consistent with the results of previous works on ITO surface.[22,26] The initial potential is the determining factor controlling the density of initial nucleation sites and hence the cohesion and the conductivity of resulting films. We also obtained a PTFPT film on nickel. But we could not get the electrochemical data because of the complicated surface of nickel electrode.

### Effects of Dopants on the Conductivity of the Polymer

The nature of the dopant strongly affects the morphology and conductivity of PTs. Highly conducting PTs are generally electrosynthesized using small anions from strong acids such as $ClO_4^-$, $PF_6^-$, $BF_4^-$, and $CF_3SO_3^-$. We compared the effects of these four anions on the properties of polymer PTFPT here. Table V shows the conductivities of PTFPT with various dopants. The polymers were synthesized under the optimal electrosynthetic current density ($J = 0.5 \, mA \, cm^{-2}$) in $PhNO_2$ on Pt. We found that free-standing films could be only obtained using $Bu_4NBF_4$ and $Bu_4NPF_6$. Slack and brittle films were deposited on the electrode using $Bu_4NClO_4$ and $Bu_4NCF_3SO_3$. From data in Table V $Bu_4NBF_4$ and $Bu_4NPF_6$ lead

**Table V.** Conductivity of PTFPT with various dopants[a]

| Dopant | Conductivity s cm$^{-1}$ |
|---|---|
| Bu$_4$NPF$_6$ | 0.1 |
| Bu$_4$NBF$_4$ | $7.0 \times 10^{-2}$ |
| Bu$_4$NClO$_4$ | $2.0 \times 10^{-4}$ |
| CF$_3$SO$_3$Bu$_4$N | $9.0 \times 10^{-4}$ |

[a] Synthesized polymer in PhNO$_2$ (deposited charge, 7.2 C cm$^{-2}$).

to higher conductivity of PTFPT effectively. The mechanism for the effects of anions on the properties of PTs has not been clearly elucidated due to the unknown effects of original counterions on structures of the polymers. The conducitivity of PTFPT was twice that of poly[3-(propoxy)thiophene].

## CONCLUSION

Correlations between properties of poly[3-(2,2,3,3-tetrafluoropropoxy)thiophene] and factors of electrochemical polymerization have been shown. Under well-controlled preparation conditions, the conductivity of polymer film can reach values close to 0.1 s cm$^{-1}$, which is one order of magnitude greater than that of poly(3-alkoxythiophene).

Analyses of conductivity, electrochemical and spectroscopic properties of the polymer as functions of electrosynthetic current density showed that the mean conjugation length in the polymer chains was more extended at lower current density. Both solvents and working electrodes also exert noticeably strong effects on the properties of the polymer electrochemically prepared.

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