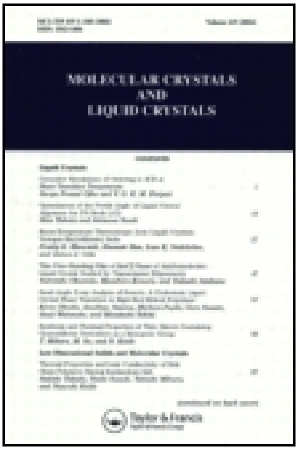

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# The Preparation and Characterization of Ester Functionalized Poly(3-Alkylthiophene)S

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# THE PREPARATION AND CHARACTERIZATION OF ESTER FUNCTIONALIZED POLY(3-ALKYLTHIOPHENE)S

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**Abstract** Soluble ester group substituted polythiophenes and copolymers of substituted polythiophenes with 3-octylthiophene were prepared. The decreased conductivities and blue shifts were observed for the substituted polythiophenes. These results indicate the shortening of conjugating length due to the steric repulsion of the ester substituent.

## INTRODUCTION

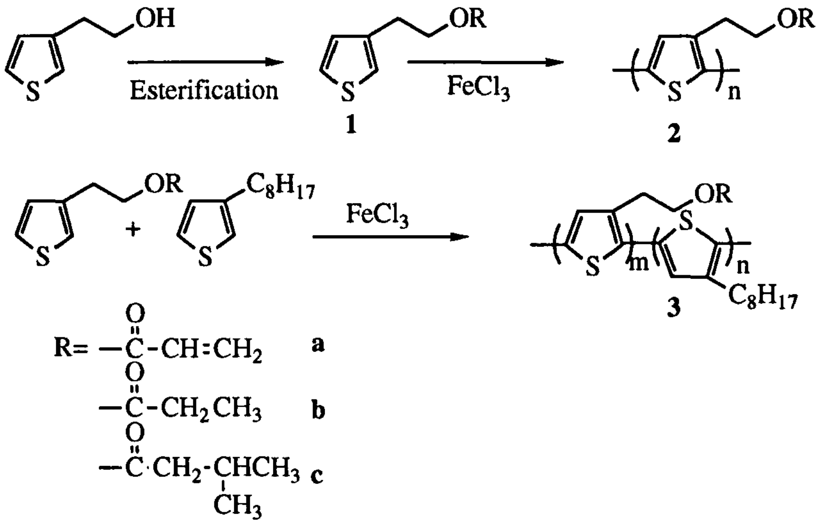
Processability is one of the requirements of the conducting polymers for practical applications. Introducing long and flexible alkyl side chains at the 3-position of thiophene enables the poly(3-alkylthiophene)s (PATs) soluble and fusible in their dedoped (neutral) state.[1] The alkyl substitution also induces properties of thermochromism[2] and solvatochromism[3] which are not observed from the unsubstituted polythiophenes.

Applications of soluble PATs were proposed *i.e.*, batteries, field-effect transistors, light-emitting diodes, Schottky barrier diodes, and etc.[4-6] Most of the applications listed above requires a good thermal stability, good metal-polymer adhesion, well defined semiconductor characteristics and etc. To meet these requirements it is important to understand the structure-property relationships of PATs.

Much works have been devoted on the synthesis of PATs with different substituents and the examination of substituents effects.[7-15] The introduction of sulfonate[13] and amino acid group[14] to the alkyl side chain allowed the polymer soluble in water and DMSO. Bathochromic shifts were observed for the electron-donating alkoxy-substituted polythiophenes.[7]

Recently, Andreani *et al.* has reported synthesis of a soluble ester substituted polythiophene.[15] But the effects of the ester substituent were not reported. It is

Scheme I



expected that the ester substitution imparts polar characters to PATs and disturb the side chain ordering of PATs.

This paper describes synthesis of soluble ester substituted PATs and the effects of substituents on the properties of PATs.

## EXPERIMENTAL SECTIONS

### MATERIALS AND SYNTHESES

The acrylated thiophene **1a** was prepared by the reaction of acryloyl chlorides and 3-thienyl-2-ethanol in the presence of triethylamine at 0 °C. Propanoated **1b** and isovalerated thiophene **1c** were prepared by the esterification of the corresponding acid and 3-thienyl-2-ethanol. Products were purified by vacuum distillation.

Nickel catalyzed coupling reaction of 3-bromothiophene and octylmagnesium bromide was used to synthesize 3-octylthiophene.

The literature procedure was followed for the synthesis of poly(3-octylthiophene) (POT).[1] To a stirred suspension of anhydrous FeCl$_3$ in chloroform was added dropwise a solution of 3-octylthiophene in chloroform at room temperature. The resulting dark brown solution was stirred for 2 days and poured into methanol to precipitate POT. The purified and dedoped POT obtained by Soxhlet extraction with methanol was red brown solid which is stable in air. Polymerization of **1**'s and copolymerization of **1**'s with 3-octylthiophene were performed as above except that acetonitrile was used instead of chloroform.

## CHARACTERIZATION AND MEASUREMENTS OF PHYSICAL PROPERTIES

NMR spectra were recorded on a Bruker AM 300 FT Nuclear Magnetic Resonance Spectrometer. Infrared spectra were recorded on a DigiLab FTS-20/80 Spectrophotometer. A Waters Model R401 Gel Permeation Chromatography (GPC) was used to determined the molecular weight distribution relative to the polystyrene standard. UV-vis spectra were recorded on a Guided Wave Model 260 Spectrophotometer.

Films of PATs were prepared by casting the solution and drying under dynamic vacuum. The films were subjected to the measurements of static water contact angle (RAN-HART Model 100) and X-ray diffraction (Rigaku D/MAX IIIB). Four probe conductivity measurements were conducted for the doped films which were prepared by dipping the films into a 0.1M solution of $FeCl_3$ in acetonitrile for 5 min, rinsing with acetonitrile and drying under the reduced pressure.

## RESULTS AND DISCUSSIONS

The chemical oxidative polymerization of 3-alkylthiophenes was well established to give soluble PATs. However, ester substituted poly(thiophene)s **2**'s prepared under the same conditions were only partially soluble in chloroform and THF. Further extensive methanol extraction and stirring with aqueous hydrazine did not improve the solubility of the insoluble parts of the polymer **2**'s.

Switching the solvent from chloroform to acetonitrile improved the yields of soluble **2**'s, where the products were readily dissolved into chloroform and THF after dedoping and the reaction was completed in a shorter period of time (5 hrs instead of 48). From the analysis of $^1H$ NMR spectrum of **2b** it was observed that the ratio of head to tail and head to head configurations of **2b** were changed from 4:1 to 1.2:1 when solvent was changed from chloroform to acetonitrile. Thus, polymerization in acetonitrile produced **2b** with less stereoregularity. The enhanced polymerization rate of **1b** in the more polar medium may cause the reduced stereoregularity of **2b**.

Copolymerization of **1**'s with 3-octylthiophene was performed to give **3**'s which were soluble in chloroform and THF. When the feed ratio of **1**'s and 3-octylthiophene in acetonitrile was 1:1, approximately the same amounts of monomer units exist in the copolymer.

It is not clear at present why solubility of **2**'s are poor when chloroform is used as polymerization solvent while **2**'s prepared in acetonitrile are soluble in chloroform and THF. There exist possibilities of partial cross linking, and/or partial hydrolysis of ester groups, which reduce the solubility of polymers. Since this behavior was only observed with ester group substituents, the ester functional group is believed to exercise some effects on the polymerization process of **1**'s in chloroform medium.

FT-IR spectra of **2a** and **3a** are shown in Figure 1. The peaks at 1724 $cm^{-1}$ and 1627 $cm^{-1}$ are assigned to the stretching of the unsaturated carbonyl ester and stretching of the unsaturated double bond, respectively. Thus, the double bonds in **2a** and **3a** were intact during the oxidative polymerization. More evidences can be seen from $^1H$ NMR spectrum of copolymer **3a** (Figure 2). The peaks around 6.0 ppm are typical splitting patterns from the protons attached at the acrylic double bond.

To the best of our knowledge, this is the first example of soluble PATs with a pendant double bond in the side chain. The double bond in the side chain of **2a** and **3a**

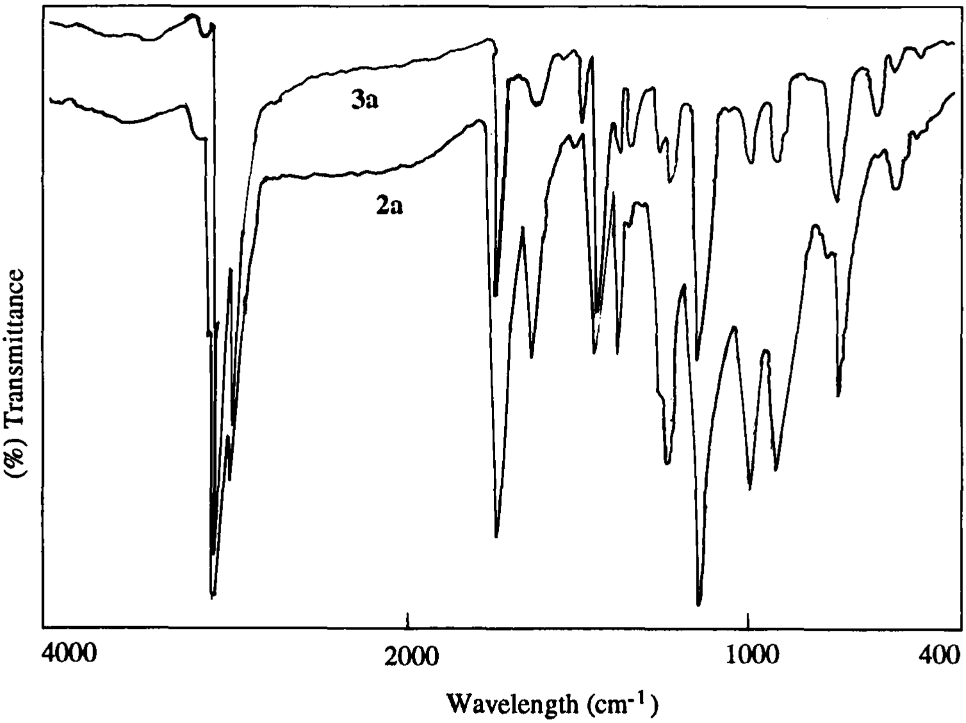


Figure 1. FT-IR spectra of **3a** and **2a**

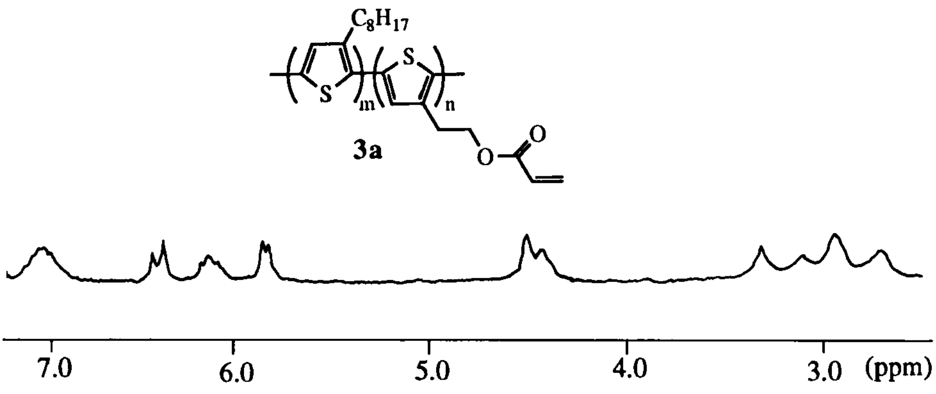


Figure 2. $^1$H NMR spectrum of **3a** (To clarify, part of the spectrum was shown.)

can serve as the reactive site for further functionalization. The cross linking of double bonds in **2a** by electron beam irradiation[16] may be utilized for lithography.

Table 1 lists yields and GPC results of the prepared PATs.[17] The average molecular weights relative to the polystyrene standard are between 4.2 x $10^4$ and 7.8 x $10^4$. The molecular weights and related parameters are comparable to the reported values of PATs.[8]

It is expected that the polymer **2**'s should be more polar than POT due to the introduction of ester functional group at the side chain. To examine the substituent effect the solubility of **2b** and POT in hexane and ethyl acetate were examined. POT was slightly soluble in hexane whereas **2b** was insoluble in hexane. In ethyl acetate the solubility of **2b** is higher than that of POT. The results of the water contact angle measurements of the cast films indicated that the film surface of **2b** is more hydrophilic than that of POT, **3a** and **3b** due to the presence of the ester substituent in the side chain.[17] The contact angles of **3a** and **3b** are the same as that of POT within

TABLE 1. Yields and molecular weights of the prepared poly(thiophene)s[17]

| | 2b | 2c | 3a | 3b | 3c |
|---|---|---|---|---|---|
| Yield (%) | 45 | 45 | 50 | 50 | 50 |
| $\overline{Mw}$ | 7.8 x $10^4$ | 7.1 x $10^4$ | 5.5 x $10^4$ | 5.4 x $10^4$ | 4.2 x $10^4$ |
| $\overline{Mn}$ | 1.3 x $10^4$ | 3.9 x $10^4$ | 2.0 x $10^4$ | 1.9 x $10^4$ | 2.1 x $10^4$ |
| $\overline{Mw/Mn}$ | 5.9 | 1.7 | 2.7 | 2.7 | 2.9 |

TABLE 2. Contact angle measurements of PATs[17]

| | POT | **2b** | **3a** | **3b** |
|---|---|---|---|---|
| Angle (degree) | 100 | 72 | 102 | 97 |

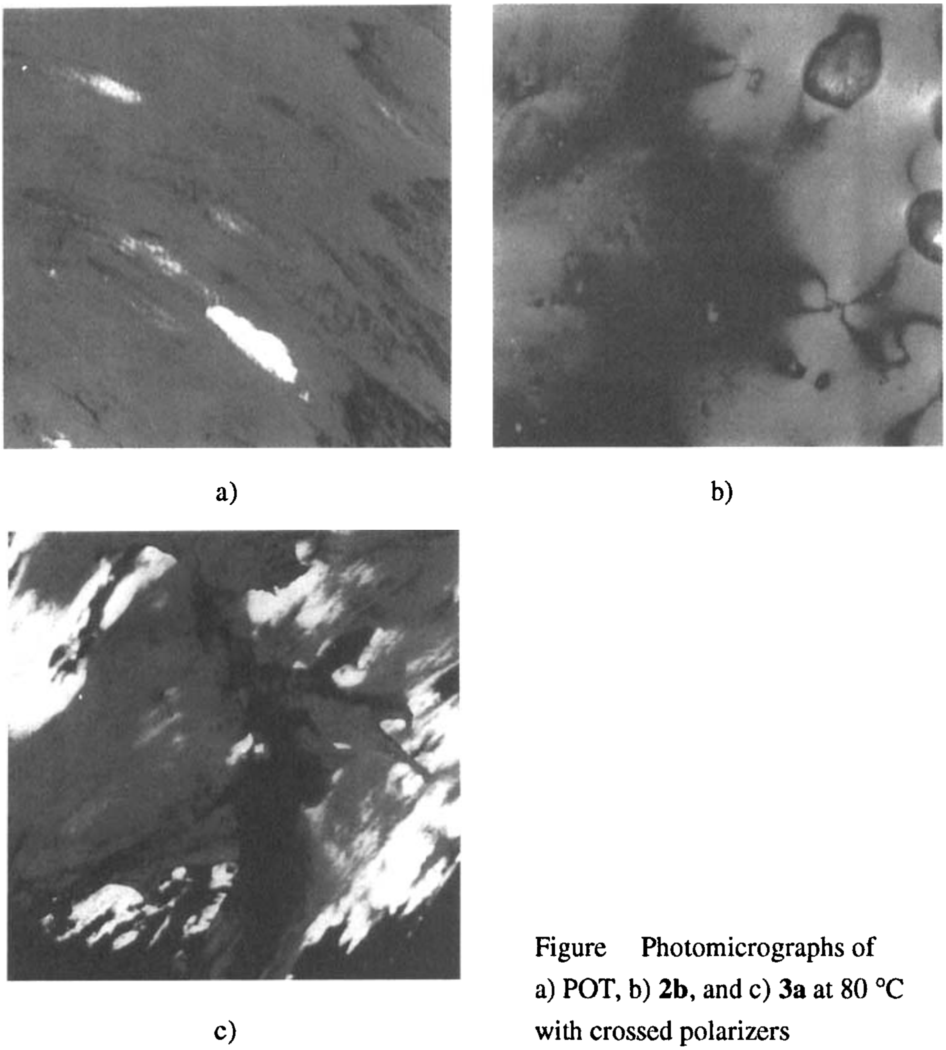
the experimental error. The polar ester group in the side chain is probably buried under the hydrophobic alkyl side chain. Thus, the surface of film POT, **3a** and **3b** has similar water wettability.

X-ray diffraction studies were performed on the cast films of **2b** and **3a**.[17] A small but sharp peak at 4.2° and broad peaks at 8° and 11° were observed for **3a**. In case of **2b** a broad maximum peak at 12° and a very small peak at 5.6° can be seen. The results indicate that the introduction of ester group in the side chain perturbs the interplanar and intraplanar packing which causes the decrease of crystallinity of PATs. Optical microscopic examination with crossed polarizers showed that **2b**, **3a** and POT have crystalline domains in the polymer matrices (Figure 3). Under the microscopic examination at 80 °C, the more fluid like (less viscous) behavior was observed for **2b** when compared with POT probably due to the reduced interchain interaction in **2b**.

UV-vis spectra were recorded for the PATs in THF. The absorption maxima and conductivities are shown in Table 3. POT and copolymer **3a**, **3b** and **3c** have all similar $\lambda_{max}$ at about 432 nm, and **2b** and **2c** have $\lambda_{max}$ at 412 and 402 nm respectively.[17] Conductivity measurements also show the same trend. The shift to the shorter wavelength and the decrease of conductivity are related to the shorter conjugating lengths of polythiophene chain. The ester substituents in the side chain of PATs may introduce more steric hindrance between the neighboring thiophene rings which leads to a shorter conjugation length and higher band gap.

## SUMMARY

Synthesis of soluble PATs with the ester group in the side chain was realized. Incorporation of the double bond via acrylated thiophene into the side chain was also achieved. The results from X-ray diffraction, UV-vis spectra and conductivity measurements indicate that the ester substitution in the side chain of PATs introduces steric repulsion between neighboring thiophene rings. This leads to the conformational rotation of main chain and increase of interchain distance which result in a higher band gap and lower conductivity.



a)

b)

c)

Figure Photomicrographs of a) POT, b) **2b**, and c) **3a** at 80 °C with crossed polarizers

TABLE 3. UV-Vis absorption maxima and conductivities of PATs[17]

| | POT | 2b | 2c | 3a | 3b | 3c |
|---|---|---|---|---|---|---|
| λmax (nm)[a] | 434 | 412 | 402 | 432 | 428 | 430 |
| Conductivity[b] (S/cm) | 5.1 | $1.8 \times 10^{-3}$ | $0.7 \times 10^{-3}$ | 3.2 | 0.14 | $5.0 \times 10^{-3}$ |

a) THF solution, b) after doping by $FeCl_3$

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