

First approach to ester-functionalized poly(3-alkylthiophene)s

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Summary

The monomer 2-(3-thienyl)ethylene hexanoate can be chemically polymerized and copolymerized with an equimolar amount of 2-(3-thienyl)ethanol to afford the two first examples of soluble ester-functionalized poly(3-alkylthiophene)s. The undoped polymers are readily processable into uniform films by solution-casting.

Introduction

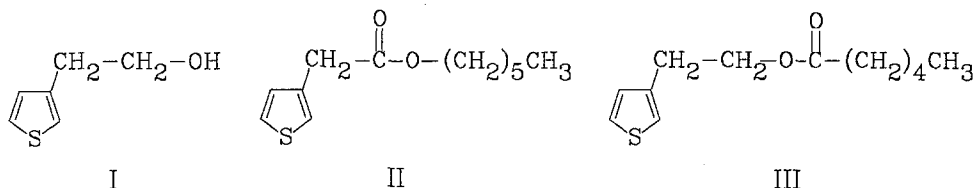
The incorporation of relatively long and flexible side chains is a common technique for preparing conducting polymers that are either melt or solution processable while maintaining their electrical properties (1-6). This paper reports the first results on the chemical synthesis and characterization of two soluble 3-alkylester-substituted polythiophenes. The work constitutes part of a study carried out to obtain a better understanding of the influence of new side chains on the physical properties of substituted polythiophenes.

Materials and measurements

The microanalyses were carried out by Redox Laboratories (Cologno M., Milano); the Fe content was determined by atomic absorption technique. IR spectra of solution-cast films were recorded using a Perkin Elmer 1750 FTIR spectrophotometer. ¹H- and ¹³C-NMR spectra were run on a Varian Gemini 200 FT-NMR spectrometer in CDCl₃ with TMS as the internal standard. The common two-probe technique was used to measure the room temperature dc conductivities of undoped polymer films and of powder pellets of doped polymers, pressed at 976 MPa.

Monomers and polymers

Our approach to the synthesis of monomeric 3-alkylester substituted polythiophenes was based on commercially available 3-thienylacetic acid and 2-(3-thienyl)ethanol (I). A convenient one-pot transformation of the carboxylic group (7), led to the formation of



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n-hexyl-3-thienyl acetate (**II**) and 2-(3-thienyl)ethylene hexanoate (**III**). These monomers were polymerized by chemical oxidation in anhydrous nitromethane under argon using anhydrous iron(III) chloride following a procedure similar to that of Sugimoto (8). However an oligomeric mixture was produced from monomer **II**, as shown by the low viscosity of the dedoped reaction mixture. Efforts to obtain a clean separation of definite oligomeric structures by column chromatography were unsuccessful. On the contrary, chemical oxidation of monomer **III** alone and of a 1:1 mixture of monomers **I** and **III** afforded doped polymers **IV** and **V**, respectively. They were dedoped by chloroform extraction after treatment with aqueous HCl, and then doped again with FeCl₃. This two-step process enabled uniform doping to be achieved via the solution-doping technique. A detailed account of the polymerization as well as the dedoping and doping procedures will be published elsewhere.

Synthesis of 2-(3-thienyl)ethylene hexanoate (III)

N,N'-carbonyldiimidazole (3.25 g, 20 mmol) was added at room temperature to a solution of hexanoic acid (2.32 g, 20 mmol) in CHCl₃ (20 ml) under stirring. After the vigorous reaction had subsided, the mixture was refluxed for 0.5 h, then 2-(3-thienyl)ethanol (**I**) (2.56 g, 20 mmol) and 1,8-diazabicyclo[5.4.0]-7-undecene (3 g, 20 mmol) were added and the mixture was stirred under reflux for 6 h. The solvent was removed at reduced pressure and the residue was dissolved in ether (200 ml). The solution was washed with 5% HCl (3 x 100 ml), 5% NaHCO₃ (3 x 100 ml) and water, then dried (Na₂SO₄) and concentrated under reduced pressure. The crude oily residue (4.4 g, 97%) was distilled in vacuo through a Vigreux column; yield: 3.6 g, 80%; b.p. 88-91°C/13-20 Pa.

ANAL Calcd for C₁₂H₁₈O₂S: C, 63.68; H, 8.02; O, 14.14; S, 14.17. Found: C, 63.6; H, 8.1; O, 14.0; S, 14.1.

¹H-NMR (CDCl₃): δ 7.27 (dd, 1H); 7.04 (d, 1H); 6.98 (dd, 1H); 4.29 (t, 2H); 2.97 (t, 2H); 2.3 (t, 2H); 1.7-1.52 (m, 2H); 1.4-1.2 (m, 4H); 0.9 (t, 3H).

FTIR (neat, on KBr discs): 3103, 2957, 2931, 2872, 2861, 1735, 1247, 1172, 1099, 1012, 861, 835, 775 cm⁻¹.

Characterization

The empirical formulae of the poly(alkylester thienylene)s as calculated from the elemental analyses are given in Table 1. The amount of residual iron is negligible as expected for dedoped polymers while the chlorine content is surprisingly high.

Thus some chlorination reaction is likely to have taken place. Losses of carbon, hydrogen and oxygen also suggest a partial cleavage of the ester function or, in the case of copolymer **V**, a preferential incorporation of monomer **I** relative to monomer **III**. This situation is apparently unaltered by the successive doping reaction, apart from the addition of the dopant species, as deduced from the elemental analyses of doped polymers not reported here. FTIR spectra of undoped polymers are reported in Figure 1.

Table 1. Theoretical and empirical formulae for undoped polymers.

Polymer	Theoretical ^a	Empirical ^b
IV	C ₁₂ H ₁₆ O ₂ S	C _{10.83} H _{14.01} O _{1.73} S ₁ Cl _{0.21} Fe _{0.003}
V	C ₁₈ H ₂₂ O ₃ S ₂	C _{16.90} H _{19.82} O _{1.96} S ₂ Cl _{0.84} Fe _{0.003}

^a Calculated for an infinite-length chain and in the case of polymer **V** with a 1:1 feed molar ratio of the two monomers. ^b Calculated from the experimental microanalysis data and given as atom mole ratios, normalized to sulfur.

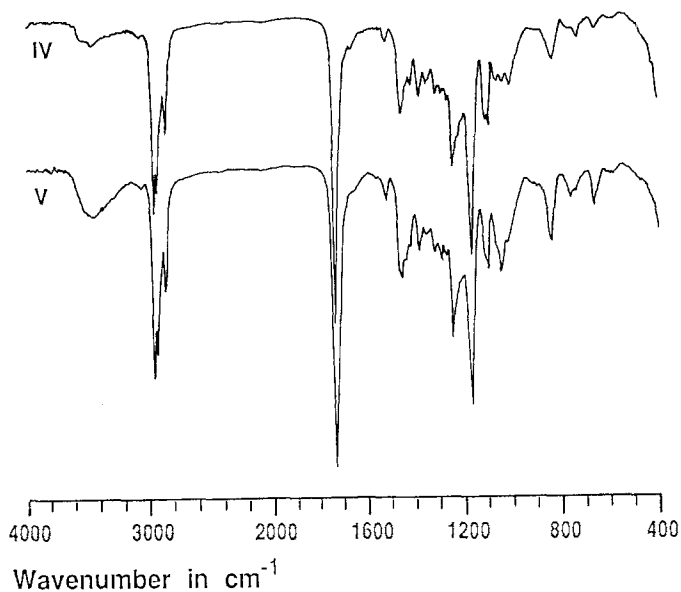


Figure 1. FTIR spectra of polymers **IV** and **V**.

The sharp and strong absorption band at about 830 cm^{-1} (C-H out-of-plane vibration), characteristic of 2,3,5-trisubstituted thiophenes, is in agreement with α - α coupled monomers and therefore indicates a linear polymer chain structure (9). Other characteristic bands confirm the structure of the side chains on the polymer backbones. A moderate O-H stretching absorption band is also observed in the spectrum of polymer **IV** thus indicating some ester cleavage during the preparation or handling of the polymer.

The structural analogies between polymers **IV** and **V** are further corroborated by $^1\text{H-NMR}$ (Figure 2) and $^{13}\text{C-NMR}$ spectra. In particular the $^{13}\text{C-NMR}$ spectrum of copolymer **V** revealed two distinct signals of similar intensities at about 63.0 and 44.4 ppm which correspond to methylene groups bonded to OH and Cl, respectively. The same two peaks also appear, with noticeably reduced relative intensities, in the spectrum of polymer **IV**. A further study of the FTIR and NMR spectra is still required in order to determine the detailed polymer structures corresponding to calculated empirical formulae as well as to

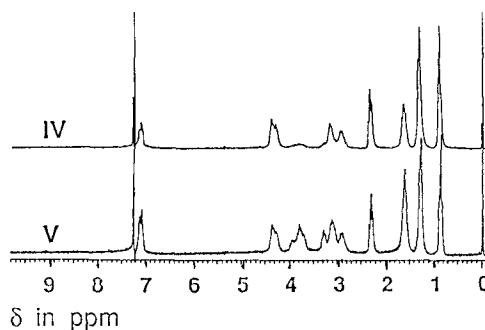


Figure 2. $^1\text{H-NMR}$ spectra of polymers **IV** and **V**

elucidate the configuration of 2,5- linked thiophene rings. However, the reported spectroscopic observations, the analytical data and a rough estimate of $^1\text{H-NMR}$ intensity ratios already indicate that the side chains of the two polymers are ester functionalized up to more than 80% of the expected values. Moreover, the polymers contain hydroxyethyl and chloroethyl side chains in small but not negligible amounts. Their precise origin, especially in homopolymer IV, is not yet established, but we hope that the homopolymerization of monomer I, which is in progress, will contribute to provide more information.

Properties

Some physical properties of 3-alkylester-substituted polythiophenes are reported in Table 2. Both undoped polymers are soluble in common organic solvents such as methylene dichloride, chloroform, toluene, and tetrahydrofuran, and can be readily processed into uniform films by casting their solutions. We have preliminarily found that the solution-cast films can also be stretched up to several times their initial length.

Table 2. Physical properties of polymers

Polymer	Color	UV (CHCl_3) $\lambda_{\text{max}}(\text{nm})$	Conductivity (S/cm)
IV undoped	orange-red	415	$3.1 \cdot 10^{-12}$
IV doped	blue-black		$1.1 \cdot 10^{-3}$
V undoped	orange-red	414	$8.7 \cdot 10^{-16}$
V doped	blue-black		$4.9 \cdot 10^{-5}$

Conclusions

The new ester-functionalized alkyl group positioned as a side chain on the backbone of polythiophenes makes the polymers soluble and readily processable. Even though some loss of ester function occurs during polymerization or dedoping, this kind of functionalization is quite stable to the doping reaction as can be deduced from the elemental analyses of doped polymers. The observed conductivity values of our unstretched and doped alkylester-substituted polythiophenes are lower than those observed for poly 3-alkyl-substituted thiophenes with a comparable side chain length. This result is not clear at present and further work is required to elucidate the several not easily separable factors which can determine the macroscopic conductivity. It should be noted, however, that the conductivity data presented here suggest that the conductivity increases with increasing ester content, at least for polymers containing the same alkylester side chain, prepared and doped in similar conditions.

Acknowledgements

Acknowledgements are made to the Ministero dell' Università e della Ricerca Scientifica e Tecnologica and to the Consorzio Interuniversitario di Fisica della Materia for support of this research.

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Accepted September 4, 1991 C