# Synthesis and Characterization of Poly(3-alkylthiophenes) with NLO Chromophoric Groups in Side Chains

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**Summary**: Polythiophene copolymers containing alkyl side chains of different length and partially functionalized with chromophoric groups have been synthesized by $FeCl_3$ oxidative coupling of 3-alkylthiophenes and functionalized 3-alkylthiophenes. Composition, molecular weigth and configuration of the soluble fraction of the copolymers have been investigated and some structure-property correlations have been evidenced.

## Introduction

Over the last decade, organic materials exhibiting non-linear optical (NLO) properties have been the subject of intensive investigations for their possible technological applications such as data storage and data transmission. In particular, polymers containing NLO active chromophores seem to be very promising for these purposes.[1,2] A first approach is to consider a polymer as an inert system in which to dissolve NLO active molecules (guest-host system). However such a dispersion of molecules presents many problems as, for instance, their usually low solubility within the polymer matrix which limits the magnitude of the NLO response. In order to overcome these problems the chromophores can be incorporated into the main or side chain of the polymer so as to enhance the chromophore concentration and consequently the non-linear activity.

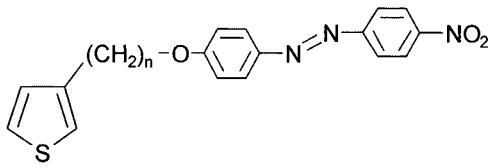
In the present paper the chromophore incorporation method was tested on 3-alkyl substituted polythiophenes which are characterized by good thermal and chemical stability. A chromophore was grafted directly to the side chains of 3-alkylthiophenes and the functionalized monomers were then copolymerised with 3-alkylthiophenes as plastifying comonomers to improve solubility. New processable polythiophene-based materials functionalized with NLO chromophoric units were thus obtained.

 CCC 1022-1360/00/$ 17.50+.50/0

**Experimental**

All chemical reagents including 3-hexylthiophene (3-HT) and 3-dodecylthiophene (3-DDT) were purchased from Aldrich.

The functionalized monomers **1a** and **1b** (Figure 1) were synthesized by the corresponding ω-bromoalkylthiophenes[3,4] with the azo dye 4-hydroxy-4'-nitroazobenzene[5] in a polar solvent and in the presence of potassium carbonate. The yield of monomer **1a** can be improved by using the *p*-toluenesulfonate[6] derivative instead of the bromo derivative.




**1a** n = 2

**1b** n = 6

Figure 1. Structures of functionalized monomers.

Mixtures of 3-HT and **1a,** 3-HT and **1b**, and 3-DDT and **1b**, in a 1:1 mole ratio, were copolymerized to give copolymers **2a**, **2b**, and **2c** (Figure 2), respectively.

Copolymerization (procedure A) was carried out over a 1 hr period by initially adding a solution of $FeCl_3$ in nitromethane to a solution of the comonomers in carbon tetrachloride.[7] The final concentrations of the mixture of the two comonomers and $FeCl_3$ were fixed to 0.06 M and 0.24 M, respectively. The reaction mixture was treated with acidic methanol to precipitate the polymer and to change it to the neutral state from the form complexed with $FeCl_3$. The polymer was extracted in a Soxhlet apparatus with methanol in order to remove residual oxidant and low molecular weight materials and then with chloroform to obtain a soluble fraction. In the preparation of polymer **2a** a different procedure (B) was also experimented to obtain a higher yield of soluble fraction, consisting in the initial addition of pure carbon tetrachloride to a solution of $FeCl_3$ and comonomers in nitromethane.

The molecular weights of the polymers were determined by gel permeation chromatography (GPC) in THF using polystyrene standards as references. Polymer composition and microstructure were assessed by $^1$H-NMR spectroscopy in $CDCl_3$

solutions. Glass transition temperatures ($T_g$) were measured by DSC at a heating rate of 20°C $min^{-1}$.

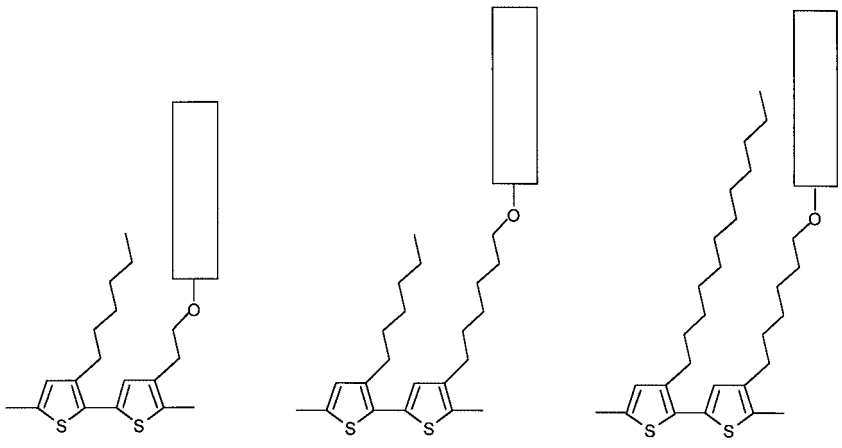



Figure 2. Structures of functionalized copolymers with different types of side chains.

**Results and discussion**

The azo dye 4-hydroxy-4'-nitroazobenzene was choosen as chromophore because it was easily grafted to the alkyl side chain of the thiophene ring. Nucleophilic substitution reactions with the appropriate thiophene intermediates led to the monomers **1a** and **1b** with a molecular hyperpolarizability, a second order NLO parameter, $\beta = 127 \times 10^{-30}$ and $144 \times 10^{-30}$ esu (measured at $\lambda = 1.06$ μm), respectively.[8]

Copolymerizations of the two monomers with procedure A (see Experimental) gave good polymer yields, that is 61 % (**2a**), 79 % (**2b**), and 61 % (**2c**), with fractions soluble in solvents such as chloroform (Table 1), from which films could be cast onto substrates. A very low amount of soluble polymer **2a** was however obtained with this procedure (see Table 1). A very substantial increase of the soluble fraction from 4 to 33% for **2a** was achieved by adopting the alternative procedure B for reagent addition. In this case the overall polymer yield is about half that obtained by method A while almost all the polymer is soluble. It is worth noting that polymer **2a** prepared according to either procedure exhibits similar composition, number average molecular weight ($M_n$) and polydispersity index ($M_w/M_n$).

Table 1. Yields and some characteristic data for the soluble fractions of the copolymers.

| Copolymer (procedure)[a] | Soluble fraction | Monomer **1a** or **b** | $M_n \times 10^{-3}$ | $M_w/M_n$ | Regioregularity |
|---|---|---|---|---|---|
| | (%)[b] | (mol%)[c] | (g/mol) | | (HT%)[d] |
| **2a** (B) | 33 | 31 | 5.5 | 2.5 | 61 |
| **2a** (A) | 4 | 30 | 6.0 | 2.7 | 64 |
| **2b** (A) | 23 | 37 | 6.6 | 3.1 | 69 |
| **2c** (A) | 16 | 28 | 11.0 | 2.5 | 75 |

[a] See experimental part.
[b] Referred to the initial weight of the comonomers.
[c] In the copolymer.
[d] HT = head-to-tail coupling.

The length of the flexible side chains seems an important parameter not only for polymer solubility but also for its microstructure. The latter was assessed by $^1$H-NMR according to regular head-to-tail (HT) coupling content calculated on the basis of the intensity of the signals relative to methylene protons in α to the thiophene ring.[7,9] As can be seen in Table 1, the HT configuration content increases as the length of the alkyl chain increases in either one or the other comonomer. The lowest value is found for polymer **2a,** regardless of the polymerization method adopted, whether A or B.

A reverse trend was found for the glass transition temperature in the series of the polymers obtained with the procedure A; $T_g$, which is 50°C for **2a**, 40°C for **2b**, and -17°C for **2c**, decreases as the length of the alkyl chain increases.

A characteristic common to all the synthesized copolymers is the difference between comonomers feed ratio (1:1 mole ratio) and final polymer composition. The amount of chromophoric monomer in the soluble fractions is at best 37 mole% (Table 1) instead of the expected 50%. In comparison, the insoluble part of the polymers is always enriched in this monomer, as can be seen from the relative intensity of the bands in the FT-IR spectra of both soluble and insoluble parts.

**Conclusions**

In conclusion, a copolymerization route for obtaining new soluble poly(3-alkylthiophene)s functionalized with NLO chromophoric groups was

successfully found. The polymerization procedure appears to be of primary importance for achieving a good amount of soluble polymer. Structure-property correlations for the new polymers were investigated and the importance of side chain length clearly emerged.

**Acknowledgements**

This work was supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica and by the Università di Bologna (funds for selected research topics), Italy.

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