

Poly(3-alkylthiophene) Modifications

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Received 04.11.1997

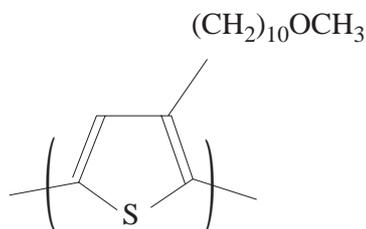
Introduction

Poly(3-alkylthiophenes) are currently investigated for their interesting electrooptical properties. These polymers are promising for their application in electronic devices and the tailoring of their structure has the aim of optimizing both the electrooptical properties and the quality of the active thin film utilised in the devices. In this work some methods followed to modify PAT structures are presented together with some properties of the corresponding polymers.

Results and Discussion

The synthesis of new kinds of poly(3-alkylthiophene)s (PATs) with improved properties has attracted a great number of researchers. In particular the preparation of PATs with functionalised side chains seems to be very promising for tailoring the electrooptical properties of this class of polymers¹.

In this view, a PAT containing -OCH₃ groups as side chain end group has been prepared in our laboratories. The structure of this polymer is given in Figure 1, hereafter called PDMT: it was synthesized with the NiCl₂dppp catalyst and showed a head to tail connection of about 85 % as determined by ¹H-NMR.



^X
Figure 1.

The electronic properties of this polymer are not so different from those of other PATs. The presence of -OCH₃ groups does not influence the electronic structure of the backbone due to the great distance from it. The advantage of this polymer with respect to the previously synthesized PATs is that a stable monolayer

at the air water interface is obtained on a Langmuir through a surface pressure of 17 mN/m. The monolayer can be transferred from the water surface onto solid substrate through a Z type deposition by means of Langmuir Blodgett (LB) technique.

We have recently shown² that a few monolayers of PDMT can be transferred onto ITO covered glass. After covering the obtained multilayered structure with Al electrode, the system was found to work as a light emitting diode by applying a voltage between ITO and Al. It was also shown that, due to the LB deposition method which is able to orient the macromolecular chains in the dipping direction, a polarized electroluminescence was observed².

Following the idea of functionalizing the side chain groups of PAT, we have recently prepared a tetrahydropyranil functionalised polymer which after deprotection gives a -OH terminally substituted PATs³. The unprotected polymer was found to be soluble only in N-methylpyrrolidinone, and the spreading of this solution onto the water surface revealed that the polymer was soluble in water.

So, a new strategy, in order to prepare -OH functionalized PAT, is under investigation and it is related to the possibility to have a copolymer structure both with -OH terminally substituted monomers and the usual aliphatic chain. To reach this goal we have tried a chemical modification of PDMT. In fact it is reported⁴ that -OCH₃ groups can react with BBr₃ in CH₂Cl₂ and 15-crown-5 ether in NaI ether solution to give a -OH function.

In a typical preparation, 50 mg of the polymer was dissolved in 10 ml of CH₂Cl₂ which was left for 10 hours on molecular sieves under nitrogen atmosphere. 3.5 ml of a saturated solution of 15-crown-ether in anhydrous CH₂Cl₂ (crown ether concentration 0.33M) was added to the polymer solution. The mixture was then cooled under nitrogen to -30°C and 0.6 ml of 1 M solution of BBr₃ in CH₂Cl₂ was added (molar ratio BBr₃/methylether 3/1). After reacting for 3 hours at -30°C the solution was left at room temperature for 1 hour, washed with a NaOH water solution and the precipitated polymer dissolved in CH₂Cl₂ and dried. Not all of the resulting polymer was found to be soluble in organic solvents: 30 % of the initial weight was insoluble. The characterization of the soluble polymers was performed with FTIR, UV-visible spectroscopy and ¹H-NMR.

A band at 3400 cm⁻¹ characteristic of the O-H stretching mode appears in the FTIR spectrum of the deprotected polymer. Moreover, the disappearance of the C-H deformation band of the CH₃ groups (1388 cm⁻¹ in PDMA) indicates that this group has been removed and substituted by the hydroxyl group. In addition the band at 1122 cm⁻¹, that we attributed to the C-O stretching of the ether function, a new band strongly decreasing in intensity, characteristic of the C-O stretching in alcoholic groups, appears at band 1050 cm⁻¹.

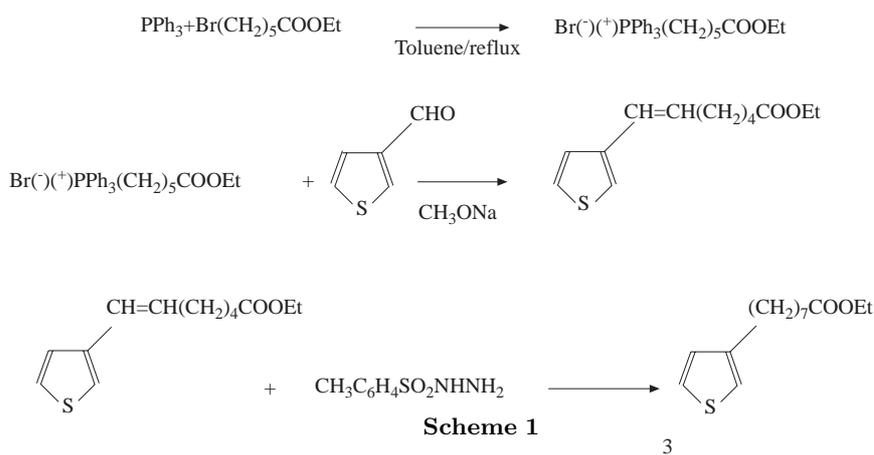
The UV-visible spectrum of the deprotected PDMT is equivalent to the spectrum of the protected polymer: no shift in the absorption maximum ($\lambda_{\max} = 430$ nm) has been observed indicating that chain degradation does not occur during deprotection reaction.

The ¹H-NMR of PDMT shows the following peaks (CDCl₃): $\delta = 3.30$, singlet due to the CH₃ of the methoxy group; $\delta = 3.35$, triplet due to CH₂ connected to oxygen. After deprotection a new peak appears at $\delta = 3.64$ while the 3.30 singlet and 3.35 triplet peak decrease in intensity. This new peak at 3.64 ppm has been attributed to a CH₂ group bearing an hydroxyl group. From a simple calculation based on the area ratio between the triplet at $\delta = 3.64$ and the sum of the peak at $\delta = 3.31$ and 3.64 an average degree of deprotection may be calculated. This value was found to be near to 25 % indicating that the deprotected polymer better results in a copolymeric structure formed by the hydroxy functionalized side chain monomers (25 %) and methoxy functionalized side chain monomers (75 %). The behavior of this copolymeric structure at the air water interface is currently under investigation.

As our aim was to obtain functionalized PAT. We tried new ways to obtain these polymeric structures. Moreover, we believe that the introduction of polar groups at the end of the side chain may greatly improve the possibility to obtain stable and transferable monolayers at the air water interface which is the first step for the preparation of well ordered multilayered structures.

We recently developed a new synthetic procedure for the formation of an ester modified PAT through a new synthetic pathway.

This method can be applied only with the FeCl_3 type polymerization and leads to high molecular weight polymers: the synthetic procedure for the monomer synthesis and polymerization is reported in Scheme 1. The unusual method followed for monomer synthesis (see Scheme 1) allowed us to obtain yield of 25 % for it which make this system comparable with other synthetic procedure utilised for introduction of particular function at the ω position of the side chain. In fact monomer **3** can easily further be modified to give other function such as $-\text{COOH}$ or $-\text{OH}$ by means of a usual saponification or reduction with LiAlH_4 respectively. So the synthetic pathway indicated for monomer synthesis can be an alternative route to the already diffused method for preparation of these compounds.



However, the polymeric structure obtained from polymerization of monomer **3** with FeCl_3 are insoluble probably because of formation of complexes between FeCl_3 and the ester group of the monomers. In order to improve the solubility of the polymer a copolymeric structure was realised by copolymerising 3-hexylthiophene (x) and monomer **3** (y).

Different copolymer composition, ranging from $x/y = 7/3$ to $x/y = 9/1$, were obtained by varying the ratio between the two monomeric units in the alimentation. By increasing the amount of ester functionalized monomer in the alimentation feed an increased amount of insoluble copolymer was found. These copolymers showed absorption spectra with maxima at 436 nm in agreement with other PATs obtained with FeCl_3 . We are currently investigating a chemical method in order to restore the $-\text{COOH}$ group of the ester function without degradation of the copolymer. In fact the first saponifications performed in THF/KOH solution revealed a degradation of the copolymer as shown by the blue shift of the absorption maxima of the UV-vis spectra.

References

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