

Preparation of carboxylic- and hydroxylated-functionalized polythiophenes and their VOCs sensing properties

V. C. Gonçalves^{(1)*} and D. T. Balogh⁽¹⁾

(1) Instituto de Física de São Carlos, USP, CP 369 - São Carlos-SP- Brazil e-mail:
vanessa@if.sc.usp.br.

* Corresponding author.

Abstract – Two functionalized polythiophene, poly(3-thiophene acetic acid)- PTAA and the poly[3-(2-hydroxyethyl)thiophene] - PHET, were synthesized by oxidative polymerization. The influence of these side chains on their volatile organic compounds(VOCs) sensing properties was investigated by recording Visible spectra of cast films upon exposure to n-hexane, dichloromethane, chloroform, toluene, tetrahydrofuran, methanol and humidity, a common interfering substance in these measurements. PTAA showed no response, while PHET sensed toluene and tetrahydrofuran, in different extents. These differences in the polymers responses seem to be associated with the side-chains that interact differently with VOCs.

In the last years much effort has been made to synthesize different polythiophenes derivatives to improve their properties, such as solubility and processability, for use in technological devices. In most cases, polythiophenes derivatives have been produced by the introduction of various side groups at the 3-position of thiophene ring. Examples of these derivatives are poly(3-alkylthiophene)s, poly(3-alkoxythiophene)s and poly(3-alkylesterthiophene)s. They have been used in solar cell, electrochromic devices, polymer light-emitting diodes and sensors [1].

In this study, our purpose is to synthesize a carboxylic- and a hydroxylated-functionalized polythiophene by oxidative polymerization and to study the use of these polymers as active layers in optical sensors for VOCs (volatile organic compounds) as well as to investigate the effect of the side chain in this behavior. These polymers are the poly(3-thiophene acetic acid) and the poly[3-(2-hydroxyethyl)thiophene] named here as PTAA and PHET, respectively. Their structures are shown in Fig. 1.

Such polymers have been synthesized by previous workers using different conditions of polymerization from that presented here [2, 3]. However, they obtained only PHET insoluble [3]. Here the polymers were synthesized via oxidative polymerization using ferric trichloride. Under nitrogen atmosphere the monomers were dissolved in nitromethane and solid ferric chloride was added quickly to the mixture by a powder addition funnel under magnetic stirring. In the next step, chloroform was added to the mixture which was magnetic stirred for 4h. In the end, the polymers were isolated by precipitation in methanol. The occurrence of the polymerizations and the chemical structures of the polymers were confirmed by FTIR. Only the number-average molecular weight (Mn) value of PHET was estimated by HPSEC, using N-methyl-2-pyrrolidone (NMP) as solvent, and it was around 13.000 g/mol. The value of PTAA cannot be obtained because of its insolubility in NMP.

The PTAA was dissolved in DMF and the PHET was dissolved NMP and insoluble products were removed by filtration. Cast films were prepared from these solutions under vacuum at 30 and 60°C, respectively. Their optical sensing response were investigated for various VOCs (n-hexane, dichloromethane, chloroform, toluene, THF, methanol) and humidity by UV-vis spectroscopy. The UV-vis spectra of PTAA did not show any change for all analytes. In contrast, the maximum of the absorption peak (λ_{max}) of PHET showed a blue shift in the presence of toluene and THF, and response for THF was greater than for toluene. From these results, we infer that these differences in responses from both PTAA (no response) and PHET seem to be associated with the side-chains, which interact differently with VOCs.

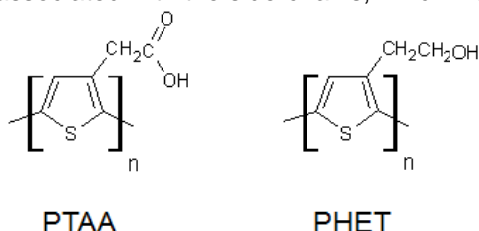


Figure 1: Chemical structures of PTAA and PHET.

References

- [1] H. S. on Chan and S. C. Ng, Prog. Polym. Sci. 23 (1998) 1167-1231.
 [2] S. V. Mello, E. C. Pereira and O. N. Oliveira Jr, Synth. Met. 102 (1999) 1204.
 [3] C. Della Casa, E. Salatelli, F. Andreani and P. Costa Bizarri, Makromol. Chem. Macromol. Symp. 59 (1992) 233.