

Electrochemical formation of a copolymer of 3-methoxyethoxythiophene and thiophene

Sandrine Pouzet and Alain Ricard*

Laboratoire der Physicochimie des Matériaux Organiques, ENSIGC-INPT, Chemin de la Loge, F-31078 Toulouse Cedex, France

Summary

The electrochemical polymerization of 3-methoxyethoxythiophene yields to a polymer which is soluble in organic solvents. However, the solution is not stable in air. The blue solution, characteristic of the polymer in the doped state, turns to red due to the anion undoping process. We have found that this behaviour can be modified when a copolymerization is performed with thiophene; the copolymer is soluble in organic solvents and stable in air.

Introduction

Conductive polymers such as polypyrroles or polythiophenes have been extensively studied (1-3) and they have potential applications in various domains : battery, electrocatalytic materials, electromagnetic shielding. However, their main drawback is their insolubility. Therefore, many studies have been devoted to the development of processible conducting polymers. To that purpose, pyrrole and thiophene have been substituted in 3-position by alkyl chains (4-7) and thiophene by alkyl sulfonate chains (8,9). After polymerization of these substituted heterocycles, the polymers show indeed new properties as fusibility or solubility. In the last few years, an other route to obtain organosoluble polymers has been developed by substituting the thiophene ring with an ether moiety. The simplest of these molecules is the 3-methoxythiophene which can give by electropolymerization a polymer which is soluble in the organic solvents with a blue coloration in the doped state and a red colour in the neutral state (10,11). A series of polyalkoxythiophene with chains of different length (12) and other molecules with several ether functions and with the first oxygen atom spaced from the thiophene ring by one or two CH₂ groups (13,14) have also been prepared. Roncali (14) reported that the polymer obtained from the monomer which contains two CH₂ groups between the thiophene ring and the first oxygen atom, and with two ether functions, has a greater stability by comparison with the other molecules of the series. The preparation of disubstituted molecules (11,12,15) has also been described.

We investigate here the synthesis of a thiophene derivative functionalized with a 3-methoxyethoxy moiety and the electropolymerization and copolymerization with thiophene.

*Corresponding author

Monomer synthesis

The synthesis of the 3-methoxyethoxythiophene was carried out following the method reported by Bryce et al. (16) 220 ml of 3-methoxyethanol were added to 4.0 g of sodium. When all the sodium was reacted, 2.5 g of copper(II) oxide and 0.1 g of potassium iodide were introduced in the reaction vessel, followed by 10 g of 3-bromothiophene. The mixture was stirred and maintained at 100°C during 3 days. 0.1 g of potassium iodide was then added and the reaction was run 2 more days. The solution was then filtered, and poured into 150 ml of distilled water and extracted twice with ether. Organic phases were dried over magnesium sulfate, then filtered and evaporated. The 3-methoxyethoxythiophene was subsequently purified by vacuum distillation.

3-methoxyethoxythiophene polymerization

In order to determine the oxidation potential of the monomer, a linear voltammogram was performed with a scan-rate of 1 mV s⁻¹. Experiment was carried with a solution of 3-methoxyethoxythiophene in acetonitrile (SdS) containing lithium perchlorate (0.1 M ; Fluka) at a platinum electrode. Potential was applied from a EGG 273 Potentiostat and referred to a saturated calomel electrode. The voltammogram presented in figure 1 shows that the oxidation of the 3-methoxyethoxythiophene appears between 1.6 and 2.3 V. The constant potential polymerization of 0.1 M of 3-methoxyethoxythiophene at 1.8 V in the same electrolyte yields to the formation of a polymer which is soluble in the reactive medium : a blue cloud comes off from the anode.

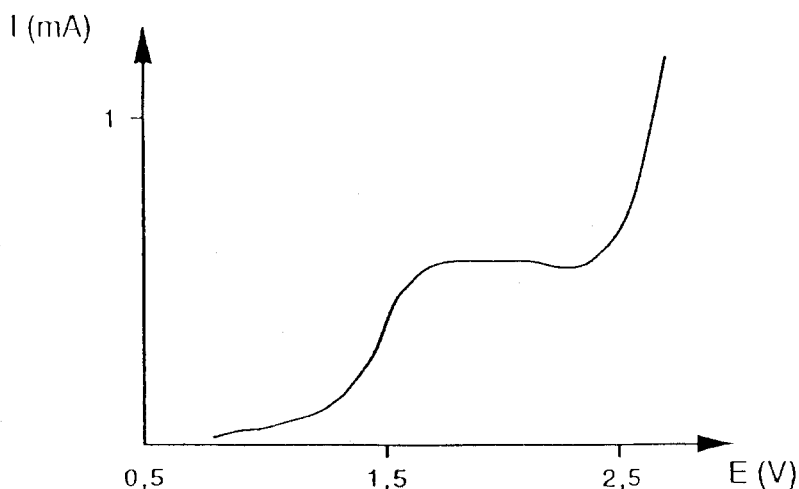


Figure 1 : Linear voltammogram of the 3-methoxyethoxythiophene in acetonitrile containing 0.1 M of LiClO₄. Scan-rate : 1 mV s⁻¹. Potentials are expressed versus saturated calomel electrode.

A polymer deposit on the electrode can be obtained when a mixture of acetonitrile and water (1:2) is used instead of pure acetonitrile. In these conditions, the poly-3-methoxyethoxythiophene forms a blue-black film on the anode and can be solubilized afterwards in organic solvents yielding to a blue solution. This coloration, which is characteristic of the doped state (11), may be associated with the formation of bipolarons. However, the polymer in solution is not stable in air and the blue coloration turns to red, characteristic of the neutral polymer. This instability of the doped state is due to a relatively high oxidation potential (17).

The evolution with the time of the visible absorption spectrum of the poly-3-methoxyethoxythiophene in acetonitrile is reported in figure 2. It was performed on an PYE UNICAM SP 8-100 spectrometer. In the doped state, it exhibits a maximum of absorption at 800 nm (a) and when the solution becomes red, this band decreases whereas an absorption at 500 nm increases (b and c). The three curves intersect at the same point which is called the isobestic point. This one gives evidence of the existence of a chemical balance between two species : the polymer can be switched between the doped and the neutral form. Furthermore, the neutral poly-3-methoxyethoxythiophene shows a maximum absorption at 500 nm which can be related to a quite highly conjugated backbone (12,14,15,17).

The infra-red absorption spectrum (figure 3) of the poly-3-methoxyethoxythiophene in the doped state was obtained from a Perkin Elmer 1760 X spectrometer, and compared with the one of the polymer in the neutral state obtained by reduction with hydrazine. The dopant (ClO_4^-) has an absorption band which is expected around $1100\text{-}1025\text{ cm}^{-1}$ but it could not be observed because it was masked by several bands attributed to the polymer. However, the spectrum of the polymer in the doped state shows an absorption band beginning at 4200 cm^{-1} which can be attributed to bipolarons.

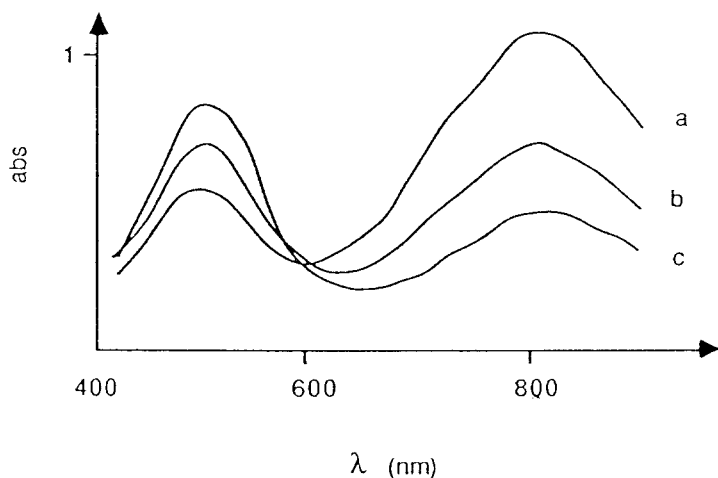


Figure 2 : Visible absorption spectrum of the 3-methoxyethoxythiophene in solution in acetonitrile. The signification of a, b and c are given in the text.

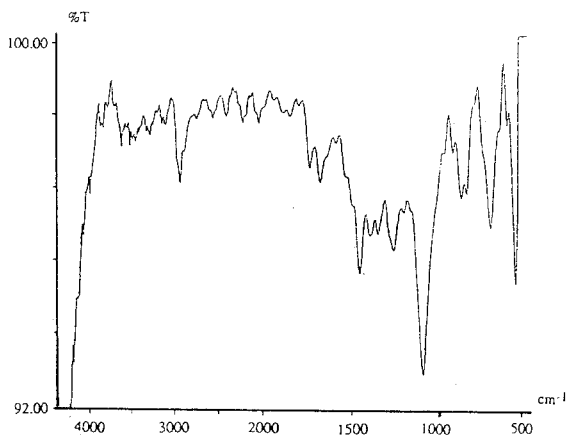


Figure 3 : Infra-red absorption spectrum of the 3-methoxyethoxythiophene.

Copolymerization of 3-methoxyethoxythiophene and thiophene

As it has been pointed out in the first part of this study, the 3-methoxyethoxythiophene is soluble in organic solvents, but it is not very stable. So, we tried to copolymerize it with thiophene. The constant potential copolymerization was performed in the same electrolyte as before with monomer concentrations of 0.03 M for the 3-methoxyethoxythiophene and 0.05 M for the thiophene. A black film was formed on the anode and it was soluble in organic solvents. The solution took a blue coloration and was stable in air.

The visible absorption spectrum was recorded and is shown in figure 4. There is a broad absorption between 600 and 900 nm and a little peak at 520 nm. This latter one, is characteristic of the presence in the chain of a little segment in the neutral state and indicates that the conjugated backbone is longer than in the polymer which has an absorption at 500 nm.

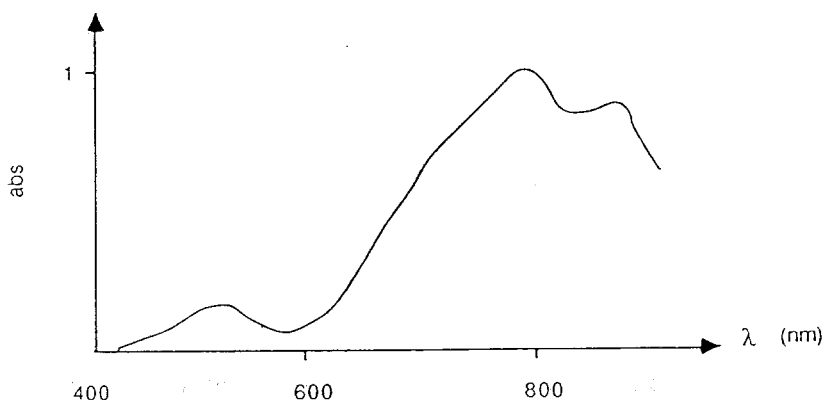


Figure 4 : Visible absorption spectrum of the copolymer of 3-methoxyethoxythiophene and thiophene in solution in acetonitrile.

In summary, this study shows that the copolymerization of the 3-methoxyethoxythiophene with thiophene allows to obtain a material with a highly conjugated backbone, soluble in organic solvents and stable in air. Further investigations are in progress to characterize this copolymer.

References

1. Handbook of Conducting Polymers, Ed. T.A. Skoteim, M. Dekker, New York, (1986)
2. Makromol. Chem., Macromol. Symp., 8 (1987)
3. D. Curran, J. Grimshaw, S.D. Perera, Chem. Soc. Rev., 20, 391 (1991)
4. G. Gustafsson, O. Iganäs, J.O. Nilson, Synth. Met., 28, C427 (1989)
5. K. Yoshino, S. Nakajima, R. Sugimoto, Jpn J. Appl. Phys., 26, L1038 (1987)
6. H. Masuda, S. Tanaka, K. Kaeriyama, J. Chem. Soc., Chem. Commun., 725 (1989)
7. K.Y. Jen, G.G. Miller, R.L. Elsenbaumer, J. Chem. Soc., Chem. Commun., 1346 (1986)
8. A.O. Patil, Y. Ikenoue, N. Basescu, N. Colaneri, J. Chen, F. Wudl, A.J. Heeger, Synth. Met., 20, 151 (1987)
9. A.O. Patil, Synth. Met., 28, 495 (1989)
10. R.L. Blankespoor, L.L. Miller, J. Chem. Soc., Chem. Commun., 90 (1985)
11. T. Yamamoto, A. Kashiwazaki, K. Kato, Makomol. Chem., 190, 1649 (1989)
12. M. Feldhues, G. Kampf, H. Litterer, T. Mecklenburg, P. Wegener, Synth. Met., 28, C487 (1989)
13. M.R. Bryce, A. Chissel, P. Kathirgamanathan, D. Parker, N.R.M. Smith, J. Chem. Soc., Chem. Commun., 466 (1987)
14. J. Roncali, Thesis of the University Paris Nord (1989)
15. M. Leclerc, G. Daoust, J. Chem. Soc., Chem. Commun., 273 (1990)
16. M.R. Bryce, A.D. Chissel, N.R.M. Smith, D. Parker, Synth. Met., 26, 153 (1988)
17. G. Daoust, M. Leclerc, Macromolecules, 24, 455 (1991)

Accepted January 11, 1993 C