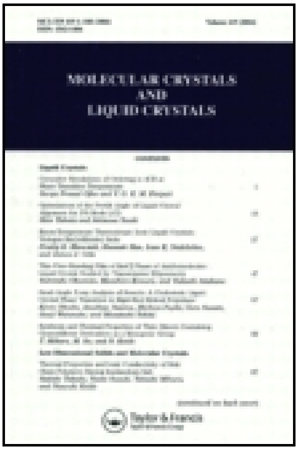

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One Step Chemical Synthesis and Doping of Poly(2,2′-Bithiophene)And Related Polymers

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ONE STEP CHEMICAL SYNTHESIS AND DOPING OF POLY(2,2'-BITHIOPHENE)AND RELATED POLYMERS

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Abstract By direct action of the oxidant $Fe^{III}(ClO_4)_3$, $9H_2O$ on 2,2'-bithiophene, 3-methylthiophene and thiophene, we have been able to synthesize the corresponding polymer. The conductivity of the poly(2,2'-bithiophene)obtained by this reaction is ca $17(\Omega\ \text{x}cm)^{-1}$. The efficiency of the polymerization process as well as the conductivity of the obtained polymers seems related to the oxidation potential of the corresponding monomers. 3-Bromothiophene does not polymerize in this way because of its high oxidation potential.

INTRODUCTION

Among the wide variety of organic conducting polymers those derived from thiophene and substituted thiophenes are depicted to show good stability toward O_2 and moisture in both doped and neutral state[1a-c]. This property is of great interest in view of polythiophene applications in electrochromic displays[2], protection of semiconductors against photocorosion[3] and energy storage[4].

Two main types of synthesis have been reported in the literature : the most widely used is the electrochemical polymerization of either thiophene[5,6,7] 3-methylthiophene, 3-bromothiophene or 2,2'-bithiophene[1b,c]. The polymers are obtained in their oxidized form and conductivities of electrochemically synthesized polythiophene lie in the range of

$10\text{-}100\,\Omega^{-1}\text{xcm}^{-1}$ [5,7,8]. The other widely used polymerization method is based on a Grignard coupling reaction starting with 2,2'-dibromo or 2,2'-diiodothiophene or 3-methylthiophene[9a-c] where the polymer is obtained in its neutral form and can be further doped.

A one step chemical polymerization and doping of thiophene has been achieved by using AsF_5 acting as an oxidant [10] and being the precursor of the dopant ion AsF_6^-. The reported conductivities rise a maximum of $2\text{x}10^{-2}\,(\Omega\,\text{xcm})^{-1}$ which is three order of magnitude smaller than those of the electrochemically prepared polythiophene[11] doped with AsF_6^-.

We reported here a method of polymerization to prepare poly(2,2'-bithiophene), poly(3-methylthiophene) and polythiophene that is already applied with success to synthesize polypyrrole and polysubstituted pyrroles : the direct action of an oxidant such as $Fe(ClO_4)_3$ on the monomers yield in one step the formation of the corresponding doped polymers. The poly-(2,2'-bithiophene) also obtained showed a good conductivity.

EXPERIMENTAL

Thiophene (Jansenn), 3-methylthiophene (Jansenn), 3-bromothiophene (Jansenn) were used as received. The 2,2'-bithiophene (Jansenn) was purified by liquid chromatography in hexane on a silica gel column, and subsequent recrystallisation at 0°C. The ferric perchlorate $Fe(ClO_4)_3{,}9H_2O$ (Fluka) was used as received. The solvent of the reactions was acetonitrile and has been previously carefully distilled on P_2O_5 in order to minimise the amount of water present during the reaction. The synthesis and the washing procedure has been performed at room temperature under Argon in a dry box.

Poly(2,2'-bithiophene)

The 2,2'-bithiophene 0.013 mole (2.16 g) was dissolved in 20 ml of acetonitrile. The amount of ferric perchlorate necessary for this reaction was calculated on the basis of the oxidative condensation reaction assuming a maximum doping level (δ) of 1 charge for three thiophene rings. So, the polymerization and doping consume about 2.66 moles of ferric perchlorate per mole of 2,2'-bithiophene (see reaction (2)). Thus 0.034 Mole (17.54 g) of $Fe(ClO_4)_3,9H_2O$ were dissolved in 80 ml of acetonitrile. As soon as the two acetonitrile solutions were admitted to contact a black precipitate appeared. The mixture was continuously stirred during 1 hour and filtered. The precipitate was washed in a Soxlet apparatus with acetonitrile for 2 hours then dried overnight under dynamic vacuum, and gives 2.17 g of a thin black powder.

Other polymers

The procedure was essentially the same as described for poly(2,2'-bithiophene) synthesis, excepted that less drastic purity conditions were admitted. The solvent, acetonitrile (Fluka, puriss) was used as received. Experiments were drive under Argon flow instead of the dry box, consequently acetonitrile was purged with argon during ten minutes. The polymer formed with 3-methylthiophene was a black and very fine powder while the polythiophene synthetized in the same conditions was brown and even more pulverulent. Addition of the 3-bromothiophene solution to the oxidant solution did not result in the formation of a precipitate.

RESULTS and DISCUSSION

The elemental chemical analysis of the poly(2,2'-bithiophene) obtained as described before gave the following formula :

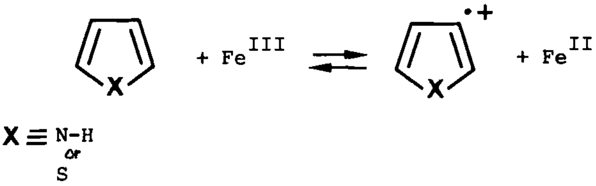
$$(C_4H_2S,(ClO_4)_{0.13},O_{0.25})$$

We first note that the dopant amount is somewhat less than expected from litterature data[1b,c,12] : there is only one perchlorate anion for about 4 bithiophene entities. As the polymer has been stored in an ampoule sealed under vacuum, the excess oxygen (0.25) cannot be attributed to a further doping by oxygen. It might be attributed to a side oxygenation reaction on the thiophene ring. The yield of the polymerization calculated with the above formula for the polymer is 88%. Conductivity measurements have been performed on a pressed pellet by the conventional four point contacts method. A value as high as $17(\Omega\,\text{xcm})^{-1}$ has been found. This conductivity is much higher than the one $(0.1\text{-}1\,\Omega^{-1}\text{xcm}^{-1})$ observed on electrochemically synthezised poly(2,2'-bithiophene)[1c,13].

The brown powder of polythiophene that we have obtained was insulating and its chemical analysis gave the following formula : $[C_4H_2S,(ClO_4)_{0.03},O]$. Thus, it appears to be very poorly doped only one perchlorate anion for 30 thiophenic units, and highly oxygenated : 1 extra oxygen per thiophene ring. The yield of this synthesis was only 31 %.

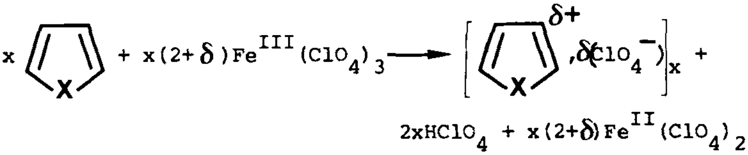
The conductivity of the poly(3-methylthiophene) synthetised by this method was $7.10^{-3}(\Omega\,\text{xcm})^{-1}$. This value compared well with electrochemically prepared poly(3-methylthiophene) chemically doped at a low level by iodine[14] but is several order of magnitude smaller than the value $(1.2\text{x}10^{2}(\Omega\,\text{xcm})^{-1}$ of the conductivity of poly(3-methylthiophene) electrochemically prepared and doped by the perchlorate anion[15]. Although the results of the elemental analysis are not yet available for this compound, we can estimate the lower limit for the yield of this reaction. If this polymer is assumed to be doped at a level of one anion for 3-4 monomer units as polypyrrole, this reaction yield would be 43 %.

Considering the mechanism of polymerization of these compounds with iron perchlorate, the failure of this method to prepare poly(3-bromothiophene) is not surprising. As a matter of fact, the electropolymerization of pyrrole has been proved to be an oxidative condensation process consisting in a first electrochemical oxidation step providing the cation radical of pyrrole, then following by subsequent dimerizations and deprotonations[16]. Such a mechanism has been extended to other polymers resembling polypyrrole, on the basis of results due to chemical investigations and physical characterization of polymers obtained from azulene[17], pyrene[18] and thiophene[1c]. Replacing the anode by Fe^{III} should results in replacing the first electronic transfer at the electrode by the following redox reaction in homogeneous phase :



(1)

and the global reaction may be written as follows :



(2)

The low level of doping of polythiophene cannot be explained in terms of thermodynamic data, because the redox potential of polythiophene (0.96[1c] V vs SSCE, 1.1[1b] V vs SCE) is sufficiently lower than those of Fe^{III} in acetonitrile (1.1 V vs Ag/10^{-2}M Ag^{+}) [19] to permit its oxidation (doping).

We suggest that besides the oxidative condensation reaction (2) a side reaction occurs giving an insulating polymer consisting in thiophene unit with a high degree of oxygenation[20]. This side reaction should become predominant when the reaction (2) is thermodynamically defavoured. In Table I are reported the yields of the synthesis and conductivities of the products obtained by action of $Fe(ClO_4)_3$ on the different monomers; It comes clearly out that the efficiency of this reaction decreases when the oxidation potential of the monomer increases.

TABLE I

Compound	2,2'-Bithiophene	3-Methylthiophene	Thiophene	3-Bromothiophene
Yield of the polymerization reaction	88%	≥43%	31%	0
σ polymer $(\Omega \cdot cm)^{-1}$	17	7.10^{-3}	insulating	-
Anodic pic potentials (V) of monomers vs SSCE[1c]	1.32	1.86	2.06	2.10
Oxidation potentials(V) of monomers vs SCE[1b]	1.20	1.35	1.65	1.85

CONCLUSION

Action of the oxidant $Fe(ClO_4)_3$ on 2,2'-bithiophene appears to be a very convenient way to synthetise in a one step the corresponding polymer doped by the perchlorate anion. Furthermore, this poly(2,2'-bithiophene) presents a high conductivity (~ 17 $(\Omega \cdot cm)^{-1}$) and is obtained with a yield as high as 88 %. Nevertheless the efficiency of this method decreases drastically when the oxidation potential of the monomer increases.

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20. The origin of the oxygen is not obvious. As we work in a dry box ($O_1 < 1$ ppm) and/or with degazed solvent, residual water in the solvent and the water of crystallization of iron perchlorate seems the only way to supply oxygen.