

Thienyl and thenyl alkyl disulfides: monomers and polymers

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Résumé

Les thiényl et thényl alkyl disulfures sont synthétisés par réaction d'un mercaptan et d'un dialkylazodicarboxylate; l'addition d'un second mercaptan conduit au disulfure dissymétrique. Le disulfure cyclique, dithiéno[3,2-c:2',3'-e][1,2] dithiine est obtenu en plusieurs étapes à partir du 2,2'-dibromothiophène. Ces dérivés thiophéniques comportant un second système redox sont des précurseurs potentiels de polymères. La polymérisation chimique conduit à de nouveaux matériaux.

mots-clés : thiophène, disulfure, polymérisation, passivation.

Abstract

Thienyl and thenyl alkyl disulfides are synthesized by reaction between a mercaptan and dialkylazodicarboxylate; the addition of a second mercaptan gives the unsymmetrical disulfide. The cyclic disulfide, dithieno[3,2-c:2',3'-e][1,2] dithiin is obtained from the 2,2'-dibromobithiophene. These thiophene derivatives including a second redox system are potential precursors for polymers. Chemical polymerization affords new materials.

key-words : thiophene, disulfide, polymerization, passivation.

INTRODUCTION

The sulfur-sulfur bond is widely known in organic chemistry and biochemistry, specially because of the frequency of disulfides bridges in the structure of many proteins and enzymes. If symmetrical disulfides are numerous, their synthesis involving direct oxidation through radical dimerization of the corresponding mercaptans, unsymmetrical ones are not so easy to generate [1,2]. Most of the methods in the literature are not at all selective and often provide a mixture of disulfides with generally low yields, so the reaction between a mercaptan and sulfenyl thiocarbonate or sulfenyl chloride [3,4]. The thiosulfate procedure described by Alonso [5] is only available for unsymmetrical dialkyl disulfides.

RESULTS AND DISCUSSION

We need unsymmetrical disulfides with thienyl or thenyl groups to further polymerization reactions. These materials exhibit a range of remarkable solid state properties and offer technological potential, e. g. in the fabrication of molecular electronic devices and solid state batteries. We found that the addition of a mercaptan to diethylazodicarboxylate, as a strong hydrogen acceptor, giving the corresponding adduct which reacts with the second mercaptan (3-mercaptothiophene and 3-mercaptomethylthiophene) [6] is the best way to obtain the unsymmetrical disulfides [7].

One limiting point of this method was the formation of the symmetrical disulfide unspecified in the reference. To avoid this inconvenience we achieve the reaction in CCl_4 at low temperature, generally during one night at -18°C .



Scheme 1 *Conditions:* diethylazodicarboxylate 1 eq., mercaptan 1 eq. CCl_4 , -18°C , 3 days

Diisopropylazodicarboxylate can be used with the same reaction time of 3 days at -18°C , monitored by NMR. The N-alkanesulfenylhydrazodicarboxylates have been

isolated, purified and identified. In the second step, the mercaptan reacts with these adducts and leads after the nitrogen-sulfur bond cleavage to the unsymmetrical disulfide identified after chromatography purification.



Scheme 2 Conditions: **1** 1 eq. and the second mercaptan 1 eq., CCl₄ heating, stirring, 3 days

Table 1 N-Alkanesulphenylhydrazodicarboxylates **1** and Unsymmetrical disulfides **2**

	R ₁	R ₂	Scheme 1	Scheme 2	Yield %	R _F	n_D^{20}	Polymer σ (Scm ⁻¹) 10 ⁻⁵
1a *	n C ₄ H ₉		CCl ₄		73			
1b **	n C ₄ H ₉		-18°C		79		1.459	
1c **	n C ₁₂ H ₂₅		3 days		65		1.460	
2a	n C ₄ H ₉	Thienyl		CCl ₄	87	0.43	1.583	25
2b	n C ₁₂ H ₂₅	Thienyl		boiling	81	0.48	1.532	5
2c	n C ₄ H ₉	Thenyl		3 days	90	0.33	1.576	0.1
2d	n C ₁₂ H ₂₅	Thenyl			76	0.32	1.529	0.5

* azodicarboxylatediethyl derivative, ** diisopropyl derivative. All experiments were carried out under an Argon atmosphere.

Chemical polymerization was carried out at room temperature using a solution of FeCl₃ (4 eq.) in chloroform. The black precipitates obtained were washed with water then methanol. The d.c. conductivity measurements of the oxidized polymers were measured on compressed pellets using a two-probe technique. The conductivity data for the polymers are listed in Table 1.

The polymerization of the dithieno[3,2-c:2',3'-e][1,2]dithiin was achieved with Cu(ClO₄)₂·6H₂O in acetonitrile at 20°C to give a doped material, C₈H₂S₄(ClO₄)_{0.32}(H₂O)_{0.84} with a 0.32 doping level and a powder conductivity value of 10⁻² Scm⁻¹.

The electrochemical behaviour of disulfides and dithieno[3,2-c:2',3'-e][1,2]dithiin was investigated. Figure 1 shows the first and the second cyclic

voltammogram scans of 10^{-2} M disulfide **2a** solution in acetonitrile with 0.1 M LiClO_4 at room temperature. The first scan shows a typical aspect for disulfide oxidation with two irreversible peaks at 1.30 and 1.60 V [8]. In the second scan the electrochemical behaviour becomes quite different. The electrode is passivated as shown by a drastic diminution of current due to brown species observed at the electrode surface.

Figure 2 shows the three first cyclic voltammograms of dithieno[3,2-c:2',3'-e][1,2]dithiin. The first one exhibits four irreversible peaks at 0.98, 1.33, 1.52 and 1.72 Volt. During the second scan a passivation phenomena appears with a drop of the current intensity of each peak, the third scan completes the passivation. If the first scan is limited to a less high potential-at the value of the second anodic wave-we observe the reversibility of the two first peaks ($v_B=10 \text{ V}\cdot\text{s}^{-1}$) that reveals the stability of the generated cationic species.

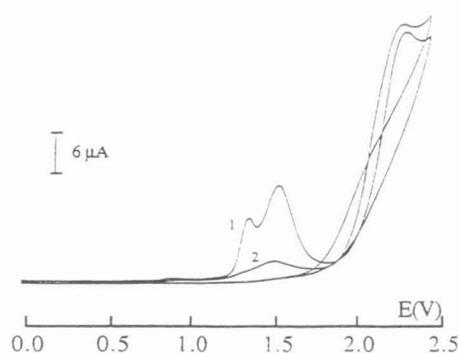


Figure 1 Cyclic voltammograms of **2a**
First and second scan. 10^{-2} M, CH_3CN ,
0.1 M LiClO_4 , Pt electrode, $v_B=100\text{mVs}^{-1}$

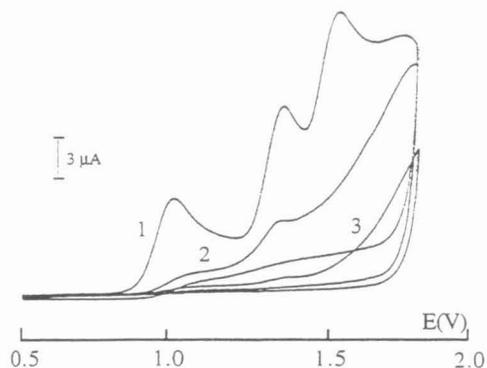


Figure 2 Cyclic voltammograms of dithieno
[3,2-c:2',3'-e][1,2]dithiin. First, second and third
scan.(same experimental conditions).

CONCLUSION

The disulfide function which is more easily oxidized than the thiophene ring could capture the radical cations produced by the oxidation of the thiophene ring and secondly prevents further reaction by passivating the electrode. So, we have now to investigate other systems containing thiophene rings with oxidation potentials lower than those of the disulfide function linked to these rings.

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