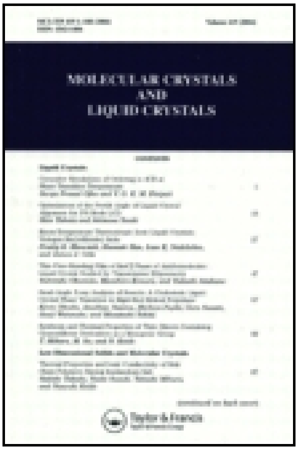

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New Aspects of the Solid-State Structures and Electrochemical Properties of Aromatic Poly(1,3,4-Oxadiazole)S

Burkhard Schulz [a]

[a] Forschungsgruppe Dünne Organische Schichten bei der Universität Potsdam, Kantstrasse 55, D/14513, Teltow, Germany

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NEW ASPECTS OF THE SOLID-STATE STRUCTURES AND ELECTROCHEMICAL PROPERTIES OF AROMATIC POLY(1,3,4-OXADIAZOLE)S

BURKHARD SCHULZ
Forschungsgruppe Dünne Organische Schichten bei der Universität Potsdam, Kantstrasse 55, D/14513 Teltow, Germany

Abstract A new aprotic solvent system for POD is described allowing to develop new possibilities for processing these polymers. In comparison to concentrated sulfuric acid where the β-form is formed in the precipitation process the aprotic solvent system gives the possibility to make the POD-α-structure directly. The β-form is characterized by a predominantly two-dimensional order whereas the α-structure is distinguished by a relatively high degree of three-dimensional order. The determination of both POD-supra molecular structure by IR- spectroscopy is also described. Additional, the electrochemical doping processes of poly(p-phenylene-1,3,4-oxadiazole) (p-POD) and the corresponding m-isomer are investigated. p-POD can easily be n-doped electrochemically and the resulting electronic structure supports a facile charge transport. In contrast m-POD was electrochemically inactive. The relationship between the molecular structures as well as the supra molecular structures and the electrochemicalical behavior is shortly discussed.

INTRODUCTION

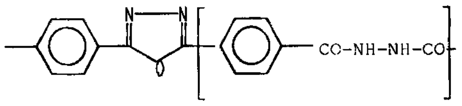
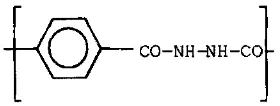
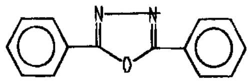
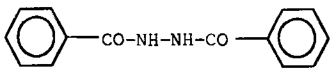
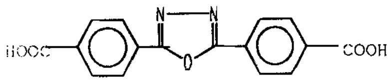
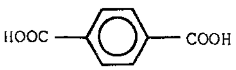
Aromatic poly(oxadiazole) fibers and films are known to have a combination of good properties, such as thermal and hydrolytic stability, strength, stiffness, fatigue resistance and a relatively low density. However, these polymers often have poor solubility in many solvents and are frequently processed from sulfuric acid solutions. Like other polymers containing aromatic and/or heterocyclic rings in their backbone, aromatic poly(oxadiazole)s exhibit minute but distinct and perceptible electronic conduction, although they are known as insulating polymers. It is known that polymer chains containing heteroaromatic repeat units can be doped electrochemically and that their p-doped forms are easier to obtain more stable and more conducting than their n-doped forms. It is of interest to find polymers with a similar structure and for which electrochemical n-doping is easy. It was demonstrated that this is true for thin p-POD films[1]. Thus, the combination of the thermostability and the electronic properties offers the possibility to construct new special polymer materials based on aromatic poly(oxadiazole)s.

SOLID STATE STRUCTURE

Recently, JENEKHE et al.[2] reported the solubility of aromatic heterocyclic rigid rod polymers such as poly(benzothiazole)s, poly(benzoxazole)s or poly(benzimidazole)s in aprotic organic solvents via reversible complex formation with Lewis acids. It was shown that the soluble polymer complex is not due to a π-electron charge transfer but a result of complexation at specific heteroatom donor sites. Nitroalkanes were used as aprotic solvents and $AlCl_3$ was the Lewis acid. We have shown for the first time that the later aprotic solvent system is also available for POD[3]. POD is also soluble in nitroethane or nitrobenzene containing Lewis acid. $FeCl_3$ can also be used as Lewis acid. As listed in the table, the oxadiazole ring is necessary for the dissolution process. If $AlCl_3$ is used two molecules of the salt are required per oxadiazole unit in the main chain. This is a hint that interactions exist between the nitrogen atoms of the oxadiazole ring and the Lewis acid molecule.

The new solvent system allowed to develop new possibilities for processing of aromatic poly(oxadiazole)s to fibers, films or membranes.

TABLE 1. The solubility of aromatic oxadiazoles and hydrazides in nitromethane/30%$AlCl_3$ at room temperature a)

soluble	unsoluble
	
	
	

a) All the compounds in this table are unsoluble in pure nitromethane

By processing POD from dilute solutions in concentrated sulfuric acid two structures distinguishable by X-ray diffraction can be obtained depending on the coagulation conditions. The β-form is caused by "hard" coagulation conditions characterized by a predominantly two-dimensional order. "Soft" coagulation creates the α-structure distinguished by a relatively high degree of three-dimensional order.

Systematic IR-spectroscopic investigations at thin POD-films have shown that there are significant differences between the α- and the β-form (see FIGURE I). While a sharp single band at 1568 cm^{-1} can be observed for samples of the α-form, the β-form mainly absorbs at 1584 cm^{-1}. Presumably these frequency positions are due to the different conformations of the two modifications. Also, the conversion from the β-form to the α-form in POD films by a treatment with 75% sulfuric acid can be easily observed by the increasing intensity of the IR-band at 1568 cm^{-1} [4].

It is important that in comparison to concentrated sulfuric acid the aprotic solvent system as has been described above gives the possibility to make α-POD directly in a simple way. Presumably by complexing of the oxadiazole unit with two molecules of $AlCl_3$ a certain pre-order in the arrangement of the polymer chains is realized prior to the following steps of coagulation and removal of the $AlCl_3$.

Successive and repeated dissolution and coagulation of the same POD-sample from sulfuric acid and nitromethane/$AlCl_3$ give reproducibly the β- and α-form respectively. Thus the observed differences in the infrared spectra cannot be caused by a change of the chemical structure.

Because the α-modification leads to higher tenacity of fibers there is a practical interest to form it directly by coagulation process. Therefore it is remarkable that by coagulation from the amidosulfuric acid reaction mixture the α-structure is formed .

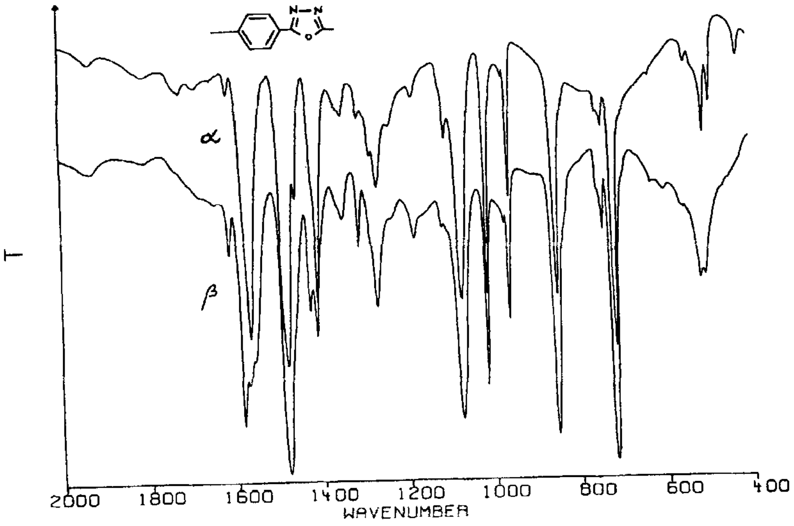


FIGURE I : FTIR - Spectra of α- and β- POD

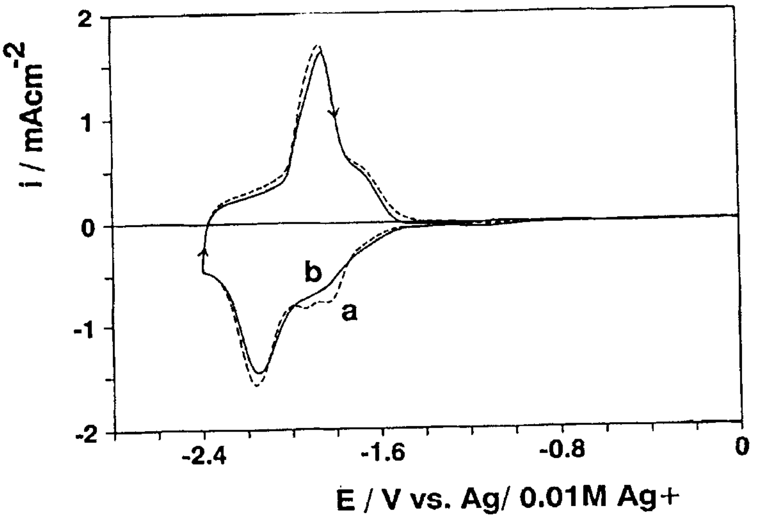


FIGURE II : Cyclic voltammogram of β- POD
(a: 1. run; b: 20. run)

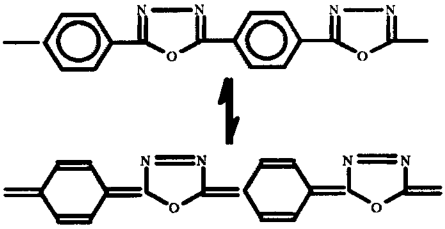
ELECTROCHEMICAL BEHAVIOUR

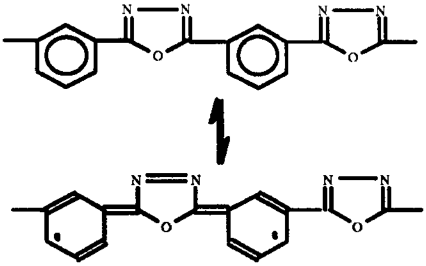
The structure of POD π-electron system suggests a possible pathway for charge delocalization and transport. Therefore we assumed that POD can be electrochemically doped and undoped either as coatings or as free standing films and fibers to yield an electrically conducting polymer.

In order to characterize the electrochemical properties of POD cyclic voltammograms and impedance spectra were measured in two different electrolyte systems. In addition UV-absorption of neutral and n-doped POD was measured.

The cyclic voltammograms in FIGURE II show that in 0.1 M $(Bu_4N)ClO_4$ the electrochemical reduction of a thin POD film on a glassy carbon is a reversible process ($Q^{ox}/Q^{red} \approx$ 0.8-1.0). In the range of 2×10^4-7×10^4 g/mol the molar mass of POD did not have any influence on the voltammograms. The number of electrons transferred in the process was found to be about 0.5 per POD repeat unit. The data exhibit a prominent cathodic peak at -2.11 V and a corresponding anodic peak at -1.82 V. The difference in peak potentials is large (ΔE_p=290±30mV) which shows a remarkable energetic stabilization of the conducting system. Large ΔE_p-values are commonly observed in the electrochemistry of conducting polymer films and are usually attributed to redox-related structural reorganization processes within the films. The reduction of POD is accompanied by a change in color from yellow to dark red which is completely reversed upon oxidation. In comparison, the UV-spectra of the neutral and n-doped films shows a bathochromic shift of the edge of the absorption plateau from 400 nm to 480 nm. This effect shows that true doping takes place, e.g., the electrons penetrating in the reduction process are able to interact with the polymer backbone resulting in new energetic states in the POD . On the other hand, the isomeric POD (using isophthalic acid as monomer) shows in the measured range (0-2.7V) no electrochemical redox processes. That means, the delocalization of π-electrons is more disturbed in the meta-POD.

No differences were observed in the electrochemical behavior of the α- and β-structures. That means, the higher order of the α-form does not improve the doping process.





The AC-impedance method was used to estimate the apparent diffusion coefficient (D_{app}) of Bu_4N^+ counter ions in POD films. The values obtained are of the order 10^{-7} cm^2s^{-1}.

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