

## SEMICONDUCTING POLYMERS WITH ROTAXANE ARCHITECTURE

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Semiconducting polymers with rotaxane architecture containing non covalently bound cyclodextrins in the main-chains were synthesized by solution polycondensation of terephthaldehyde / $\alpha$ - or  $\beta$ -cyclodextrin adduct with 1,4 phenylenediamine and blocking of the chain ends with a bulky aromatic amine, p-aminophenyl triphenylmethane. As compared with the model linear polymer synthesized in the absence of cyclodextrins, these polymers are more hygroscopically, more soluble in polar solvents such as DMF and DMSO and their IR and  $^1\text{H-NMR}$  spectra show the presence of macrocycles in the polymer structure.

*Keywords:* Aromatic azomethines, Main-chain polyrotaxane, Semiconductor, Electrical conductivity

### 1. Introduction

Electrically conducting polymers have attracted considerable attention in the last years due to both theoretical aspects and practical applications. Since all conducting polymers have a very low solubility and processing capacity, limited thermal and chemical stability, unsatisfactory mechanical properties, investigations are directed towards improving these characteristics, without sacrificing final electrical properties. Several approaches have been attempted to surpass these disadvantages namely: a) introduction of bulky substituents in the traditional monomers, b) copolymerization, and c) preparation of composite materials.

The introduction of bulky substituents on the rigid polymer backbone can significantly modify chain flexibility and improves polymer solubility. However, the processability is achieved by decreasing the conjugation and therefore the conductivity of the polymer. The same effect is observed by copolymerization. Homogeneous macromolecular composites formed from a conjugated polymer (a rigid-rod macromolecule) and a saturated polymer (a random coil macromolecule) are unlikely to be obtained, mainly from two motifs: thermodynamic considerations and the tendency of components to segregate.

An alternative strategy for improving processability of the conducting polymers is to adopt a rotaxane architecture consisting of macrocyclic molecules whose cavities are pierced by linear conjugated polymers. These structures having many cyclic molecules threaded on a linear macromolecule can be considered as molecular composites. In this case the segregation tendency is diminished because the partners are constrained to maintain their positions. This unusual architecture will confer solubility and processability and environmental stability for conducting polymer. The lack of chemical bonds between the macrocyclic and linear components means that conjugation in polymer chain and final conductivity are not altered.

Such architecture can be viewed as a molecular electrical wire, formed from a conducting polymer (core) protected from shorting by a coating of insulating compound consisting from a cyclic molecule (Fig. 1), all being at molecular level.

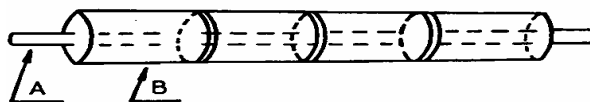


Fig. 1. Molecular insulated electrical wire - an ideal polyrotaxane: A-Conductive core (conducting polymer) B-Insulated shell (macrocyclic compound).

Polymeric rotaxanes or polyrotaxanes, in the last years have attracted growing interest due to their unique molecular architecture and properties [1-5]. Polyrotaxanes represent a relatively recent addition to the repertoire of polymer architecture [6]. Most of the polyrotaxanes already reported contain ( $\alpha$ -,  $\beta$ - or  $\gamma$ -) cyclodextrin as macrocyclic component that threads onto backbone or side chain polymers. Cyclodextrins ( $\alpha$ -,  $\beta$ - or  $\gamma$ -), cyclic oligomers of amylase with six, seven or eight glucose units have a shape like a doughnut with a hydrophobic interior able to form inclusion compounds with various substances [10]. Based on this capacity various low molecular weight rotaxanes have been obtained and used in polycondensation or polymerisation reactions to obtain polyrotaxanes. All synthesized polyrotaxane structures have showed a distinct change of solubility, thermal and mechanical properties relative to the simple linear backbone of the polymer.

Poly(azomethine)s, also known as poly(Schiff base)s have been extensively studied due to their interesting properties such as thermal and mechanical resistance, environmental stability, semiconducting or optical properties and ability to form metal chelates [11]. The azomethine linkage can be formed by a polycondensation reaction between an aromatic/aliphatic diamine and a dialdehyde or diketone partner. Aromatic polyazomethines are insoluble in common organic solvents and precipitate from the reaction medium before obtaining high molecular weight polymers. Even poly(azomethine)s containing aliphatic spacers between aromatic rings have maintained their poor solubility and good thermal stability.

Poly(azomethine)s with rotaxane architecture have synthesized by Gibson et al [12] via polycondensation of bisphenols having a preformed azomethine linkage with diacid chlorides in the presence of a crown ether.

In a previous paper we have reported the synthesis of a poly(azomethine) with rotaxane structure by polycondensation of 1,6 hexamethylenediamine/ $\alpha$ - or  $\beta$ -cyclodextrin adduct with terephthaldehyde [13]. The goal of this communication is to present the synthesis of another main-chain polyrotaxane based on wholly poly(aromatic azomethine)s as linear polymer and  $\alpha$ - or  $\beta$ -cyclodextrin as macrocyclic compound. The next step in our researches is the study of electro-optical properties of pristine and doped polymers.

## 2. Experimental part

### 2.1 Materials

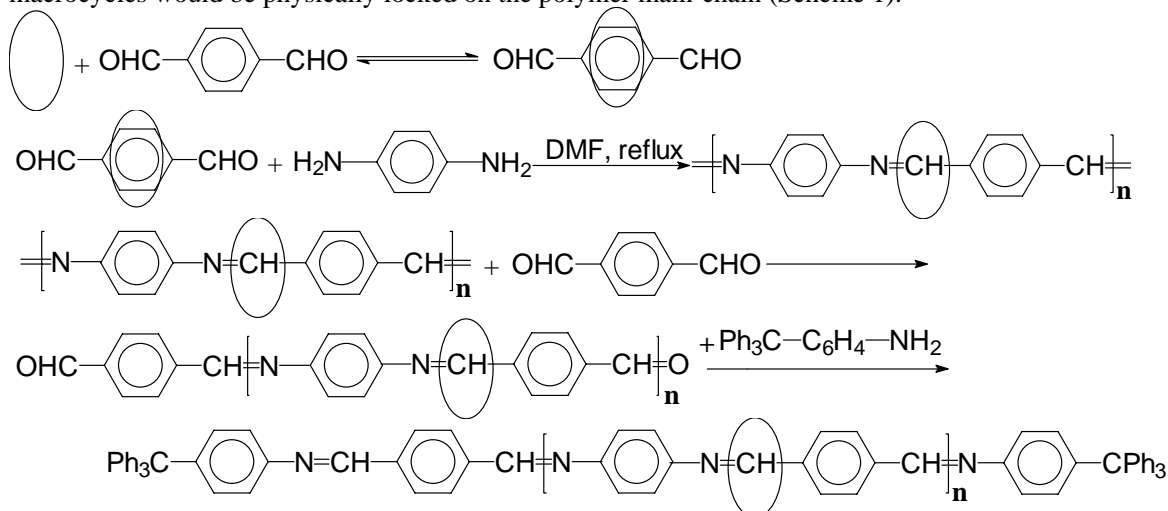
$\alpha$ - and  $\beta$ -cyclodextrin (Merck), terephthaldehyde (Fluka) and *p* toluenesulfonic acid (Aldrich) are commercially products and were used as received. 1,4 phenylenediamine (Fluka) was recrystallized from benzene just before use. Barrier compound, 4 aminophenyl triphenylmethane was synthesized from triphenylmethane chloride and aniline hydrochloride according to the published method of Witten et al. [14]. N,N-dimethylformamide (DMF) (Fluka) and toluene were dried on  $\text{CaH}_2$  and distilled under reduced pressure and deposited in nitrogen atmosphere.

### 2.2 Characterization

The infrared spectra were obtained on a SPECORD Carl Zeiss Jena Infrared spectrometer (KBr pellets).  $^1\text{H}$ -NMR spectra were registered on a JNM-C-60 HL, 60 MHz spectrometer using  $\text{DMSO-d}_6$  as solvent. The chemical shifts( $\delta$ ) are recorded in ppm and were referenced to the solvent value (2.50 ppm).

### 3. Results and discussion

The synthesis of polyrotaxanes with poly(azomethine) backbone has been performed by solution polycondensation of terephthalaldehyde/  $\alpha$ - or  $\beta$ -cyclodextrin adduct with 1,4 phenylenediamine and the capping of the polymer chain ends with bulky barriers so that the threaded macrocycles would be physically locked on the polymer main-chain (Scheme 1).



Scheme 1: Synthesis of semiconducting polymer with rotaxane architecture.

#### 3.1 Synthesis and characterization of terephthalaldehyde $\alpha$ - or $\beta$ -cyclodextrin adduct

Terephthalaldehyde is soluble in warm water, while cyclodextrin is soluble even in cold water since all of the hydroxyl groups are situated on the outer surface of the macrocycle. However, when terephthalaldehyde was added into an aqueous solution of cyclodextrins at room temperature followed by heating at about 60°C a turbid solution was obtained and a white bulky precipitate resulted when the reaction mixture was cooled at room temperature. This product was filtered, washed with water and dried. The 1:1 stoichiometry was proved by the <sup>1</sup>H-NMR spectrum of the adduct. Infrared spectrum of the adduct (Fig. 2) shows specific absorption peaks at 3370 cm<sup>-1</sup> (OH stretching H-bonded), 2930 cm<sup>-1</sup> (OH stretching), 1627 cm<sup>-1</sup> (OH bending), 1368 cm<sup>-1</sup> (OH deformation), 1243 cm<sup>-1</sup> (OH bending), 1156 cm<sup>-1</sup> (COC stretching and OH bending), 1079 and 1032 cm<sup>-1</sup> (COC stretching) characteristic for cyclodextrins, together with the peaks at 1700 cm<sup>-1</sup> (C=O), 1600 cm<sup>-1</sup> (C=C) and 700-900 cm<sup>-1</sup> (CH aromatic) attributed to terephthalaldehyde.

#### 3.2 Synthesis and characterization of polymers

The adduct with  $\alpha$ - or  $\beta$ -cyclodextrin was polycondensed with 1,4 phenylenediamine using DMF as solvent and p-toluenesulfonic acid as catalyst for 28 hours. The polycondensation reaction needs a very long time because by inclusion of terephthalaldehyde inside of cyclodextrins, aldehyde groups are more less accessible to diamine attack. At the end of polycondensation a slight excess of terephthalaldehyde (~ 2%) was added and aldehyde chain ends were coupled with a bulky monofunctional aromatic amine, 4 aminophenyltriphenyl methane. The polymer remained partially in solution during the reaction, but it precipitated by cooling at room temperature. After cooling the polycondensation mixture at room temperature, the DMF insoluble fraction was separated by filtration, dried and then washed with large quantities of water, acetone and methanol to remove the free macrocycles. The polycondensation yield was approximately 38%. The polymer was fractionated in two fraction: one insoluble in warm DMF and other one soluble in DMF and insoluble in water.

The IR and <sup>1</sup>H-NMR analyses were performed for the DMF soluble fraction of the polymer.

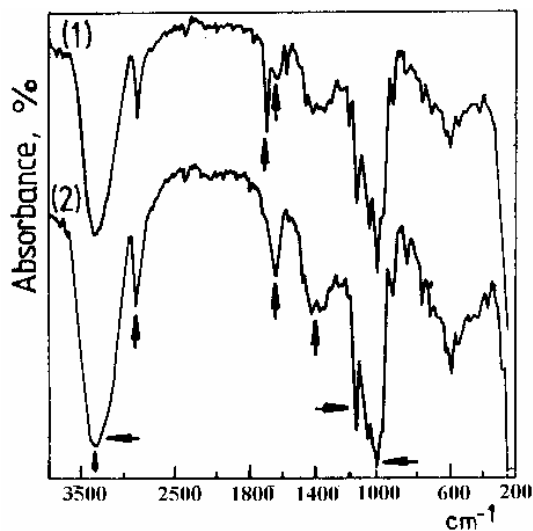


Fig. 2. IR spectra of : (1)  $\beta$ -cyclodextrin / terephthalaldehyde adduct; (2)  $\beta$ -cyclodextrin.

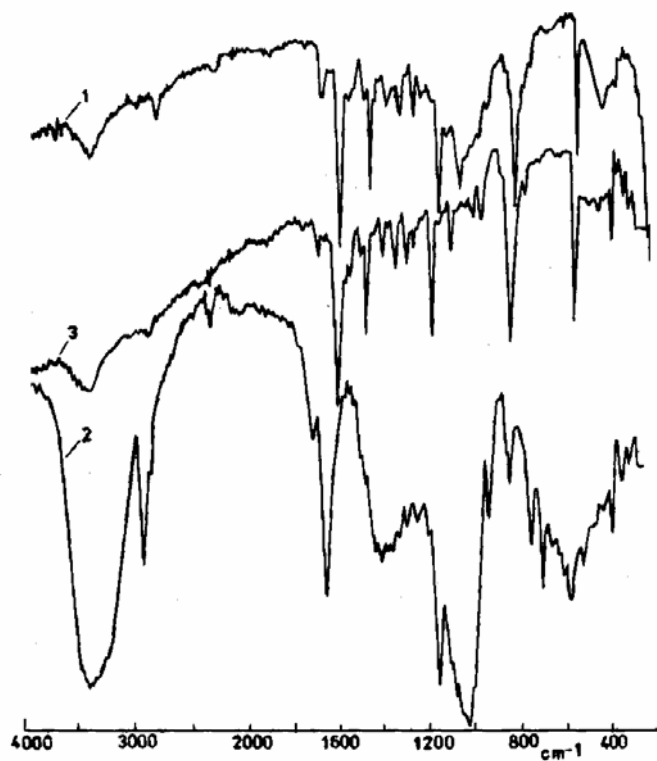


Fig. 3. IR spectra of: (1) polymer without rotaxane architecture; (2) polymer with rotaxane architecture DMF – soluble fraction; (3) polymer with rotaxane architecture DMF-insoluble fraction.

Fig. 3 presents IR spectra of polymers with classic and rotaxane architecture. The C=N double bond stretching absorption ( $1630\text{ cm}^{-1}$ ) is present in all polymers and it is characteristic to azomethine linkage. The absorptions characteristic for  $\alpha$ - or  $\beta$ -cyclodextrin (3370, 2926, 1627, 1368,

1243, 1156, 1080 and 1032  $\text{cm}^{-1}$ ) are present in spectra of soluble (strong) and insoluble (very slight) polymer fraction with rotaxane architecture, and absent in the spectrum of the polymer synthesized in the absence of cyclodextrins. The intensity of the peaks characteristic for  $\alpha$ - or  $\beta$ -CD remains unchanged after two precipitations (from DMF) and washings with water.

Fig. 4 presents  $^1\text{H}$ -NMR spectrum of the polymer (DMF-soluble fraction). The aromatic protons from phenyl groups appear at about 7 ppm, while protons of  $\text{CH}=\text{N}$  unit appear at about 7.9 ppm. The signals situated in the range 3-6 ppm are attributed to the protons from cyclodextrins. These signals are weak, their interpretation being very difficult. The appearance of such signals is probably caused by the high conjugate structure of the polymer and the interactions that can occur in solution between the polymer and the solvent at certain temperature. A more clear separation between these peaks is observed if the same sample is scanned after 10 days (Fig. 4, curve 1). We believe that this is due to the relative freedom of move along polymer backbone and aggregation of the cyclic species without dethreading by keeping the rotaxane polymer in solution. A similar behaviour was observed by Gibson et al. [15] for a series of polyesters rotaxane with crown ethers as macrocycles.

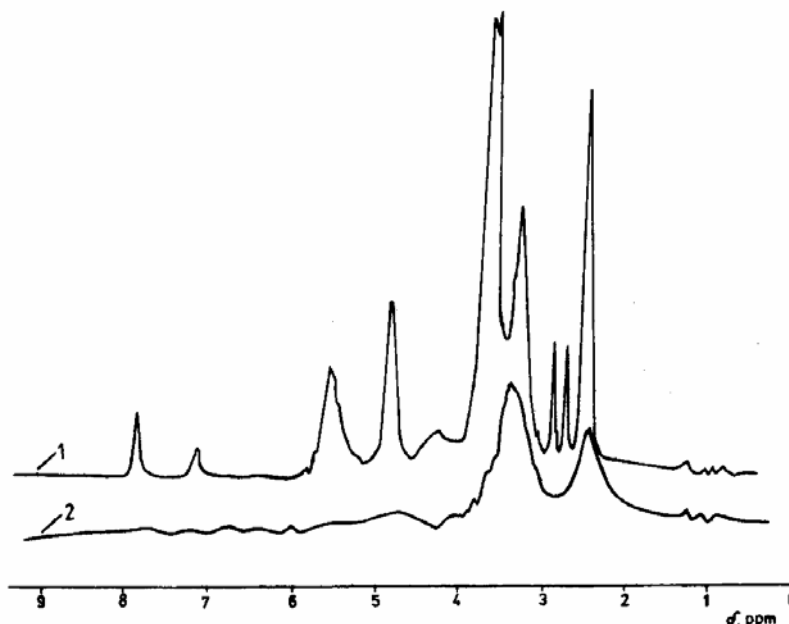


Fig. 4.  $^1\text{H}$ -NMR spectra (DMSO- $d_6$ , 70°C) of polymer with rotaxane architecture: (2) DMF-soluble fraction, fresh solution and (1) after 10 days.

The polymer without the rotaxane architecture is insoluble in common organic solvents and it can not be characterized by  $^1\text{H}$ -NMR method.

The number-average molecular weight ( $M_n$ ) of the polymer determined by gel permeation chromatography is 18600 g/mol and is much higher than the expected values for the polyazomethines. Usually, the number-average of most polyazomethines prepared by solution condensation fall in the 500-2000 g/mol range [11] and is attributed to the insolubility of the polymer chains in the polycondensation medium. In our experiments the polymer remains in solution during the polycondensation and this behaviour allows the attainment of higher molecular weights.

#### 4. Electrical conductivities

Electrical conductivities of the synthesized polymers are lower than  $5.6 \times 10^{-9} \text{ S} \times \text{cm}^{-1}$ . Doping of these polymers is performed both in solution and solid state using iodine as acceptor. In solid state doping is carried out by exposing the polymer powders to dopant vapours (760 mm Hg, room temperature) and subsequently to  $10^{-2}$  mm Hg for 30 minutes to remove excess dopant. The doping level is determined by weight measurement.

The conductivity of the powders doped with iodine is situated in the range of  $10^{-7}$ - $10^{-6}$  S cm<sup>-1</sup>, and it was measured by the standard four point probe. The electrical conductivity of the iodine doped polymers is similar as compared to other polymers noncontaining rotaxane architecture. Therefore, the presence of the macrocycles permits the obtaining of soluble polymers, but has not an unfavourable effect on polymer electric properties.

## 5. Conclusion

Semiconducting polymers containing  $\alpha$ - or  $\beta$ -cyclodextrin rings threaded on the main chain polymer can be synthesized by solution polycondensation of the terephthaldehyde/  $\alpha$ - or  $\beta$ -cyclodextrin adduct with 1,4 phenylenediamine and blocking of the chain ends with a bulky barrier. As compared with the model linear polymer without rotaxane architecture, this polymer is more hygroscopically and soluble in polar solvents and spectral data support the presence of cyclodextrins in the polymer composition. Therefore, we conclude that this approach will offer a broadening of possible application.

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