# SYNTHESIS AND CHARACTERIZATION OF A NEW CONJUGATED POLYAZOMETHINE

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Polyazomethine with rotaxane architecture was synthesized by polycondensation of terephtalaldehyde/β-cyclodextrin adduct with 2,7-diaminofluorene. The IR, ^{1}H-NMR, GPC and DSC data evidenced the presence of cyclodextrin in the polymer chain. As compared to the polymer obtained in the absence of β-cyclodextrin, the polyazomethine rotaxane is more hygroscopic and more soluble in polar solvents such as DMF and DMSO, while the electroconducting properties of polyazomethine rotaxane are similar to those of its polyazomethine analog.

## INTRODUCTION

Much attention has been directed last years toward the construction of micrometer to nanoscaled architectures from bulk materials by using the new concepts of host-quest chemistry, molecular recognition and supramolecular science.

Polymeric polyrotaxanes, are of interest not only because of their unique structures, but also for their implication in the construction of self-assembled materials and of more complex systems with interesting properties and functions. Polyrotaxanes are novel molecular composites obtained as a result of threading of linear macromolecules through a macrocycle with no chemical bonding between the cyclic and the linear components. They are typical examples of *host-guest* complexes.[1-7]

Cyclodextrins (CDs) which are a class of cavity containing, non-reducing oligosaccharides (comprised of six, seven or eight glucopyranose rings and known as α-, β- and γ- CDs, respectively) are the most used cyclic components. Their ability to host a wide variety of guest molecules and to form three-dimensional complexes is already a known and fascinating structural characteristic. The affinity of CDs to form inclusion complexes is governed by the non-covalent bonding forces between the molecules. The driving force of inclusion is a sum of hydrofobic interactions, van der Waals forces, London dispersion forces, hydrogen bonding, etc.

Studies on azomethine-based polymers have been conducted by many research groups and a great diversity of structures was obtained. It is well-known that fully aromatic Schiff base polymers are high performance polymers presenting high thermal stability, good mechanical strength and semiconducting properties. Their poor solubility makes difficult the obtaining of high molecular weight polymers and the determination of their structural and macromolecular features. Moreover, the transition temperatures of conjugated polyazomethines are situated in many cases over the decomposition limit and their technical applications are strongly limited by their sensitivity to acidic hydrolysis and thermal exchange reactions between different azomethine groups. The inclusion of polyazomethines in rotaxane architecture was already proposed as a useful method to improve their processability.[8-13] Generally, polyazomethines are synthesized by polycondensation reactions, method that has some disadvantages, among them being a high reaction temperature and the use, in some cases, of specific catalysts.

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The paper describes the synthesis and characterization of a soluble aromatic polyazomethine, starting from terephthalaldehyde/β-cyclodextrin (β-CD) adduct and 2,7-diaminofluorene. The resulting fluorene containing azomethine polymer would be expected to show not only high thermal and thermo oxidative stability, but also good semiconducting properties. Preliminary results indicate that this material possesses multifunctional properties and it is a promising candidate for photonic applications.

## RESULTS AND DISCUSSION

A new aromatic polyazomethine with rotaxane architecture was synthesized by solution polycondensation of terephthalaldehyde/β-CD adduct with 2,7-diaminofluorene according to Scheme 1. A polymer without rotaxane architecture was synthesized under the same experimental conditions by polycondensation of 2,7-diaminofluorene with terephthalaldehyde.
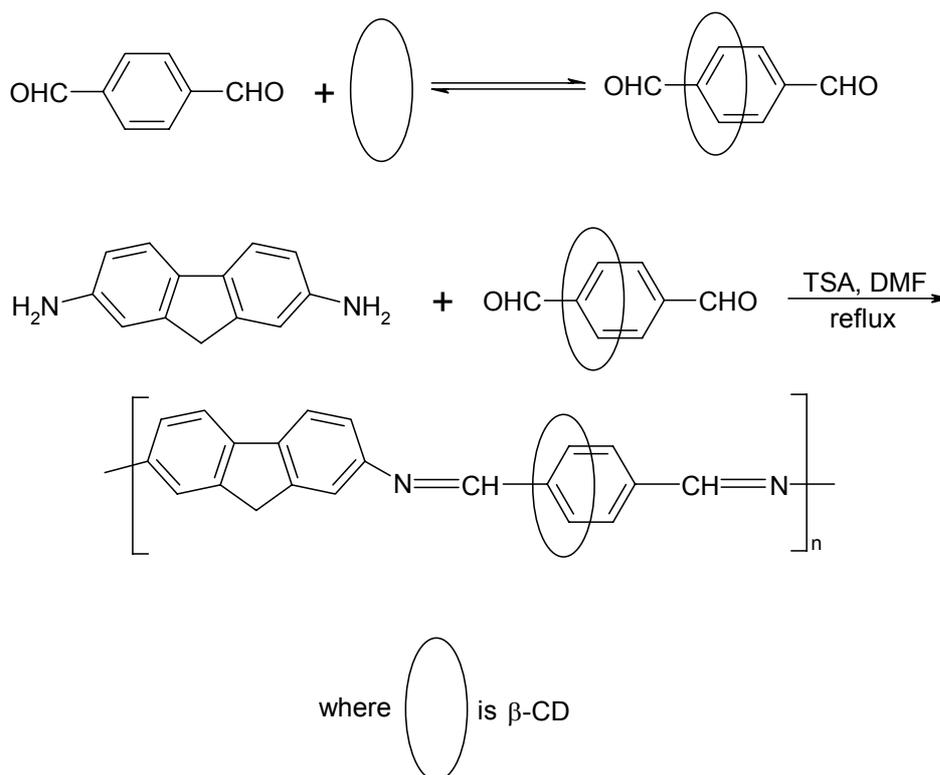


Scheme 1 – Synthesis of polyazomethine/β-CD rotaxane.

### Characterization of polymers

The structures of polyazomethine and of polyazomethine rotaxane were determined by IR and NMR analysis.

The infrared spectrum of the polyazomethine rotaxane shows specific absorption peaks at 3370 cm$^{-1}$(OH stretching H-bonded), 2930 cm$^{-1}$ (OH stretching), 1627 cm$^{-1}$(OH bending), 1368 cm$^{-1}$ (OH deformation), 1243 cm$^{-1}$(OH bending), 1156 cm$^{-1}$(COC stretching and OH bending), 1079 and 1032 cm$^{-1}$(COC stretching) characteristic for β-cyclodextrin. After a second reprecipitation in water of the rotaxane solution in DMF, the intensity of the characteristic bands of cyclodextrin remained unchanged. The characteristic absorption

of azomethine linkages (1618 cm$^{-1}$, C=N stretching vibration) and the absorption characteristics of fluorene rings (798, 1413, 1660 cm$^{-1}$) are present in IR spectra of both polymers.

The $^1$H-NMR spectrum (DMSO-d$_6$, 400 MHz, 23$^0$C) of polyazomethine rotaxane is presented in Figure 1. The polymer shows signals at 7.96 ppm attributed to the –CH=N- proton and 7.86 ppm (2H, d), 7.49 ppm (2H, d), 5.87 ppm (2H, d) attributed to fluorene and phenylene ring. The signals situated in the range 3.0-5.7 are attributed to the protons of β-CD. The amount of β-CD incorporated in the polymer, as calculated from $^1$H-NMR analysis by using the integration ratio of CH=N- to CD protons is about 0.7 macrocycle molecules to one polymer repeating unit, lower

than expected. Probably, during the polycondensation reaction, a part of CD macrocycles are dethreaded from the terephthalaldehyde molecules. Thus, the polymer chain contains complexed and non complexed structural units.
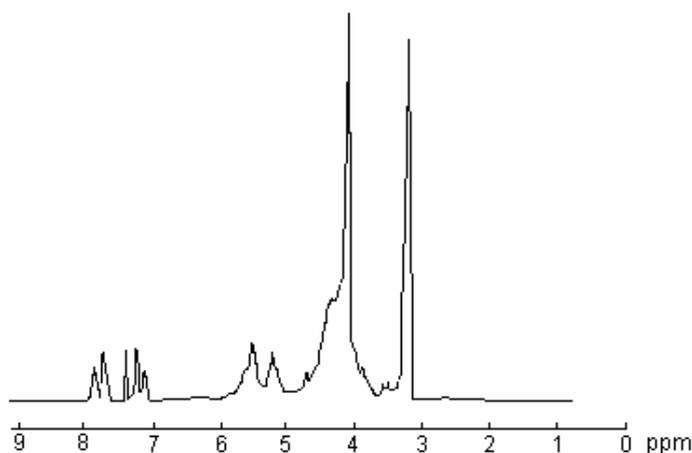


Fig. 1 – $^1$H-NMR spectrum of polyazomethine/β-CD rotaxane.

The polymazomethine rotaxane showed marked contrasting properties as compared to the polymer without rotaxane architecture. The polyazomethine rotaxane is soluble in hot DMF while the polyazomethine itself shows a poor solubility. While the polymer obtained in absence of β-CD is a yellow-orange colored product, the polyazomethine/β-CD rotaxane is a light-yellow product.

A number-average molecular weight, Mn, of 15600 g mol$^{-1}$ was determined for polyazomethine rotaxane by gel permeation chromatography, a much higher value than that expected for the polymer without rotaxane architecture, insoluble in DMF. The GPC curve (Figure 2) shows nearly unimodal distribution, denoting the presence of a unique structure, i.e. a rotaxane polymer and not a physical mixture of the polyazomethine and CD.
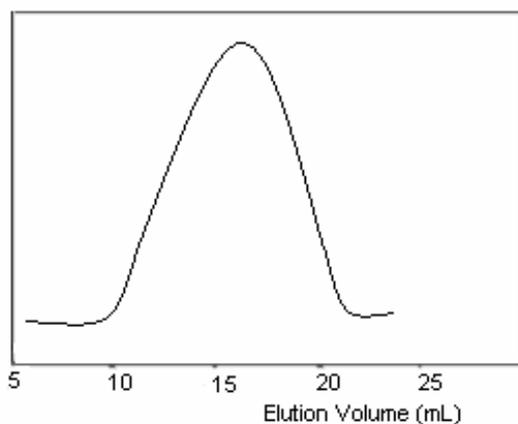
The thermal stability of polyazomethine and of polyazomethine/β-CD rotaxane was determined by TGA. As revealed by the weight loss curves in Figure 3, both polymers present three stages decomposition processes within the intervals 200-300$^0$C, 450-500$^0$C and 500-700$^0$C, but the weight loss of the rotaxane is lower as compared to the non-complexed polyazomethine. Moreover, the first decomposition temperature of the rotaxane is 310$^0$C, somewhat higher than that of β-CD (300$^0$C), denoting a thermal stabilization of the macrocycle by the polyazomethine chain.

Pure polyazomethine and polyazomethine/ β-CD rotaxane showed similar conductivities of 5.6 10$^{-11}$ S cm$^{-1}$ and 4.2 10$^{-11}$ S cm$^{-1}$, respectively. After doping, the conductivities of polymers were increased, but the conductivity of polyazomethine rotaxane (1.8 10$^{-10}$ S cm$^{-1}$) was about two orders of magnitude lower than that of polyazomethine (8.9 10$^{-9}$ S cm$^{-9}$).



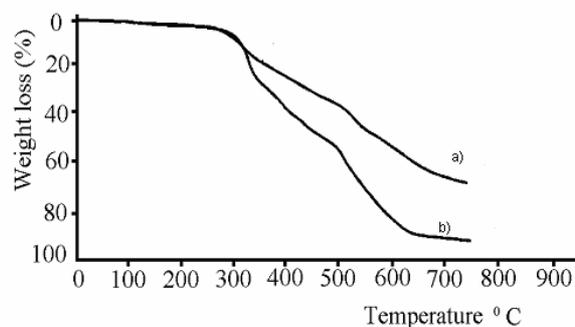Fig. 2 – GPC curve of polyazomethine/ β-CD rotaxane.



Fig. 3 – Weight loss curves of (a) polyazomethine/β-CD rotaxane; b) polyazomethine.

## EXPERIMENTAL PART

### Materials

β-Cyclodextrin (Merk), terephthalaldehyde (Fluka), 2,7 diaminofluorene (Aldrich) and p-toluenesulfonic acid (Aldrich) are commercially products and were used as received. N,N-dimethylformamide (DMF) (Fluka) and toluene were dried on $CaH_2$ and distilled under reduced pressure.

### Polymer synthesis

Into a 50 mL three-neck round bottom-flask equipped with a reflux condenser, a gas inlet-outlet, a Dean-Stark trap and a magnetic stirrer, 0.908 g (0.8 mmol) β-CD and 0.107 g (0.8 mmol) terephthalaldehyde in 5 mL DMF were placed. The reaction mixture was heated and stirred at $50^0$C for 14 h. After 6 h, the mixture became turbid and this is the first observation that β-CD formed a complex with terephthaldehyde. To assure the completeness of the adduct formation the mixture was stirred at room temperature, under a nitrogen atmosphere for 2 days. Then 0.158 g (0.8 mmol) 2,7-diaminofluorene dissolved in 10 mL DMF was added and the solution were stirred for additional 12 h at room temperature. Finally, two crystals of p-toluenesulfonic acid dissolved in 1 mL DMF and 4 mL toluene were added and the polycondensation was started by heating the reaction mixture to reflux temperature. The reaction was carried out for 40 h with continuous removal of water by azeotropic distillation with toluene. After cooling at room temperature, the polymer was separated by precipitation in water which is known as a good solvent for the macrocycle, but which is a non-solvent for the polymer. A turbid solution was obtained by adding water and the polymer precipitated in time. The polymer was separated by filtration, washed with methanol and acetone and dried. Yield = 46.5 %. The polyazomethine without rotaxane architecture was synthesized under the same experimental conditions by polycondensation of terephthalaldehyde and 2,7-diaminofluorene in the absence of β-CD. Most of the orange-yellow polymer precipitated during the polycondensation reaction. This polymer was washed with methanol. Yield = 68.9 %.

### Doping of polymers

Doping of the polymers was performed in solid state by exposing the polymer powder to iodine vapors (760 mm Hg, room temperature). The iodine excess was subsequently removed in vacuum ($10^{-2}$ mm Hg) for 30 minutes. The doping level was determined by weight measurement. The polyazomethine rotaxane proved an affinity (absorbed amount) of ca. 1.3 wt. % toward iodine.

### Characterization methods

^{1}H NMR spectra were obtained on a Bruker Avance 400 MHz spectrometer in DMSO-$d_6$, at 23 $^0$C. The relative molecular weights were determined by gel permeation chromatography (GPC) in DMF as solvent and using a Polymer Laboratories (PL-EMD 950) instrument equipped with an evaporative mass detector. Polystyrene standards were used for calibration. The infrared spectra were obtained on a SPECORD Carl Zeiss Jena device (KBr pellets). The thermal analysis was performed on MOM (Budapest-Hungary) thermobalance apparatus, in air and a heating rate of $14^o$C/min. The conductivity measurements were performed on disc-shaped samples (13 mm diameter) prepared by pressing the polymer powder in a mould under a pressure of $10^5 N/cm^2$. The discs were provided with vacuum evaporated silver electrodes of circular form. In order to remove current leakages on the surface, the electrodes had a diameter of only 10 mm and were centrally placed on both sides of the disc. The conductivity measurements were carried out in dry $N_2$ at normal pressure.

## CONCLUSIONS

A new aromatic polyazomethine having rotaxane architecture in the main chain has been prepared and compared with classical aromatic polyazomethine, without rotaxane architecture. Incorporation of β-CD into an aromatic polyazomethine backbone gave an easily soluble and processable compound. The polyazomethine rotaxane is more hygroscopic and soluble in polar solvents. The luminescent properties of new material are under investigation.

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