SYNTHESIS OF INSULATED MOLECULAR WIRE : CONFORMATION OF A POLYROTAXANE (SEMI-CONDUCTING-POLYMERS COMPLEXED INSIDE SHEATHS OF CYCLODEXTRINS) : DETERMINATION OF THE MASS AND THE NUMBER OF CYCLODEXTRINS PER DIMER.

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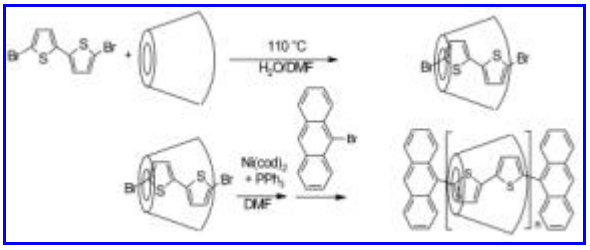
One of the focuses of our laboratory is to synthesize insulated molecular wires by using semi-conducting polymers complexed in insulated sheaths of b-cyclodextrins.

The most promising synthesis in which a polythiophene (semi-conducting polymer) is complexed in β-CD sheath is pictured below:



We have isolated the complex, polymerized it[1] and then selected the molecules which are soluble in water. We have characterized these wires with MALDI TOF which is a mass spectrometer using a laser to ionize a matrix containing our sample, and small angle neutron scattering performed at LLB in 2001-2002.

MALDI TOF measurements (figure 1) only yield the mass of the polymer chain because cyclodextrin molecules are destroyed by the ionization of the laser. From this analysis, it is apparent that we have synthesized a **water soluble** polythiophene with a **degree of polymerization of 24**. It is interesting to note that usually polythiophene is not soluble in any solvent beyond a polymerization degree of 6.

To gain additional information about the size, shape and mass of the molecular wire, we performed neutron scattering measurements at LLB (exp. N° 6205) (figure 2). We fit the data from SANS measurements of this PT-Pr with a cylindrical model with the following dimensions: diameter 8.3 Å, length 75 Å. To be soluble in water, the polymer must be complexed in a cyclodextrin sheath. It will be interesting to estimate the number of cyclodextrins that contribute to the sheath.

By calculating the polyrotaxane mass from SANS experiments and extrapolating to q = 0, we have learned that some β-CD escaped from the polymer during the polymerization resulting in a Polyro-taxane composed of 24 thiophene units complexed in only 7 β-CD. To confirm this hypothesis, we then fit the experimental data with a polyrotaxane model composed of a 24 monomer units complexed in 7 β-CD [2].

We are now confident that the polyrotaxanes contain less than one cyclodextrin per dimer of thiophene. This information, obtained via SANS is a major contribution to our understanding of the solubility of the wire and the doping necessary for upcoming measurements of the conductivity of this insulated molecular wire. In the future, this type of measurement will help us to control the degree of insulation of the wire, which is fundamental to measurements of conductivity.

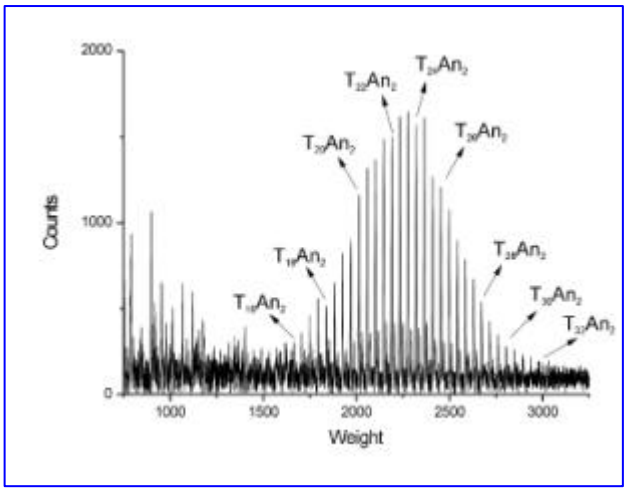


Figure 1. Maldi-TOF spectrum of the polythiophene polyrotaxane in a Dithranol matrix..

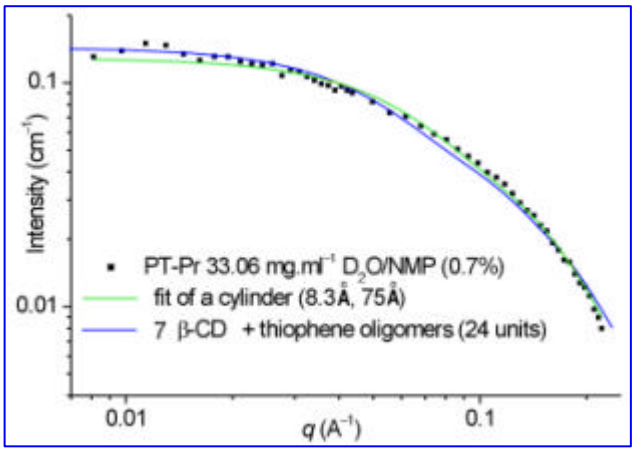


Figure 2. Small angle neutron scattering measurements on polythiophene polyrotaxane.
We can reach the number of cyclodextrin by extrapolating the mass at q=0 and by fitting with models

References

[1] T. Yamamoto, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z.-H. Zhou, Y. Nakamura and T. Kanbara, *Macromolecules*, 25, (1992**)** p. 1214

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[3] M. van den Boogaard, PhD dissertation **2002**, University of Groningen, NL, *Cyclodextrin-containing supramolecular structures*, http://www.ub.rug.nl/eldoc/dis/science/m.van.den.boogaard/