CONJUGATED POLYMERS WITH ROTAXANE ARCHITECTURE

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The review is devoted to polymers with rotaxane architecture in the main or side chain having cyclodextrins or crown ethers as host molecules and semi- or conducting polymers as guests. Due to their architectural differences as compared to conventional polymers, polypseudorotaxanes or polyrotaxanes have unique properties. Recent progress in conjugated polymers with rotaxane architecture is reviewed.

INTRODUCTION

The electronic properties of conjugated polymers have acquired a growing importance in many areas of modern chemistry and physics of condensed matter. During the past 10 years these conjugated polymers have given rise to an impressive amount of experimental and theoretical work devoted to:

Analysis of their structure and properties using a whole arsenal of physical techniques;

Development of synthetic methods allowing a better control of their structure and electronic properties;

Synthesis of functional polymers in which the electronic properties are associated with specific properties afforded by covalently attached prosthetic groups;

Analysis of their multiple technological applications extending from bulk utilizations such as antistatic coatings or energy storage materials to highly sophisticated electronic, photonic, and bio electronic devices.

Among conjugated polymers, those with extended systems involving alternating C=C and C-C bonds are predominant. This is the case for many conjugated polymers, such as polyacetylene,[1] poly(*p*-phenylene),[2] and poly(*p*-phenylene-vinylene).[3] New classes of conjugated polymers such as polypyrrole, polyaniline, polyazomethine or polythiophene have been also developed.

Until now, the utilization of conjugated polymers remained limited. The insolubility makes difficult the obtaining of high molecular weight polymers as well as their structural characterization.

An alternative strategy for improving the processability of these polymers is to include them in polyrotaxane architectures. Polyrotaxanes possess mechanically linked subunits, the connecting forces being non-covalent interactions, while conventional polymers have only covalent linkages. Because there is no covalent bond between their linear and cyclic components, polyrotaxanes can be viewed as composites at a molecular level.

The paper reviews the recent progress in conjugated polymers with rotaxane architecture.

POLYROTAXANES

Starting from 1967 when Harrison reported the first inclusion complex,[4] large series of pseudo- or polyrotaxanes were prepared and described. In simple instances a rotaxane can derive from the two distinct components: a sufficiently large macrocycle, which acts as a wheel, and an acyclic component, which, by threading the wheel, acts as an axle. The insertion of two bulky stoppers at the ends of the axle inserted into the wheel yields a rotaxane.

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Molecular architectures that consist of cyclic molecules threaded onto linear polymer segments and bulky end groups able to block the dethreading of the cyclic component are called polyrotaxanes, and polypseudorotaxanes when blocking groups are not present.[5, 6]

Generaly, two main routes were employed for the preparation of polyrotaxanes: (a) the polymerisation of a monomer with pseudorotaxane structure and (b) the inclusion of a preformed macromolecular chain in the inner cavity of a cyclic compound. Depending on the location of the rotaxane unit, polyrotaxanes can be divided into two principal types: main-chain, and side-chain polyrotaxanes.

Due to their architectural differences as compared to conventional polymers, these architectures have unique properties. These unique features offer the possibility to design nanoscopic equivalents of bearings, joints, motors, rotors, pistons and other macroscopic assemblies, composed of interlocked mechanical parts. Besides nanotechnology, polyrotaxanes have been also proposed in the macroscopic side of science as "smart" materials for sensor or data storage applications.[7]

CONJUGATED POLYMERS WITH ROTAXANE ARCHITECTURE

Conjugated polymers have attracted widespread interest due to their applications in light-emitting diodes,[8] field effect transistors[9] and photovoltaic devices.[10] They are often loosely described as molecular wires because of the high charge-mobility along individual polymer chains.[11] The rotaxane concept allows a single conducting polymer chain to be encapsulated into a supramolecular architecture. Research in this domain focused primarily on the synthesis of conducting molecules and the evaluation of their ability to transport charges.

Recently, the formation of inclusion complexes in which aniline or pyrrole covered by α- or β-CD was reported and these complexes were polymerized.[12] Blocking the macrocycles on the polymer chain was performed with a bulky group (p-aminophenyl triphenyl methane) (Scheme 1). This yielded a semi-polyrotaxane having a conjugated polymer as thread and cyclodextrins as rings. The obtained semi-polyrotaxane was proposed to be an insulated molecular wire. The insulation effect of an inclusion complex formed by polyaniline and β-cyclodextrin in solution was reported by Shimomura et al. [13]

The structural configurations of inclusion complexes between thiophene and cyclodextrin molecules (CDs) have been investigated by the combined quantum mechanics / molecular mechanics (QM/MM) method.[14] It has been found that the configuration of polythiophene in CDs is close to a planar structure and there is no charge transfer between CDs and polythiophene. This indicates that the CD complexes can be used as ''insulated'' molecules. Also, the crystal structure of the complex of β-cyclodextrin with bithiophene and their oxidative polymerization in water were reported.[15] To obtain pseudorotaxanes the polymerization of inclusion complexes was carried out in water using $FeCl_3$ as an oxidative initiator.
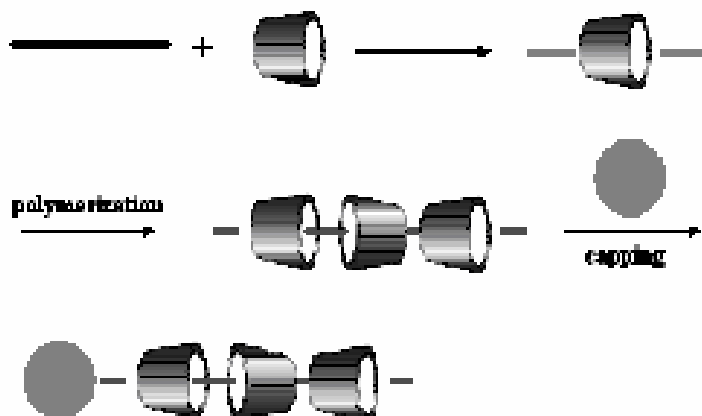

Scheme 1 – Synthesis of conducting polymers with semi-rotaxane architecture.

Polyazomethines or polyazines have gained widespread interest during the last two decades due to their useful electronic, optoelectronic, electrochemical, and nonlinear optical properties.[16] Polyazomethines with aromatic backbones are attractive conducting polymers but their insolubility in common organic solvents

limits their processability and characterization. Over the past 25 years, different methods have been adopted to yield processable polyazomethines by incorporating nonconjugated linkages into the main chain[17] through copolymerization,[18] by attaching functional groups or flexible chains as branches onto the main chain[19] or by a combination of both.[20] In most cases, the polymers were still insoluble and, hence, the problems of processability and characterization remain unsolved. Modifying the conjugated chain by solubilizing groups disturbs the electron delocalization and affects the interesting properties of the conducting polymer. Recently, the concept of polymerization in the cyclodextrin cavity has been introduced[21] and also applied to the synthesis of polyazomethines, leading to soluble rotaxanes.[22]

Geckeler and coworkers prepared the first fullerene-terminated soluble polyazomethine based polyrotaxane with β-CD as the macrocyclic component in order to improve the solubility of polyazomethine.[23] The polycondensation in the presence of an excess of CD and using C60 as the end-capping agent led to a high molecular mass soluble polyrotaxane.

Soluble aromatic polyazomethines with rotaxane architecture were also prepared starting from aromatic diamines (p,p-diaminobiphenyl or 1,4-phenylenediamine) / β-CD adducts and N-*n*-butyl-3,6-diformyl carbazole (Scheme 2).[24, 25]
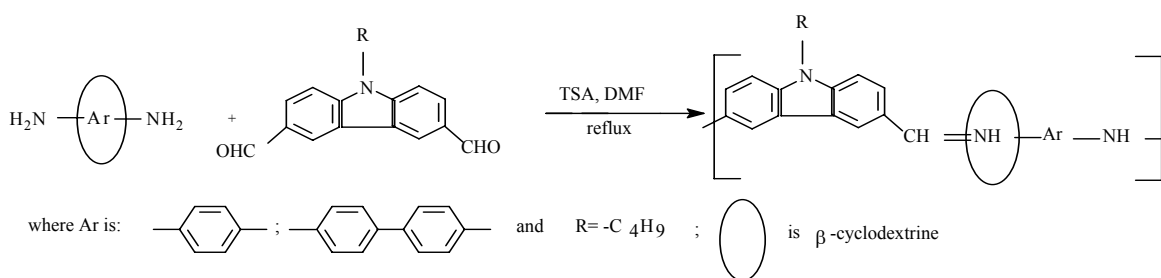
Scheme 2 – Synthesis of aromatic polyazomethine with rotaxane architecture.

The threading of CD macrocyles on aromatic polyazomethine chains does not change the specific electrical properties of these conjugated polymers. Other fully aromatic polyazomethines with rotaxane architecture have been prepared by polycondensation of aromatic diamines (1,4-phenylenediamine or p,p' diaminobiphenyl) with terephthalaldehyde / β-CD adduct and blocking the chain ends with a bulky aromatic amine (p-aminophenyl triphenylmethane).[26,27] The conductivity of the powders doped with iodine was similar to that of polymers without rotaxane architecture.

Cyclodextrin-threaded conjugated polyrotaxanes as insulated molecular wires with reduced interstrand interactions were synthesized by Anderson's group.[28- 31] This group reported the synthesis of poly-*para*-phenylene, or poly(4,4'-diphenylenevinylene), and polyfluorene, threaded through α- and β-cyclodextrin macrocycles.

A copolymer based on polyfluorene with pseudorotaxane architecture in the side chain was prepared through nickel(0)-catalyzed couplings between 2,7-dibromo-9-ethylcapronatefluorene / 24-crown-8 as adduct and 9,9-bis(2-ethylhexyl)-fluorene.[32] The chemical modification of this copolymer was performed by saponification in the presence of a LiOH solution and resulted in ionic structures. The polymer presents semiconducting properties with the activation energy of the electrical conduction of 1.41 eV that makes it suitable for electronic solid state devices.

The first example of α-cyclodextrin induced color change of polymerized diacetylene film sensor was reported by Kim et al.[33] The polydiacetylene film was prepared from a diacetylene monomer containing a terminal anilide moiety and was found to preferentially interact with α-CD causing a color transition which is both time and concentration dependent. Other linear and cyclic polysaccharides were found to be ineffective in their ability to promote a color transition in this polydiacetylene film.

CONCLUSIONS

Due to their novel topologies, polyrotaxanes have different properties, including solubility, stability, photoelectronic properties, viscosity, phase behavior as compared to conventional polymers. Their versatile characteristics provide unique opportunities for high performance applications.

These polymers are investigated in different laboratories as supramolecular materials that open new prospects in both fundamental and applied material science.

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