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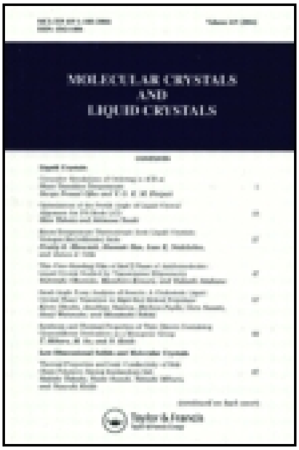

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Functional Conjugated Polymers for Molecular Electrochemical and Electron Ic Devices

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FUNCTIONAL CONJUGATED POLYMERS FOR MOLECULAR ELECTROCHEMICAL AND ELECTRONIC DEVICES

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Abstract The basic structural electronic and steric parameters involved in the substitution of conjugated poly(thiophenes) have been analyzed. These analyses led to the concept of functionalization space which allows the design of extensively conjugated and highly conducting functional polymers capable to exhibit specific interactions with their chemical environment.

INTRODUCTION

Recent years have wittnessed the emergence of a second generation of conducting polymers in which the electronic, optical and electrochemical properties of the conjugated backbone are coupled and/or altered by specific properties afforded by covalently attached prosthetic groups[1].

In this context, poly(thiophene) derivatives (PTs) have attracted particular interest owing to their stability, high conductivity and structural versatility[1]. The applications of functional conjugated polymers in electronic, optical or electrochemical molecular devices are conditioned by their ability to interact with and monitor their chemical environment and to respond to the information provided. However, the design of chemically active functional conjugated polymers capable of such selective interactions imposes severe conditions to the possible modifications of the basic monomer structure. As a matter of fact, any substitution of the thiophene ring must remain fully compatible with *(i)* the polymerization reaction and *(ii)* the persistence of an extensively conjugated π system in the resulting polymer since this structural parameter controls the ionization potential, energy gap, electroactivity and conductivity of the substituted polymer.

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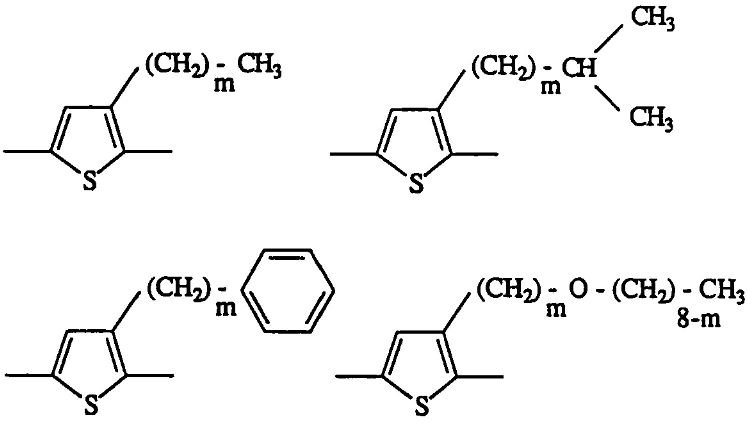
In an attempt to solve these problems, the electronic and steric effects associated with various types of substitution of the thiophene ring have been analyzed, leading to the definition of the basic structural conditions allowing the synthesis of extensively conjugated and highly conducting functional PTs. On the basis of these analyses, various series of functional PTs showing specific interactions with their chemical environment have been synthesized and characterized.

STRUCTURAL BASIS FOR FUNCTIONALIZATION

In order to define the structural conditions allowing the derivatization of PT while preserving the relevant electronic and electrochemical properties of the conjugated backbone, we have carried out a systematic analysis of the effects of the distance between a bulky and/or electron withdrawing group and the thiophene ring (m) on the structure and properties of the corresponding polymers (scheme 1).



SCHEME 1

For each polymer serie, a spacer group of minimal length is required to neutralize the steric and electronic substituent effects and hence to obtain extensively conjugated and highly conducting substituted polymers[2]. These results can be rationalize by means of the concept of functionalization space, defined as the volume in which a given substituent must be introduced in order to preserve both the polymerizability of the

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monomer and an extensive conjugation length in the resulting polymer. This volume is determined by the spacer length required to neutralize the electronic substituent effects and by the acceptable limits of intra-chain distortion and inter-chain distance (Fig. 1).

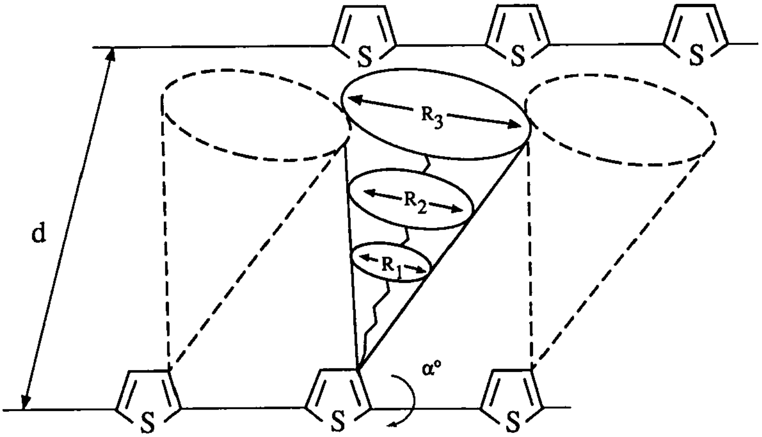

FIGURE 1 Functionalization space of poly(thiophene)

DERIVATIZED POLY(THIOPHENES)

Substituted Phenyl Groups

The insertion of a spacer of adequate length between the thiophene ring and the substituent allows the analysis of the effects of the interactions between substituents electronically and sterically decoupled from the conjugated system. This is examplified in the case of polymers (a-c), in which the electronic and steric decoupling of the substituents is confirmed by the invariance of the absorption maximum (Fig. 2).

On the other hand, the dependence of the resolution of the vibronic fine structure (FS) on the substitution of the phenyl ring shows that interactions among substituted phenyl groups indirectly control the rigidity of the polymer framework[3]. Furthermore, the correlation of the n doping level with the FS resolution indicates that cation doping depends much more on this parameter than anion doping.

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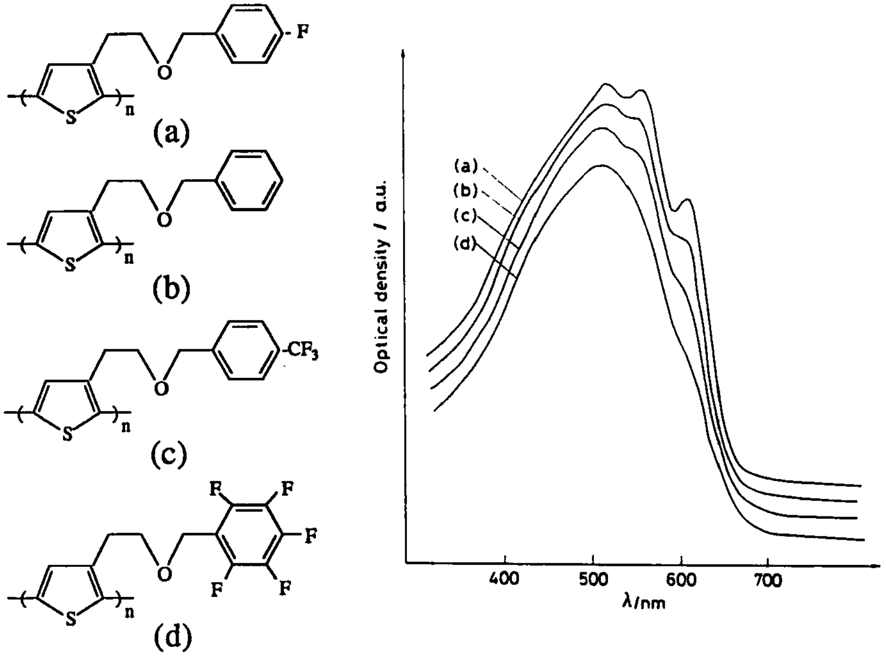


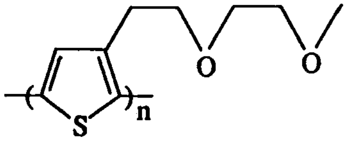
FIGURE 2 Electronic absorption spectra of polymers a-c

Chiral Groups

Chiral conducting polymers have been synthesized by electropolymerization of enantiomeric monomers designed according to the above described conception rules. These polymers exhibit high stability and conductivities in the range of 1-10 S cm^{-1}. Their high specific rotations have been interpreted by a macromolecular asymmetry arising from an helical polymer structure. The analysis of the electrochemical behavior these polymers in presence of chiral anions has provided first evidences for enantioselective molecular recognition on a chiral conducting polymer[4].

Polyether Chains

Conjugated polymers derivatized by polyether complexing groups are another new class of electroactive materials with potential applications in selective electrodes and membranes and all-polymer solid-state batteries. As a matter of fact, when electronically decoupled from the conjugated backbone, polyether chains lead to interesting modifications of the electronic and electrochemical properties of the conjugated backbone. These original properties have been extensively analyzed on (PDHT) which represents a good compromise between the conservation of extensive conjugation and high conductivity and the emergence of new properties afforded by the polyether chain[5,6].



(PDHT)

Thus, the grafting of oligo(oxyethylene) side chains produces a considerable increase of hydrophilicity which allows PDHT to remain fully electroactive in aqueous media contrary to the case of poly(3-alkylthiophenes)[7] (fig. 3).

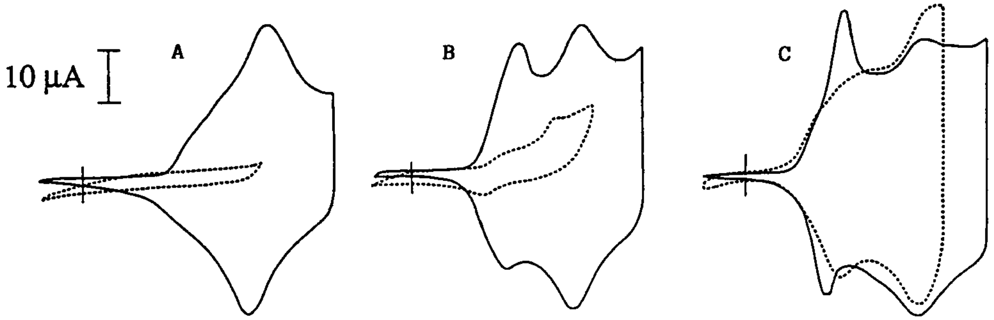


FIGURE 3 Cyclic voltammograms of (a) poly(3-heptylthiophene), (b) poly[3-(3-oxaheptyl)thiophene)] and (c) PDHT
Solid line: Between - 0.2 and 1.1 V/SCE in 0.5 M $LiClO_4$/MeCN, dotted line: between - 0.2 and 0.9 V in $LiClO_4/H_2O$, scan rate 30 mV/s

PDHT exhibits a specific electrochemical response in presence of Li^+. These specific interactions with Li^+, make PDHT the first example of poly(heterocycle) capable to dope n with alkali cations[5].

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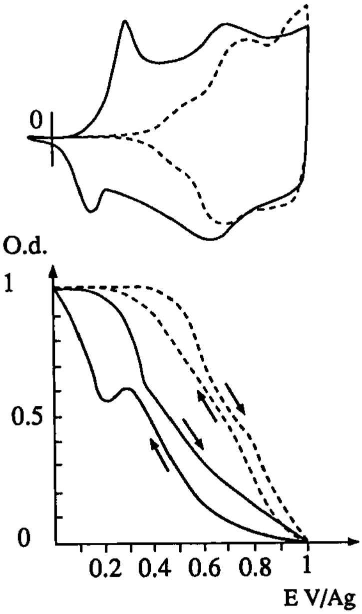

FIGURE 4 Simultaneously recorded cyclic voltammetric and voltabsorptometric responses of PDHT. Solid line: in 1M $LiClO_4$/MeCN, dotted line: in 1M Bu_4NClO_4/MeCN.

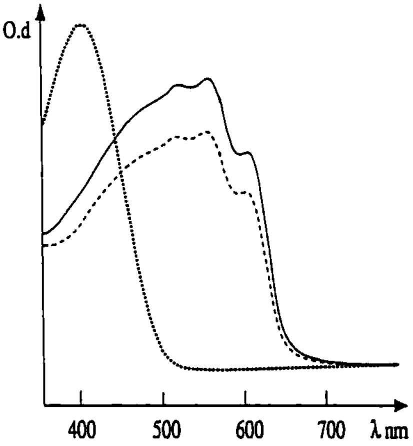

FIGURE 5 Electronic absorption spectra of undoped PDHT on ITO solid line: electrochemically undoped in 1 M $LiClO_4$/MeCN dotted line: same film immersed in hexafluoroisopropanol dashed line: same film after recycling in 1 M $LiClO_4$/MeCN

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As consequences of this high sensitivity toward environmental factors, reversible and correlated modifications of the cyclic voltammogram and of the optical spectrum can be induced by the solvent or the cation of the electrolytic medium in which the polymer has been cycled, or by immersion in strong hydrogen-bonding solvents[8,9] (fig. 4 and 5). These first evidences for solid-state solvatochromic and ionochromic effects have been interpreted in terms of feed-back control of the conformation and rigidity of the conjugated backbone by the interactions between the oligo(oxyethylene) side chains and the chemical environment[9].

Crown Ethers

Conjugated polymers derivatized by macrocycles could constitute an interesting extension of this new class of functional conducting polymers. However, the size of such substituents and the steric constraints imposed by the conservation of the effective conjugation require spacer groups of considerable length. Such long spacers groups will severely limit the interactions between the crown ether and the conjugated π system and hence the possibility to address the cation-binding properties of the macrocyclic cavity through the redox state of the conjugated PT backbone. A possible answer to this problem consists in the simultaneous formation of the macrocyclic cavity and conjugated backbone by using as substrate for electropolymerization two thiophene rings linked together by an oligo(oxyethylene) chain (Fig. 6).

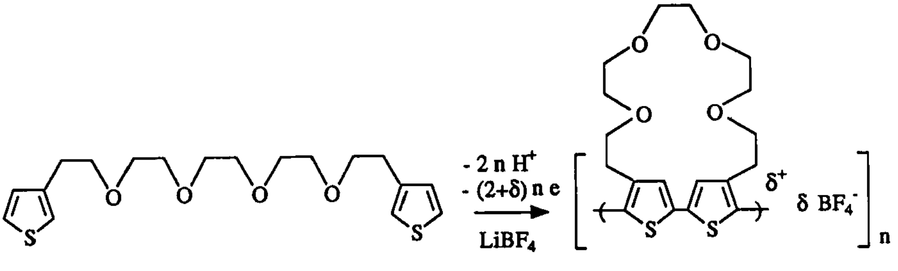

FIGURE 5 Electrosynthesis of Conjugated Polymers Containing Macrocyclic Cavities

Preliminary investigations have shown that, in presence of Li^+, this substrate electropolymerizes at a potential 300 mV lower than PATs, indicating possible template assisted ring closure[10]. Furthermore, although less conjugated than some PTs substituted by linear polyether chains, the obtained polymer is highly electroactive, demonstrating thus the feasability of this new approach.

CONCLUSION

In summary, through a systematic analysis of the structural factors involved in the substitution of poly(thiophene), the basic structural conditions allowing the synthesis of extensively conjugated derivatized polymers have been defined. The practical applications of these concepts have been demonstrated by the synthesis and characterization of several new classes of electroactive conjugated polymers in which the electronic and electrochemical properties of the conjugated backbone are associated with original new properties such as molecular recognition and specific electrochemical and/or optical responses to their chemical environment.

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