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Paper 105

New Perspectives in the Preparation of Functional Materials Using Furan Chemistry

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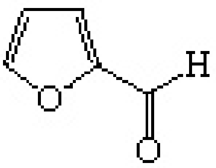
Abstract: *This lecture deals with recent advances in the use of furan compounds to prepare novel oligomers and polymers with functional properties. The topics covered include: (i) the synthesis and characterisation of conjugated oligomers bearing a terminal aldehyde group and their possible applications as semi-conductors, liquid crystals, luminescent compounds and photosensitive moieties; and (ii) the application of the Diels-Alder reaction for the preparation of thermally reversible networks. Apart from the intrinsic interest of these materials, the strategy underlying the whole field of furan chemistry will be emphasized in the context of the exploitation of renewable resources.*

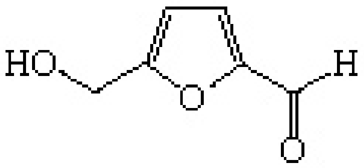
Keywords: *Furans; Conjugated oligomers; Photosensitive polymers; Thermally reversible networks.*

Introduction

Furfural (**F**) and 5-hydromethylfurfural (**HMF**) are among the several important industrial chemicals derived from vegetable renewable resources. A whole variety of natural products can be used to generate them through simple processes, including sugars and numerous by-products of agricultural and forestry activities. The investigations dealing with the use of these first-generation furan derivatives to prepare monomers and their polymers and copolymers has given rise to a whole chapter of macromolecular chemistry based on renewable resources [1,2], which stands as a counterpart to the classical petroleum and natural gas (i.e. perishing fossil sources) approach.



F



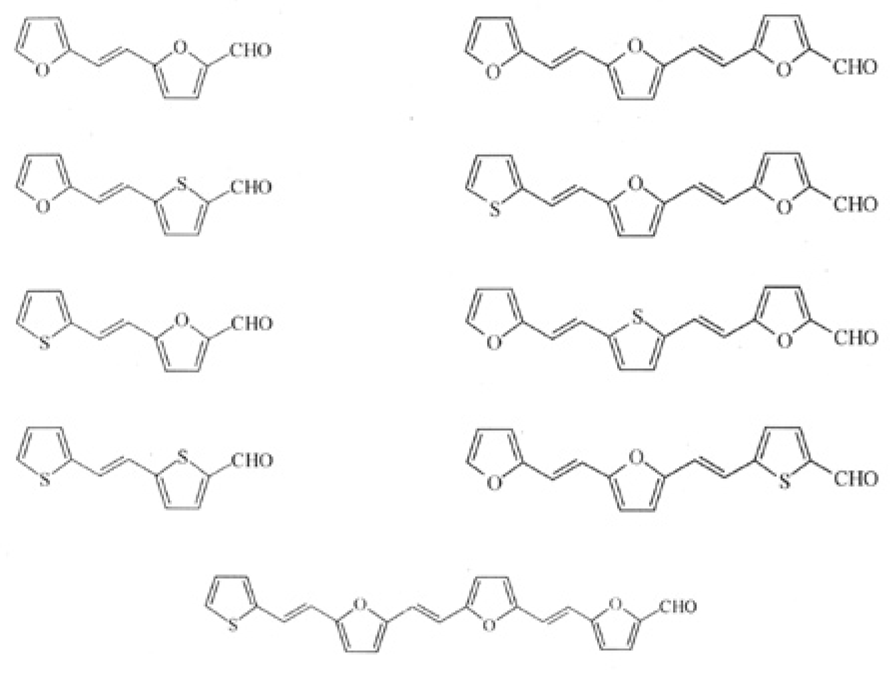
HMF

This wide spectrum of studies [1,2] covers, on the one hand, the polymerisation of furan monomers in the context of both polyaddition and polycondensation systems and the characterisation and properties of the ensuing materials, bur also, on the other hand, the exploitation of some specific features of the chemistry of the furan heterocycle to prepare polymers with original structures and properties.

The examples given here are the outcome of the continuing efforts to bring added value to this comprehensive research work and describe some of the most recent studies.

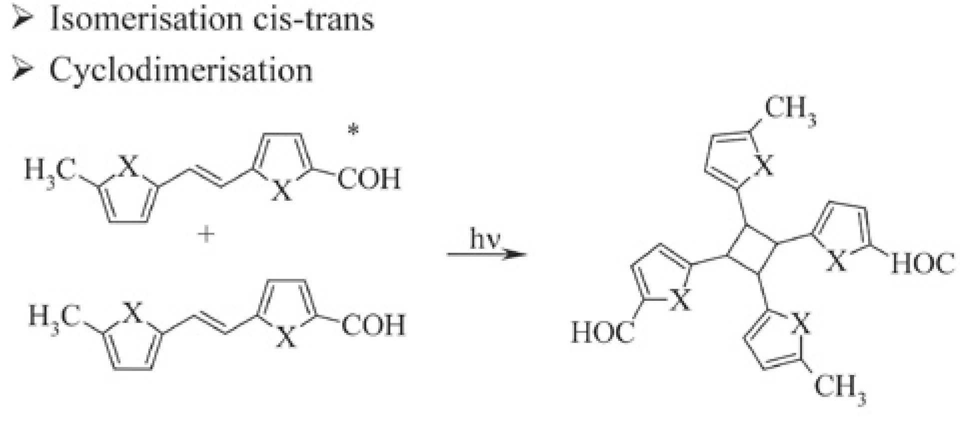
Conjugated Oligomers

Following the discovery of the possibility of polymerising 5-methylfurfural (**MF**) through a sequence of aldol-crotonic-type condensations, conjugated poly(furylene-vinylene)s with DPs of up to 100 were prepared and shown to have interesting semiconductive properties [1,2]. In order to examine the potential of these structures in other areas, it was decided to conduct a more thorough study of well-defined oligomers, each prepared and purified as a single species. This synthetic effort was also extended to the thiophene heterocycle, using the same procedures and the molecules shown below are a selection of the oligomers obtained (all as *trans* isomers):



The properties investigated included electronic conductivity (~1S cm^{-1} for oligomers with DP>4, after doping with iodine), the evolution of the uv absorption spectra as a function of the degree of conjugation (before and after protonation), the photoluminescence as a function of the DP and the furan-thiophene composition, the possibility of preparing mesogenic structures from these molecules and their photochemical behaviour. The fact that the adopted synthetic procedure left a terminal aldehyde group in each of these molecules represented a considerable advantage, because it permitted to couple them with various molecules and macromolecules bearing such reactive moieties as amines and diols.

All these aspects will be illustrated and discussed. In particular, the photochemical study of the various dimers revealed a clean *molecular* π2+π2 cyclodimerisation, only accompanied by *trans-cis* isomerisation, as shown in Scheme 1 below. This behaviour was exploited in two different macromolecular applications, both involving the photo-crosslinking of polymers bearing these pendant furanic or thiophenic chromophores: in one system, the chromophores were grafted onto poly(vinyl alcohol) through an acetalisation reaction [3], whereas the second called upon their condensation onto the chitosan NH_2 groups, to give the corresponding Schiff bases [4].



X = O, S λ_{exc}>280 nm

Scheme 1

Thermoreversible Networks

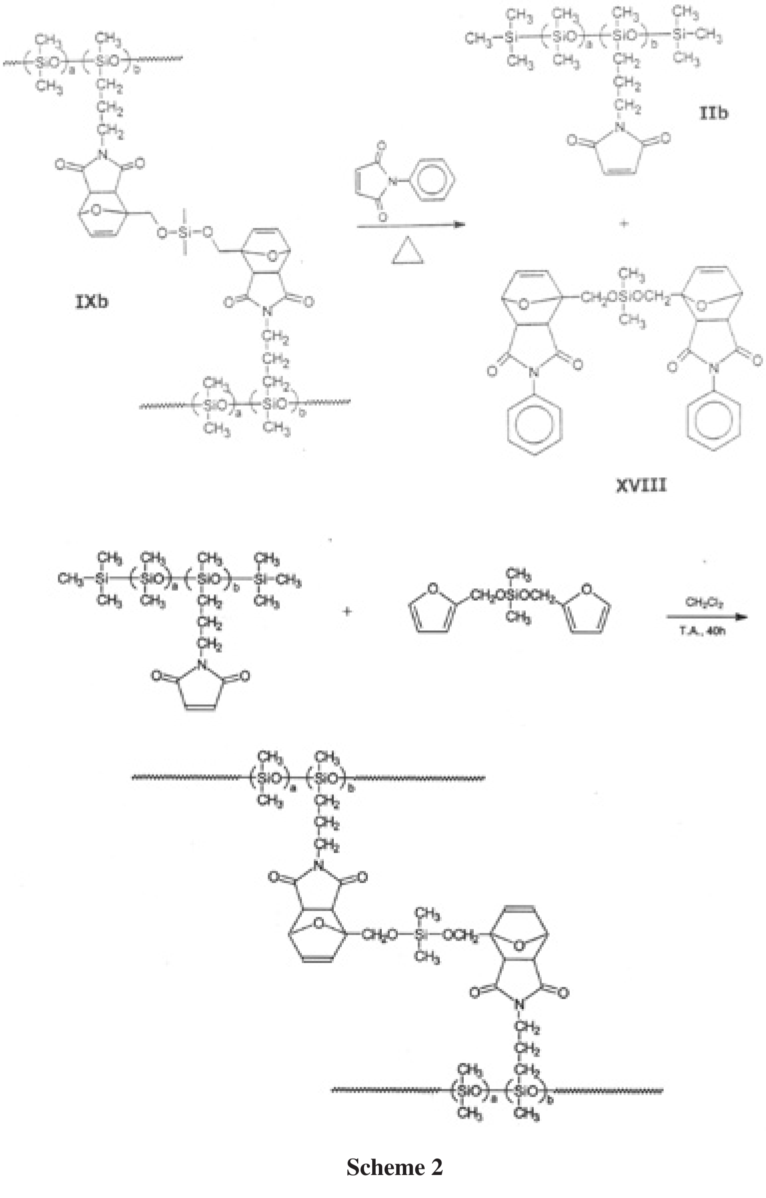
The furan heterocycle is particularly suited to intervene as a diene in the Diels-Alder reaction, which has the peculiarity of being very sensitive to reversibility with increasing temperature. These features were exploited to generate polymer networks, which can be reverted to linear thermoplastic materials by a simple thermal treatment [5,6]. The interest of this working hypothesis is, among others, the possibility of recycling used tyres.

Two different approaches were explored in view of verifying the feasibility of this idea, viz. (i) the synthesis of copolymers bearing pendant furan rings (dienes) and their cross-linking with a *bis*-maleimide (dienophile) and (ii) the preparation of copolymers bearing pendant maleimide moieties (dienophiles) and their cross-linking with a *bis*-furan compound. These procedures were successful, even with proportions of reactive groups in the copolymers as low as 5%.

The thermal de-cross-linking was carried out at ~100ºC in the presence of an excess of monofunctional reagent capable of trapping the released difunctional bridging compound. Thus, 2-methylfuran was used for approach (i) and phenylmaleimide for approach (ii). In both instances, the initial linear copolymer was recovered quantitatively, showing that recycling was indeed possible and efficient, thanks to this strategy.

The mechanisms associated with the Diels-Alder couplings and the retro-Diels-Alder reactions leading to the regeneration of the thermoplastic structures were thoroughly investigated by using monofunctional model compounds. TGA thermograms and dynamic mechanical properties showed the onset of the de-cross-linking reaction and its quantitative occurrence. Swelling measurements on the various networks provided a confirmation of their cross-link density, already obtained from the dynamic mechanical properties.

Scheme 2 illustrates the workings of one of the systems studied, with the mechanism of network formation, followed by that of the retro-Diels-Alder reaction leading to complete de-cross-linking.



Scheme 2

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