

## Polyesters bearing furan moieties

### 1. Polytransesterification involving difuranic diesters and aliphatic diols

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#### Summary

This paper describes a preliminary set of results concerning novel systems in which the synthesis of furanic polyesters was conducted according to a transesterification procedure. Regular linear macromolecular structures were thus obtained with molecular weights well above those previously reported for similar polyesters prepared by more conventional routes.

#### Introduction

The present investigation pursues the long-standing interest that one of us has devoted to the chemical exploitation of the biomass for the elaboration of novel polymeric materials (1). Within the several areas covered by that general approach, the use of furanic monomers and/or the specific chemistry of the furanic heterocycle constitutes a major field which has been the object of numerous publications and some reviews (1-4).

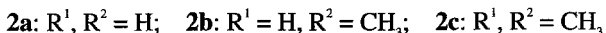
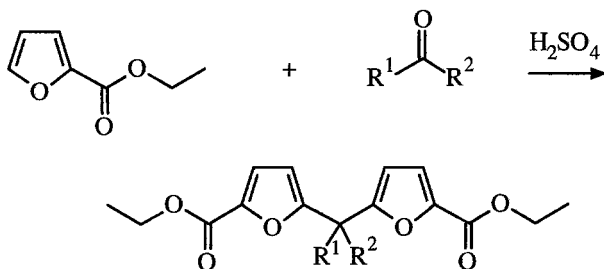
The realm of furanic polyesters has stimulated few studies. Moore *et al* (5-9) were the first to tackle the field with the intention of establishing valid reactivity and structural criteria among the various monomers used and the properties of the corresponding polymers. However, the characterization of these polyesters was relatively limited because of the lack of a complete spectroscopic assessment and the modest information obtained on DPs, which anyway were quite low. A further point on which these authors did not dwell in depth was the macromolecular regularity of their products and hence their possible crystallization. Hirai (10) was the first to envisage the use of an A-B type monomer and looked at the possibility of preparing polyesters from 5-hydroxymethyl-2-furoic acid, but obtained only linear and cyclic oligomers. Roudet and Gandini (4,11) used similar structures with an intermediate unsaturation, viz. 5-hydroxymethyl-2-furanacrylic esters and achieved regular polyesters capable of crystallizing and photocrosslinking. Storbeck and Ballauff (12) carried out an interesting investigation on the use of isosorbides, i.e. another monomer arising from renewable resources, as diol in polyesterification reactions with a number of diacid chlorides, including the 2,5-furandicarboxylic homologue. This "all sugar derived" polyester showed the expected structure, but was not characterized in detail.

The above short survey clearly suggests that much remains to be done to acquire a comprehensive knowledge of furanic polyesters, because the studies published thus far are somewhat disconnected and leave numerous questions unanswered. The purpose of this series of papers is to report a thorough investigation on furanic polyesters aimed at

filling those gaps in order to optimize the quality (structure, DPs, end groups,...) of the ensuing materials and thus be able to give a sound appraisal of their possible applications arising from a complete physical characterization. The present communication deals with a first investigation in which the main novelties are the use of difuranic monomers and the application of a transesterification technique hitherto not envisaged with these heterocyclic reagents.

### Experimental

The various diols used in this work, namely ethane diol (**1a**), 1,3-propane diol (**1b**) and 1,4-butane diol (**1c**), were distilled at atmospheric pressure in the presence of freshly ground calcium hydride. The difuranic diesters **2a**, **2b** and **2c** were prepared following the procedure described previously by Pennanen and Nyman (13). This synthesis involves the condensation of aldehydes with 2-furoic esters in sulfuric acid, viz. here the use of formaldehyde and acetaldehyde with 2-ethyl furoate. The corresponding reaction with acetone was novel and in order to make this condensation occur, we had to operate at 60°C (as opposed to 0-25°C with the aldehydes) and thus achieved 65% yield of **2c**.



The three esters, purified by vacuum distillation and characterized by FTIR and  $^1H$ - and  $^{13}C$ -NMR spectroscopy, displayed the expected structures without detectable impurities.

The preparation of the oligomeric diols (first phase of the polycondensation procedure discussed below) was followed by sampling the reaction mixture and analysing it by GLC. The criterion chosen to consider that this phase had ended was the total disappearance of the peak due to the difuranic diester used. The validity of this choice was verified by the fact that the products obtained did not show any residual ethyl end-groups, i.e. that all the initial ester moieties had been exchanged by the glycol with the corresponding release of ethanol. The operating procedures relative to the polycondensation reactions are described below together with the relevant results. During the actual polymerization phase, the reactions were followed by withdrawing samples at regular intervals and analyzing them by intrinsic viscosity measurements in DMF at 25°C. The acetylation of the polyesters was carried out by refluxing for one hour in dry pyridine using an excess of acetic anhydride and by subsequent vacuum evaporation of both solvent and excess reagent.

### Results and discussion

Polytransesterifications were conducted according to a technique which has been successfully applied to the synthesis of poly(ethylene terephthalate) (14). This procedure requires two distinct phases, namely:

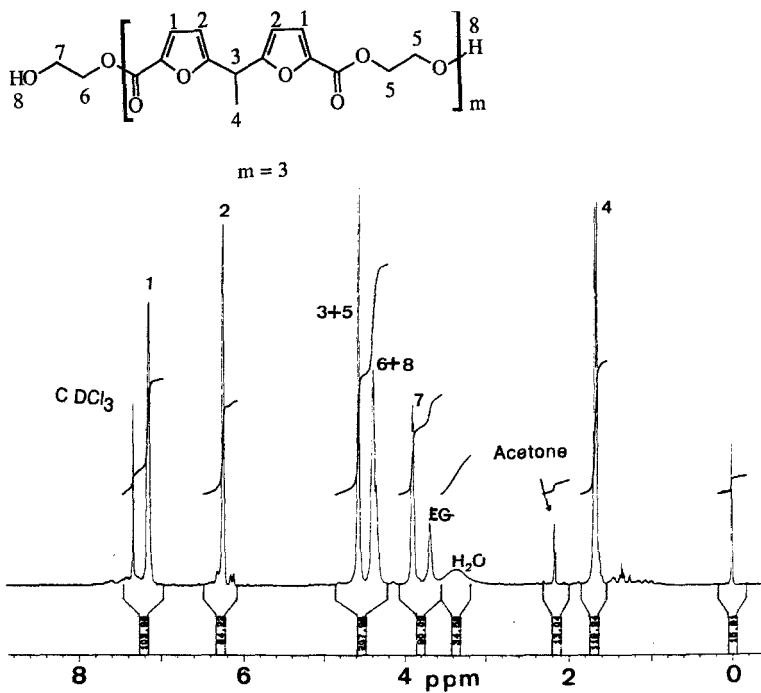


Figure 1.  $^1\text{H-NMR}$  spectrum of 3d.

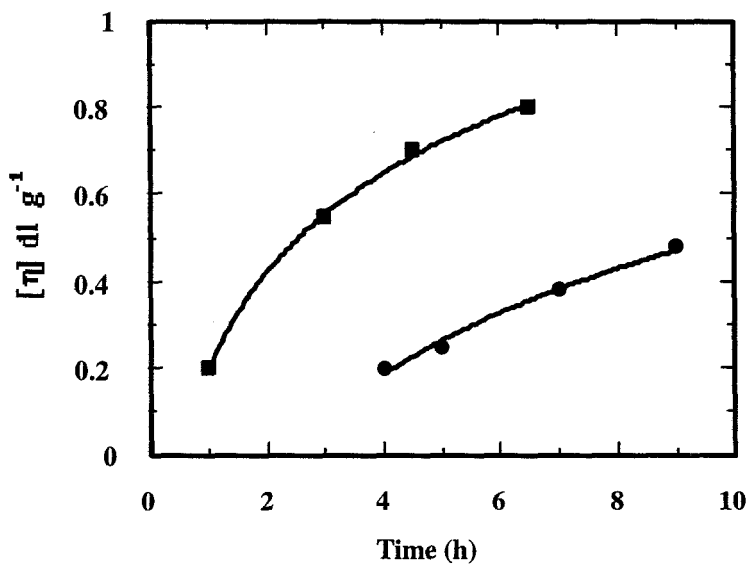
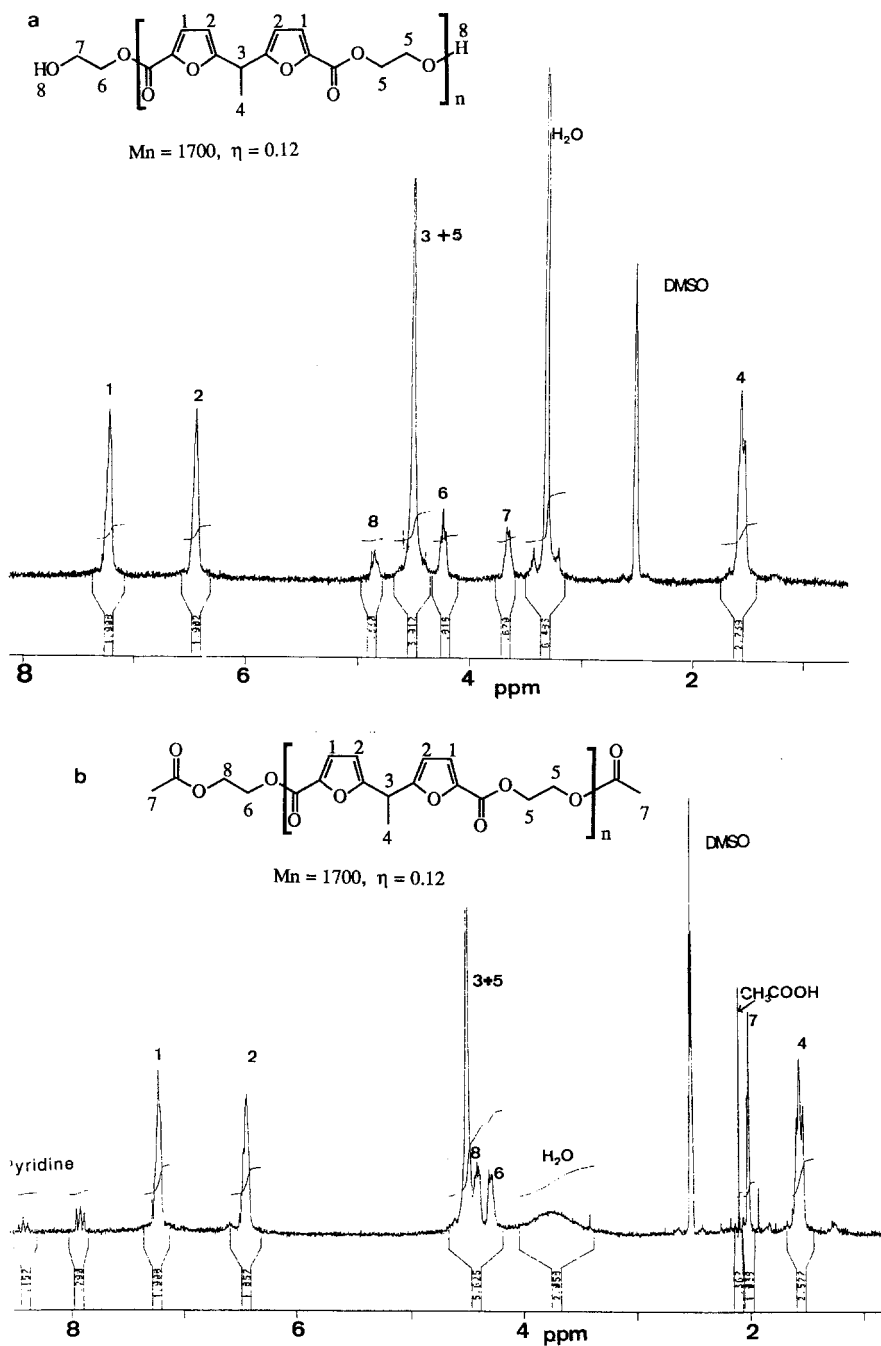
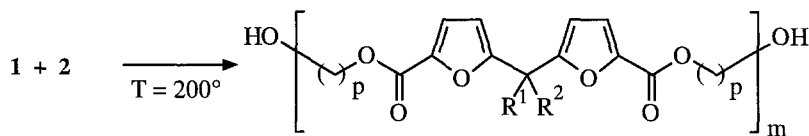


Figure 4. Viscosity of reaction medium vs. time in the polytransesterification of 3g (■) and 3e (●).

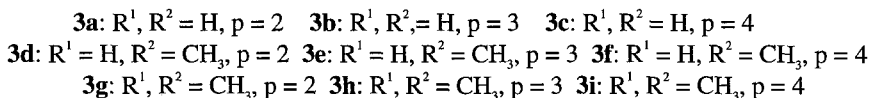


**Figure 2.**  $^1\text{H-NMR}$  spectrum of the polyester obtained from **3d**:  $M_n = 1700$ . (a): before and (b): after acetylation

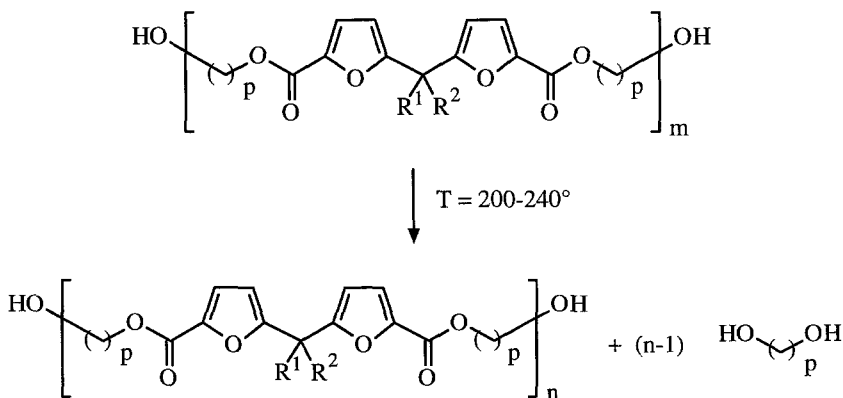
(i) An **exchange reaction** consisting of the interaction of the diester with an excess of glycol in order to obtain the oligomeric structures **3**, with  $m$  varying from 1 to 3, depending on the conditions. These transesterifications were carried out at 200°C for several hours in a stream of dry nitrogen which removed the ethanol. Among the catalysts used, the following order of activity was found: titanium tetra-*n*-butoxide > zinc acetate > calcium acetate > potassium bicarbonate. With the latter two catalysts the reaction lasted ca. 12 h. This order applied to all combinations studied. The resulting intermediates were characterized by conventional spectroscopic techniques which confirmed in each case the expected structure. Figure 1 shows a typical <sup>1</sup>H-NMR spectrum of one of these condensation products with the corresponding assignments.



$$1 < m < 3$$



(ii): The **polytransesterification** itself, which consisted in treating the oligomers **3** with different catalysts under vacuum (ca 100 Pa) with a progressive increase in the reaction temperature, from 200 to 240°C, over a few hours. Thereafter, the evolution of the reaction medium was monitored by frequent sampling in order to follow the extent of polycondensation. Apart from the variation of the intrinsic viscosity, the progress of the reaction was clearly shown by the changes in the <sup>1</sup>H-NMR spectra of the product which revealed both a decrease in the relative proportion of end-groups and a regular linear structure devoid of detectable anomalies. These features are illustrated in Figures 2 and 3 which give typical spectra and assignments of samples of a polyester and its corresponding acetylated product, obtained at two reaction times. This general phenomenology was common to all diester/diol combinations and to the two catalysts tested, namely Sb<sub>2</sub>O<sub>3</sub> and Ti(*On*Bu)<sub>4</sub>, although the latter was found to be more active.



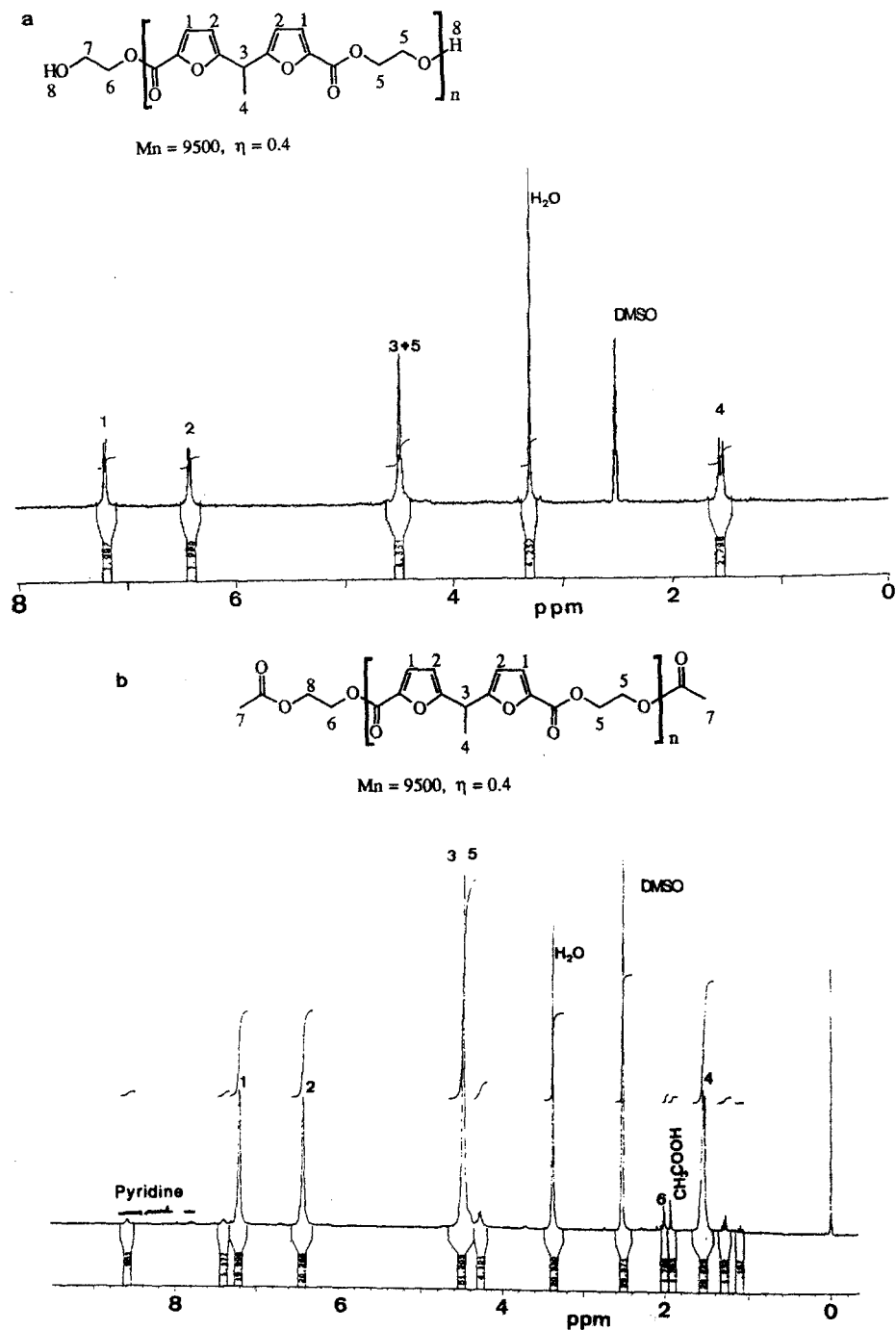


Figure 3.  $^1\text{H-NMR}$  spectrum of the polyester obtained from 3d:  $M_n = 9500$ . (a): before and (b): after acetylation

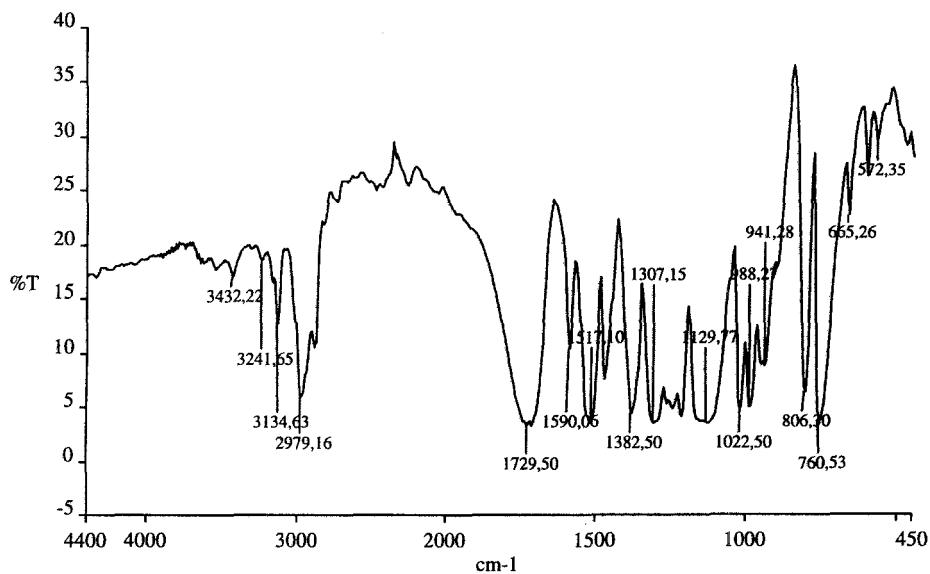


Figure 5. FTIR spectrum of the polyester obtained from 3g.

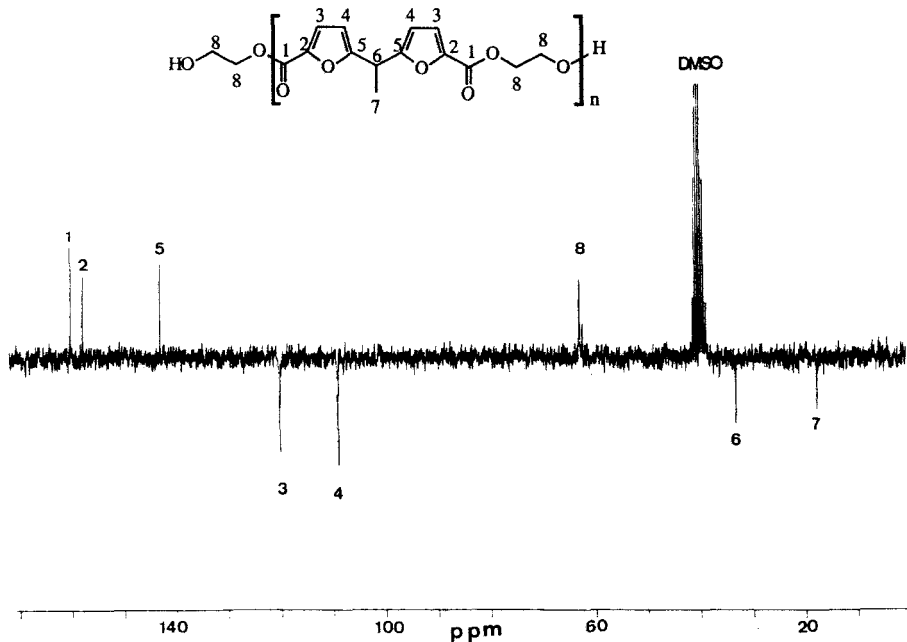


Figure 6.  $^{13}\text{C}$ -NMR spectrum of the polyester obtained from 3d.

The intrinsic viscosities attained varied between about 0.2 and 0.8 dl g<sup>-1</sup> depending mostly on the diol used. In particular, the higher values were reached with **1c**. Figure 4 shows the increase in molecular weight, through  $[\eta]$ , with reaction time for two polycondensations which only differed in the nature of the diol used.

The acetylation of some of these polyesters and the careful inspection of the ensuing <sup>1</sup>H-NMR spectra was a convenient means of determining their end-groups and therefore of calculating their molecular weight. Thus, an intrinsic viscosity of 0.12 corresponded to an Mn of 1700 and for a polyester with  $[\eta] = 0.46$ , Mn was about 9500. Since we were able to attain intrinsic viscosities of up to 0.8, it can be concluded that this technique of two-step polytransesterification leads to very satisfactory chain lengths.

The structural regularity of these materials was repeatedly corroborated by their spectroscopic features scrutinized both during the reactions and on the final products. Figures 5 and 6 give typical FTIR and <sup>13</sup>C-NMR spectra of one of these polyesters.

This investigation is being pursued along different lines, including the extension of the number and type of monomers, the optimization of the polymer syntheses and the characterization of the physical properties of the polyesters.

## Conclusion

The extrapolation of a well-known polytransesterification method, developed originally for PET, to new monomers based on difuranic diesters, proved not only feasible, but quite promising in terms of the quality of the ensuing novel materials. These furanic polyesters are now being prepared according to a systematic approach which aims at reaching more comprehensive structure/properties relationships.

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