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RAPID COMMUNICATION

The Furan Counterpart of Poly(ethylene terephthalate): An Alternative Material Based on Renewable Resources

ALESSANDRO GANDINI, ARMANDO J. D. SILVESTRE, CARLOS PASCOAL NETO, ANDREIA F. SOUSA, MÓNICA GOMES

Department of Chemistry, CICECO, University of Aveiro, Aveiro 3810-193, Portugal

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INTRODUCTION

The burgeoning surge of research on polymers from renewable resources¹ is a direct reflection of the growing concern about the dwindling of fossilized organic reserves, i.e., the materials science version of the concurrent ferment dealing with the search for alternative energy sources. Macromolecules incorporating furan heterocycles, or moieties arising from them, constitute an attractive family of such polymers, whose wide scope stems from a unique context in which two first-generation compounds, viz. furfural (F) and hydroxymethylfurfural (HMF), readily available from saccharide sources, can be converted into a whole host of monomers simulating those presently prepared from petrol and carbon chemistry.² Additionally, the well-known aptitude of the furan ring to play the diene role in the Diels-Alder reaction has spurred considerable interest in recent years in applications of this reversible click reaction to the synthesis of a variety of novel functional materials.^{2(c),3} Whereas, F has been an industrial chemical commodity for nearly a century, thanks to the exploitation of pentose-rich ubiquitously available agricultural by-products,⁴ the industrial production of HMF from hexoses has been hampered by difficulties associated with finding both an economically viable process and a sound way to store this rather unstable com-

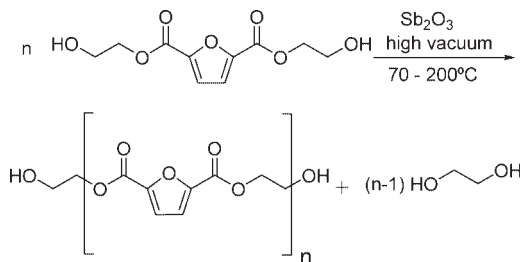
pound. Very recent work⁵ strongly suggests a reversal of this situation, whereby such a process can soon become a reality. As for the handling of large quantities of HMF, the obvious solution lies in its *in situ* transformation into stable derivatives like the corresponding dialdehyde and diacid.²

Polyesters bearing furan moieties have been actively investigated for decades, starting with Moore and Kelly's pioneering research some thirty years ago⁶ and continuing with more recent studies,² mostly based on the use of difunctional monomers derived from F. Oddly enough, however, the synthesis of the furan homologue of poly(ethylene terephthalate) (PET), poly(ethylene 2,5-furandicarboxylate) (PEF), has not been reported in the last forty years. The literature on this polymer, which stops in the late 1960s, is scanty and erratic, consisting mostly, as previously reviewed,⁷ of exotic patents and a brief communication focusing on its crystal structure.⁸

Considering that the novel approaches to the preparation of HMF⁵ open the way to the large-scale production of 2,5-furandicarboxylic acid (FCA) from C6 carbohydrates, i.e., one of the most obvious monomers derived from it, and the fact that aliphatic glycols can also be considered as future chemicals from renewable resources, given the recent intensive studies on the chemistry of glycerol,^{5(c),9} a revival of interest in PEF and its homologues seems amply justified. The purpose of this preliminary communication, which anticipates a more thorough study, is to describe a straightforward synthesis of PEF and the characterization of the ensuing material in the light of a first comparison with PET.

Correspondence to: A. Gandini (E-mail: agandini@ua.pt)

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Scheme 1. Synthesis of poly(ethylene 2,5-furandi-carboxylate).

RESULTS AND DISCUSSION

Among the various synthetic pathways tested to synthesize PEF (solution polycondensation between the FCA dichloride and ethylene glycol (EG), transesterification of the FCA dimethyl ester with an excess of EG, followed by the polytransesterification of the ensuing product), the polytransesterification of the diester diol **1** proved the most rewarding. Monomer **1** was prepared in 98% yield by reacting FCA with a hundredfold excess of EG (Aldrich > 99%) for 6 h at 75 °C in the presence of small amounts of aqueous HCl and vacuum removing the excess diol after neutralization. The spectroscopic characterization of **1** confirmed the expected structure and the adequate purity: FTIR (liquid, cm^{-1}) 3350, νOH ; 3128, furan $\nu=\text{CH}$; 2952 and 2881, νCH_2 ; 1716, ester $\nu\text{C}=\text{O}$; 1272, ester $\nu\text{C}-\text{O}$; 1582, furan $\nu\text{C}=\text{C}$; 1016, ring breathing; 963, 832, and 764 bending motions associated with the 2,5-disubstituted furan heterocycles; ^1H NMR (acetone- d_6), ppm) 7.29, s 2H, furan H3 and H4; 4.45, t 4H, $\text{CH}_2-\text{O}-\text{C}=\text{O}$; 3.96 t 4H, CH_2-OH ; 3.85, s 2H, OH.

Its reproducible bulk polymerization by transesterification, catalyzed by Sb_2O_3 (5×10^{-3} to 2×10^{-2} M) and carried out in a high-vacuum system under magnetic stirring (Scheme 1), proceeded smoothly while the temperature was raised progressively from 70 to 220 °C in the course of several hours, with the concurrent trap-

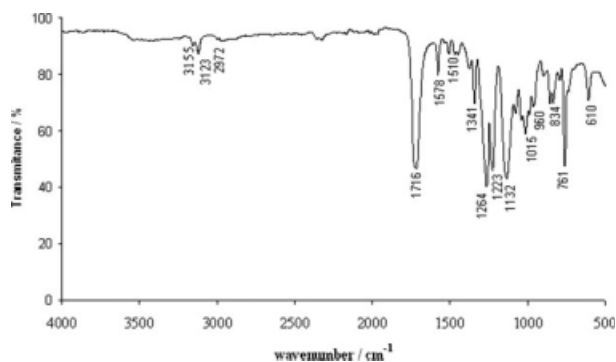


Figure 1. A typical FTIR spectrum of PEF.

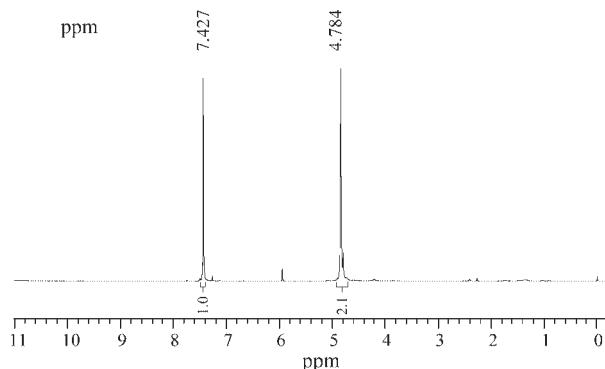


Figure 2. A typical ^1H NMR spectrum of PEF in CF_3COOD .

ping of the released ethylene glycol at liquid nitrogen temperature.

The ensuing white PEFs were found to dissolve only in trifluoroacetic acid (TFA) and in hot tetrachloroethane (TCE), among the numerous potential solvents tested. After precipitation of the TFA solutions in an excess of an EtOH/ Et_3N mixture, filtering, and washing with the same solution, the polymers were dried to constant weight (their mass reflected the amount of monomer **1** used, minus the calculated mass of ethylene glycol generated to form a high-DP product) and characterized. Figure 1 shows a typical FTIR spectrum with the corresponding peaks (cm^{-1}) attributed to the ester carbonyl and C–O moieties (1716 and 1264) and the 2,5-disubstituted furan heterocycles (3123, 1578, 1015, 960, 834, and 761). The very weak OH absorption around 3400 cm^{-1} suggested that the PEF had reached a reasonably high molecular weight.

The ^1H NMR spectra in CF_3COOD (Fig. 2) bore a striking resemblance to that of PET in the same solvent with the resonance of the H3 and H4 furan protons at 7.43 ppm, and that of the ester CH_2 at 4.78 ppm with the expected 1:2 integration ratio. The ^{13}C NMR

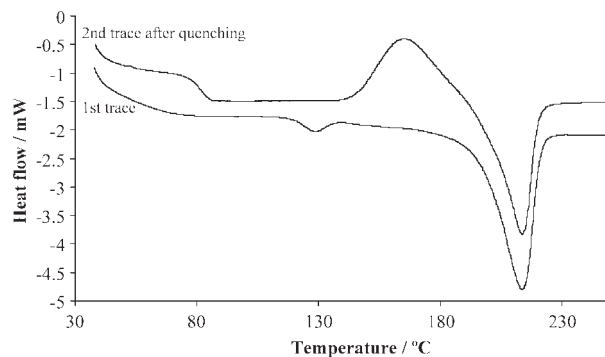


Figure 3. DSC tracing of a precipitated PEF (first trace) and of the same polymer after quenching its melt in liquid nitrogen (second trace).

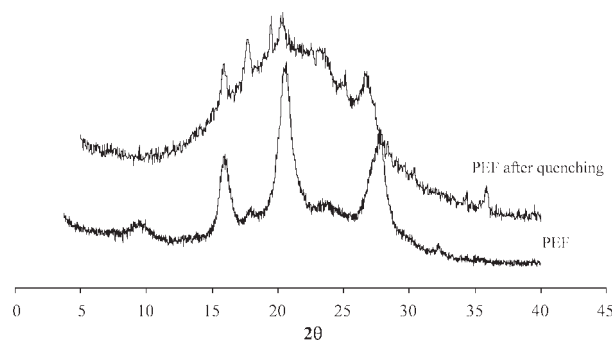


Figure 4. A typical X-ray diffractogram of PEF before and after quenching its melt.

spectra in the same solvent exhibited the peaks associated with the furan ring (C2/C5 at 147.1 ppm and C3/C4 at 121.1 ppm), with the methylene groups at 64.7 ppm and with the carbonyl moieties at 161.0 ppm. The elemental analyses of these polymers were in tune with high-DP PEFs, viz. C 52.2–52.4% (calculated for the monomer unit, 52.76% and 52.72% for a polymer with $DP_n = 200$), oxygen 44.0–44.3 (calculated 43.92 and 43.97%, respectively) and H 3.3–3.4% (calculated, 3.32 and 3.31, respectively). The slightly lower carbon and higher oxygen content could have arisen because of the presence of the few ether bridges detected by 1H NMR.

The TGA of these PEFs showed that they were thermally stable up to ~ 300 °C and degraded thereafter with a major decomposition step, which left a $\sim 20\%$ residue at ~ 400 °C, and a slower complete volatilization ending at ~ 580 °C. This behavior is similar to that displayed by PET,¹⁰ albeit with a somewhat lower thermal stability. The DSC thermograms of the precipitated polymers (Fig. 3) indicated a high degree of crystallinity, with a melting temperature of 210–215 °C, depending on the sample tested, viz some 45 °C lower than that of PET. After quenching the melted PEFs in liquid nitrogen, the tracings of the ensuing amorphous morphologies (Fig. 3) displayed a glass transition at 75–80 °C (similar to that of PET) and a crystallization exotherm with a maximum at ~ 165 °C, followed by the same melting pattern as that of the precipitated precursor.

The pronounced crystallinity of these PEFs was corroborated by the presence of three sharp signals in their X-ray diffractograms (Fig. 4), respectively, at $2\theta = 16.0$, 20.1 , and 27.8° , i.e., a pattern similar to that displayed by PET,¹¹ only sharper. After melting the polymer and quenching it in liquid nitrogen, the pattern lost most of its crystallinity features, as shown in Figure 4.

To determine the DP of these polyesters, their TFA solutions were treated with pentafluorobenzoyl chloride to esterify the two OH end-groups present on each macromolecule with a fluorine-rich moiety, precipitated and washed with an EtOH/Et₃N solution and dried to constant weight. Their elemental analysis gave C 52.2–

52.3%, H 3.3–3.4%, O 44.1–44.3% and F 0.35–0.38%, from which DP_n values of 250–300 were calculated, assuming complete esterification of the end-groups and the absence of cyclic oligomers.

SUMMARY

The preliminary evidence gathered here clearly indicates that it is readily possible to synthesize a PEF whose basic properties are comparable with those of PET, i.e., that the use of renewable resources (not only the furan monomers, but also ethylene glycol which can be prepared from glycerol) provides a means of preparing a furanic-aliphatic polyester which could be a viable alternative to its highly successful petrochemical aromatic counterpart. Work is in progress to extend the scope of this investigation in terms of (i) a thorough appraisal of the PEF syntheses with a search for alternative catalysts in replacement of the rather toxic Sb₂O₃, (ii) the characterization of its mechanical properties in comparison with those of PET, and (iii) the extension of the investigation to the use of other diols, like the propylene homologues, as well as the preparation of copolymers.

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