Synthesis and Characterization of Poly(2,5-furan dicarboxylate)s Based on a Variety of Diols

MÓNICA GOMES, ALESSANDRO GANDINI, ARMANDO J. D. SILVESTRE, BRUNO REIS
CICECO and Department of Chemistry, University of Aveiro, 3810-193 Aveiro, Portugal

Received 23 March 2011; accepted 23 May 2011
DOI: 10.1002/pola.24812

ABSTRACT: Novel polyesters from renewable resources based on 2,5-dicarboxylic acid and several diols were synthesized and characterized using different polycondensation techniques. The aliphatic diols were sufficiently volatile to allow the use of polytransesterifications, which gave high-molecular weight semicrystalline materials with good thermal stability. In particular, the polyester based on ethylene glycol displayed properties comparable with those of its aromatic counterpart, poly(ethylene terephthalate), namely, the most important industrial polyester. The use of isosorbide gave rise to amorphous polymers with very stiff chains and hence a high glass transition temperature and an enhanced thermal stability. The interfacial polycondensation between the acid dichloride and hydroquinone produced a semicrystalline material with features similar to those of entirely aromatic polyesters, characterized essentially by the absence of melting and poor solubility, both associated with their remarkable chain rigidity. The replacement of hydroquinone with the corresponding benzylic diol was sufficient to provide a more tractable polyester. This study provided ample evidence in favor of the exploitation of furan monomers as renewable alternatives to fossil-based aromatic homologs. © 2011 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 3759–3768, 2011

KEYWORDS: aliphatic, aromatic and furan diols; crystallinity; furan polyesters; 2,5-furandicarboxylic acid; polycondensation; renewable resources; thermal properties

INTRODUCTION The growing interest in the preparation of new chemicals and materials based on renewable resources has naturally led to the development of a correspondingly original realm of polymers.[1] The interest of this strategy is to provide viable alternatives to the predictable dwindling of fossil resources associated with their price increase, as well as to counteract the environmental problems related to fossil CO_2 emissions. Although these actions are more frequently and more massively directed at novel sources of energy, the production of chemical commodities from renewable resources has also become a major issue involving both academic and industrial research activities.[2]

In this context, two basic nonpetroleum monomer precursors are readily accessible from polysaccharides or sugars bearing, respectively, pentose and hexose moieties, namely the first-generation furan derivatives furfural (**F**) and hydroxymethylfurfural (**HMF**).[2,3] From them, a whole array of furan monomers can be prepared and polymerized to give materials often comparable to those derived from a whole host of monomers prepared from fossil resources, that is, the majority of today's commercial polymers.[3] While **F** has been an industrial commodity for nearly a century,[3] the production of **HMF** has been slowed down by difficulties in terms of isolating it in good yields and purity. However, in the last few years, a massive output of publications[3(a,d,e)] suggests that such a process will soon become a reality, motivated by the practical interest in optimizing its synthesis. This is understandable, because **HMF** is the obvious precursor to 2,5-disubstituted furan monomers, like 2,5-furandicarboxylic acid (**FDCA**) and its dichloride,[3] as well as to promising chemicals such as levulinic acid.[4] The key structural feature associated with these monomers is their close resemblance to aromatic counterparts and hence the interest in using them to synthesize polymers via step-growth mechanisms, namely polyesters and polyamides.

The realm of furan polyesters has been the subject of several investigations,[3] beginning with the pioneering work of Moore and Kelly[5] 30 years ago, who studied the synthesis of a number of linear polyesters prepared from **FDCA** or its dichloride. Since then, these types of structures have been virtually ignored, except for a brief study by Storbeck and Ballauf,[6] probably because of the lack of ready availability of **FDCA**. Therefore, the interest in furan polyesters shifted to the use of difuran dicarboxylic monomers prepared by the coupling of commercial 2-furancarboxylic esters through a condensation reaction involving aldehydes and, preferably, ketones. A series of systematic investigations were thus carried out covering a wide range of diols, as well as of different moieties

Correspondence to: A. Gandini (E-mail: agandini@ua.pt)
Journal of Polymer Science Part A: Polymer Chemistry, Vol. 49, 3759–3768 (2011) © 2011 Wiley Periodicals, Inc.

bridging the two furan heterocycles,[7] which provided a comprehensive set of structure–property relationships. Okada et al.[8] extended this domain using diols from renewable resources.

The prospect of **HMF** and its derivatives becoming viable commodities[3(a,d,e)] induced us to return to furan polyesters based on **FDCA** through a comprehensive investigation of their synthesis and characterization, including novel structures and the re-examination of previously reported ones, as briefly described in two preliminary communications.[9,10] Grosshardt et al.[11] concurrently tackled some of these systems.

The present detailed report marks the start of this program with a first set of furan polyesters and copolyesters based on **FDCA** and several diols, prepared by straightforward routes, using mild conditions. It is important to reiterate that at the basis of this strategy lies the pressing requirement of developing novel materials from renewable resources capable of replacing, or even surpassing, their fossil-based counterparts.

EXPERIMENTAL

Materials

FDCA was a generous gift from Dr. Claude Moreau, who prepared it during his pioneering studies related to the optimization of the preparation of **HMF**.[12] Its purity was deemed adequate for its subsequent use as a monomer precursor. D-Isosorbide and isoidide were generous gifts from Roquette France. Bis(2,5-hydroxymethyl)furan was kindly donated by TransFurans Chemicals bvba, Geel, Belgium. Ethylene glycol (99%), propane-1,3-diol (99%), 1,4-di-(hydroxymethyl)-benzene (99%), hydroquinone (99.5%), as well as all other reagents and solvents were purchased from Aldrich and used as received. D-Isosorbide, isoidide, and bis(2,5-hydroxymethyl)furan were dried under vacuum in the presence of phosphorus pentoxide and 1,1,2,2-tetrachloroethane (**TCE**), which was dried over sodium hydride.

Techniques

Molecular weights and their distributions were obtained using a home-made size exclusion chromatographer (**SEC**) equipped with a PL-EMD 960 light scattering detector. The column set consisted of a PL HFIPgel guard followed by two PL HFIP columns (300 × 7.5 mm^2), kept at 40 °C. The HPLC was set with a flow rate of 1.0 mL/min and a v/v/v mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (**HFIP**) 70/20/10 was used as the eluent. The sample solutions with a concentration of about 3 mg/mL were filtered through a **PTFE** membrane before injection. A molecular weight calibration curve was obtained with eight polystyrene standards in narrow-range of molecular weights comprised between 790 and 96,000 g/mol.

All FTIR-attenuated total reflection (**ATR**) spectra were taken with a Brücker IFS FTIR spectrophotometer equipped with a single horizontal Golden Gate **ATR** cell. ^1H and ^{13}C NMR spectra were recorded on a Brücker AMX 300 operating at 300.13 MHz for ^1H and 75.47 for ^{13}C spectra in $CDCl_3$, $C_2D_2Cl_4$, CD_3COCD_3, or $C_3F_6OD_2$. ^{13}C solid-state cross-polarized magic-angle spinning nuclear magnetic resonance (^{13}CP-MAS [hpdec] NMR) spectra were recorded on a Brücker Avance 400 spectrometer operating with a magnetic field of 9.4 T, at 9.7 kHz, using glycidine as reference.

Elemental analyses of C and H were conducted in duplicate with a Leco CHNS-932 analyzer. The duplicate elemental analysis of C, H, O, and F were carried out at the CNRS "Service Central d'Analyse," Vernaison, France.

The thermogravimetric properties were gathered using a Shimadzu TGA 50 analyzer equipped with a platinum cell. Samples were heated at a constant rate of 10 °C/min from room temperature to 800 °C, under a nitrogen flow of 20 mL/min. DSC thermograms were obtained with a Setaram DSC92 calorimeter using aluminum pans under nitrogen with a heating rate of 10 °C/min in the temperature range of 18–400 °C.

The X-ray diffraction (**XRD**) patterns were recorded with a Phillips X'pert MPD diffractometer, using Cu Kα radiation.

Monomer Synthesis

The diol comonomers were used as such and the furan monomers were prepared as described below.

2,5-Furandicarbonyl Chloride 1

1 g of **FDCA**, 2 mL of $SOCl_2$, and 20 μL of dimethylformamide (**DMF**) were introduced into a 25 mL round-bottom flask fitted with a condenser and a magnetic stirrer, and the mixture was refluxed at 80 °C for 4 h with constant stirring. The condenser was connected to a washing bottle, filled with a concentrated sodium hydroxide aqueous solution, through a glass tube packed with activated silica gel. After the reaction, the excess of $SOCl_2$ and **DMF** was removed under vacuum at room temperature and collected in a trap cooled with liquid nitrogen. The ensuing monomer was isolated and purified by high-vacuum sublimation (yield: 78%).

White crystalline powder, m.p. 79 °C. FTIR (ν/cm^{-1}): 3143 (=CH); 1737 (C=O); 1563 (C=C); 974, 824, 712 (C—H). ^1H NMR ($CDCl_3$, δ/ppm): 7.5 (s, H3 and H4). ^{13}C NMR ($CDCl_3$, δ/ppm): 155.9 (C=O); 149.3 (C2 and C5); 123.2 (C3 and C4).

Bis(hydroxyalkyl)-2,5-furandicarboxylates

The general procedure for the synthesis of these monomers deals with the classical Fischer esterification. Typically, 1 g of **FDCA** (6.41 mmol), a large excess of diol, and 1.8 mL of concentrated HCl were introduced into a round-bottom flask. The mixture was heated at 90 °C for 12 h under magnetic stirring. The excess of diol was then removed under high vacuum after neutralization with a saturated solution of sodium hydroxide in the used diol. The products were isolated by dissolution in acetone at room temperature, the impurities were filtered, and finally the solvent vacuum was removed.

Bis(hydroxyethyl)-2,5-furandicarboxylate 2. FTIR (ν/cm^{-1}): 3354 (OH); 2952, 2881 (C—H); 1716 (C=O); 1582, 1511 (C=C); 1272 (C—O); 963, 832, 764 (=CH). ^1H NMR (CD_3COCD_3, δ/ppm): 7.4 (s, H3/H4 furan ring); 4.4 (t,

CH_2—O—C=O); 3.9 (t CH_2-OH). ^{13}C NMR (CD_3COCD_3, δ/ppm): 158.7 (C=O); 147.7 (C2/C5 furan ring); 119.7 (C3/C4 furan ring); 67.6 (COO$\underline{C}H_2$—); 60.6 (—$\underline{C}H_2OH$). White crystalline powder, m.p. 91 °C.

Bis(3-hydroxypropyl)-2,5-furandicarboxylate 3. FTIR (ν/cm^{-1}): 3228 (OH); 3119 (=CH); 2930, 2873 (C—H); 1725 (C=O); 1573, 1505 (C=C); 1279 (C—O); 960, 855, 771 (=CH). ^1H NMR ($CDCl_3$, δ/ppm): 7.3 (s, H3/H4 furan ring); 4.5 (t, $C\underline{H_2}$—O—C=O); 3.8 (t, —$C\underline{H_2}$—OH); 2.0 (q, —CH_2—$C\underline{H_2}$—CH_2—). ^{13}C NMR, ($CDCl_3$, δ/ppm): 158.2 (C=O); 146.6 (C2/C5 furan ring); 118.5 (C3/C4 furan ring); 62.6 ($\underline{C}H_2$—O—C=O); 58.9 (—$\underline{C}H_2OH$); 33.9 (—CH_2—$\underline{C}H_2$—CH_2—). White crystalline powder, m.p. 79 °C.

Polymerization Procedures

Three different techniques were adopted taking into account the specific monomers involved. Solution and interfacial polycondensations were the procedures chosen for the synthesis of polyesters based on **1** and nonvolatile diols, whereas monomers **2** and **3** were submitted to a polytransesterification approach for preparing both polyesters and copolyesters. The detailed procedures are provided below.

Solution Polycondensation

The procedure was adapted from Storbeck and Ballauff[6] and Gharbi et al.[7e] The reactions were carried out at low temperature under nitrogen with magnetic stirring and **TCE** as solvent. The diol monomer (2.59 mmol) was first dissolved in 1 mL of **TCE** and, after complete dissolution, 1.7 mL of pyridine was added. This mixture was cooled to about 0 °C with an ice bath and an equal molar amount of 2,5-furandicarbonyl chloride (2.59 mmol), dissolved in 1.5 mL of **TCE**, was added. The reaction medium was kept under constant stirring at room temperature while its viscosity increased progressively before the actual precipitation of the polymer, which was isolated by filtration, washed repeatedly with methanol, and dried.

Poly(1,4-phenylbismethylene-2,5-furandicarboxylate). FTIR (ν/cm^{-1}): 3124 (=CH); 2880 (C—H); 1718 (C=O); 1578 (C=C); 1267 (C—O); 976, 826, 761 (=CH). ^1H NMR (C_3F_6DOD, δ/ppm): 7.4 (s, H9/H10/H12/H13 aromatic ring); 7.3 (s, H3/H4 furan ring); 5.4 (s, $C\underline{H_2}$—O—C=O). ^{13}C NMR, (C_3F_6DOD, δ/ppm): 160.7 (C=O); 147.1 (C2/C5 furan ring); 135.8 (C9/C10/C12/C13 aromatic ring); 128.9 (C8/C11 aromatic ring); 120.4 (C3/C4 furan ring); 68.3 ($\underline{C}H_2$—O—C=O).

Polyester from 1 and Isosorbide 6. FTIR (ν/cm^{-1}): 1713 (C=O); 1579 (C=C); 1267 (C—O); 967, 810, 761 (=CH). ^1H NMR ($C_2D_2Cl_4$, δ/ppm): 6.61–6.56 (H3/H4 furan ring); 3.40–3.29 (H7/H12); 4.76–4.71(H8/H11); 3.98 (H9); 4.38 (H10). ^{13}C NMR ($C_2D_2Cl_4$, δ/ppm): 157.07 and 157.02 (C=O); 146.13 and 145.99 (C2/C5 furan ring); 119.41 and 119.17 (C3/C4 furan ring); 73.05 (C7); 85.74 (C8); 78.84 (C9); 74.96 (C10); 80.96 (C11); 70.73 (C12).

Polyester from 1 and Isoidide 7. FTIR (ν/cm^{-1}): 1719 (C=O); 1579 (C=C); 1267 (C—O); 976, 826, 761 (=CH). ^1H NMR ($C_2D_2Cl_4$, δ/ppm): 6.61–6.56 (H3/H4 furan ring); 3.40–3.32 (H7/H12); 4.76–4.71(H8/H11); 3.97 (H9); 4.38 (H10). ^{13}C NMR ($C_2D_2Cl_4$, δ/ppm): 157.07 and 156.85 (C=O); 146.13 and 146.00 (C2/C5 furan ring); 119.41 and 119.18 (C3/C4 furan ring); 73.06 (C7); 85.74 (C8); 78.80 (C9); 74.95 (C10); 80.95 (C11); 70.76 (C12).

Interfacial Polycondensation

The reactions were carried out at room temperature using a biphase system stirred mechanically at 900 rpm, consisting of (i) a 0.19 M aqueous solution of NaOH containing hydroquinone (5.18 mmol) and tetrabutylammonium bromide (72.4 mg) as the phase-transfer agent and (ii) dichloromethane containing the 2,5-furandicarbonyl chloride (5.18 mmol). A solid precipitate appeared almost immediately and the stirring was maintained further for an hour. The medium was then acidified to pH 2, and the polyester was isolated by filtration, washed with water, ethanol and acetone, and vacuum dried.

Poly(1,4-phenylene-2,5-furandicarboxylate). FTIR (ν/cm^{-1}): 3122 (=CH); 1739 (C=O); 1573, 1572 (C=C). ^{13}C MAS (hpdec) NMR, δ/ppm: 160.6 (C=O); 147.4 (C2/C5 furan ring and C7/C10 aromatic ring); 122.3 (C3/C4 furan ring and C8/C9/C11/C12 aromatic ring).

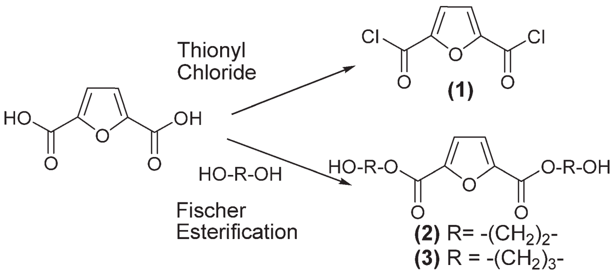
Poly(2,5-furandimethylene 2,5-furandicarboxylate). FTIR (ν/cm^{-1}): 1716 (C=O); 1580 (C=C); 1267 (C—O); 960, 821, 764 (=CH). ^1H NMR (C_3F_6DOD, δ/ppm): 7.3 (s, H3/H4 furan ring); 6.5 (s, H3/H4 furan ring), and 5.3 (s, $COOCH_2$); ^{13}C NMR (C_3F_6DOD, δ/ppm) 160.5 (C=O), 147.1 (C_2 and C_5), 127.0 ($C_{3'}$ and $C_{4'}$), 123.7 ($C_{2'}$ and $C_{5'}$), 120.0 (C_3 and C_4), and 68.0 (COO$\underline{C}H_2$).

Polytransesterification

The homopolymerization reactions were carried out in bulk using 1 g of the corresponding bis(hydroxyalkyl)-2,5-furandicarboxylate mixed with 1% (w/w) of the catalyst Sb_2O_3 in a round-bottom flask equipped with a magnetic stirrer. The flask was connected to a high-vacuum line through a trap cooled with liquid nitrogen. The mixture was heated rapidly to 70 °C and then progressively, in steps of about 10 °C at a time, to 240–250 °C, under constant stirring. The temperature increases were applied when a stagnancy occurred in the release of the glycol. The reaction was stopped when the product turned into a solid mass by letting the system return to room temperature. The ensuing polyester was dissolved in trifluoroacetic acid (TFA) or in HFIP and then precipitated into an excess of methanol, filtered, and vacuum dried.

Poly(ethylene 2,5-furandicarboxylate). FTIR (ν/cm^{-1}): 3123 (=CH); 1716 (C=O); 1578 (C=C); 1264 (C—O); 960, 834, 761 (=CH). ^1H NMR (C_3F_6DOD, δ/ppm): 7.4 (s, H3/H4 furan ring); 4.8 (s, —$C\underline{H_2}$—$C\underline{H_2}$—). ^{13}C NMR (C_3F_6DOD, δ/ppm): 161.0 (C=O); 147.1 (C2/C5 furan ring); 121.1 (C3/C4 furan ring); 64.7 (—$\underline{C}H_2$—$\underline{C}H_2$—).

Poly(3-propylene 2,5-furandicarboxylate). FTIR (ν/cm^{-1}): 3129 (=CH); 2968 and 2906 (C—H); 1715 (C=O); 1576 (C=C); 1267 (C—O); 966, 825, 763 (=CH). ^1H NMR ($C_2D_2Cl_4$, δ/ppm): 7.2 (s, H3/H4); 4.5 (t, —$C\underline{H_2}$—CH_2—$C\underline{H_2}$—); 2.3 (q, —CH_2—$C\underline{H_2}$—CH_2—). ^{13}C NMR,



SCHEME 1 The synthesis of monomers **1–3**.

($C_2D_2Cl_4$, δ/ppm): 158.3 (C=O); 146.9 (C2/C5); 119.3 (C3/C4); 62.6 ($-\underline{\mathrm{C}}H_2-CH_2-\underline{\mathrm{C}}H_2$); 28.4 ($-CH_2-\underline{\mathrm{C}}H_2-CH_2-$).

The copolymerization reactions involved monomers **2** and **3** in a molar feed of 1:3 and were conducted following the same protocol used for the homopolymerizations detailed above.

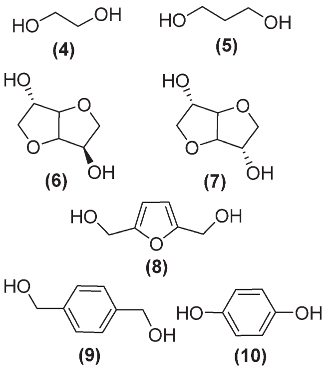
Poly(ethylene 2,5-furandicarboxylate-ran-3-propylene-2,5-furanodicarboxylate). ^{1}H NMR ($C_2D_2Cl_4$, δ/ppm): 7.2 (s, H3/H4 furan rings); 4.7 (s, $-C\underline{H}_2-C\underline{H}_2-$ 4.5 (t, $-C\underline{H}_2-CH_2-C\underline{H}_2-$); 2.3 (m, $-CH_2-C\underline{H}_2-CH_2-$ ^{13}C NMR ($C_2D_2Cl_4$, δ/ppm): 158.2 (C=O); 147.0 (C2/C5 furan rings); 119.5 (C3/C4 furan rings); 63.5 ($-CH_2-\underline{\mathrm{C}}H_2-$); 62.7 ($-\underline{\mathrm{C}}H_2-CH_2-\underline{\mathrm{C}}H_2$); 28.4 ($-CH_2-\underline{\mathrm{C}}H_2-CH_2-$).

RESULTS AND DISCUSSION

Monomer Synthesis and Characterization

The purity of the **FDCA** we used was deemed satisfactory for its use as a precursor in this study, as confirmed by TLC, ^{1}H and ^{13}C NMR spectroscopy, as well as elemental analysis. The synthetic pathways leading to the furan monomers **1–3** from it are sketched in Scheme 1, and the data relevant to their structure are summarized in Experimental section.

The FTIR spectra of these monomers were in tune with their expected structures, through the absence (for **1**) or the characteristic shift and narrowing of the OH band (from carboxylic to primary alcohol for **2** and **3**), respectively. The C=O bands of the carboxylic moieties shifted to the characteristically higher wavenumbers, compared with that of **FDCA**. Further corroboration was acquired from both ^{1}H NMR and ^{13}C NMR spectra, in which the multiplicity, integration, and assignments were in tune with each monomer structure. Interestingly, the melting temperatures of 79, 91 and, 78 °C, respectively, for **1**, **2**, and **3** were similar to those reported for their terephthalic counterparts, namely, 79–83, 109–110, and 77–79 °C, respectively, indicating that the 2,5-disubstituted furan moiety introduces a cohesive energy similar to that of the 1,4-phenylene homolog.



SCHEME 2 The diols used in this study.

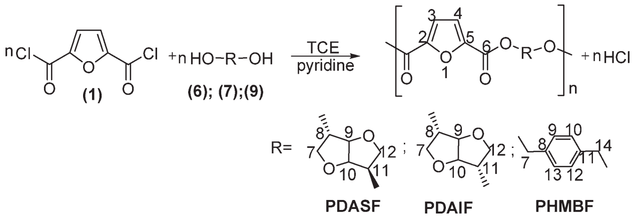
The diol comonomers **4–10** (Scheme 2) were used as received, given their high purity, and were chosen for their specific structural peculiarities. The absence of detectable impurities in these commercial products was confirmed by TLC, FTIR, and both ^{1}H and ^{13}C NMR spectroscopy. Ethylene glycol **4** and propane-1,3-diol **5** were aliphatic structures used to achieve materials with a degree of flexibility similar to that of their terephthalic polyester counterparts. With the purpose of preparing progressively stiffer polymer chains, we used D-isosorbide **6**, isoidide **7**, bis(2,5-hydroxymethyl)-furan **8**, bis-(1,4-hydroxymethyl)benzene **9**, and hydroquinone **10**. Additionally, diols **6**, **7**, and **8** were selected for the preparation of polyesters fully derived from renewable resources, considering moreover that isosorbide is a competitively priced chemical commodity. The latter considerations also apply, in principle, to **4** and **5**, because they can be prepared from glycerol, an abundant and cheap commodity produced in the preparation of biodiesel.

Polymer Synthesis and Characterization

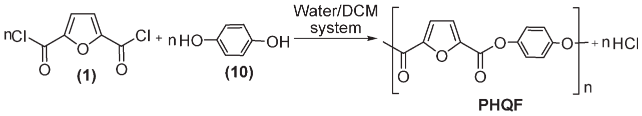
The polycondensation processes adopted here were based on well-known mechanisms and procedures, adapted to the present context and to the different types of monomers and comonomers. For the reactions conducted in solution, a proton trap insured the removal of HCl, whereas in the case of interfacial procedures, the presence of NaOH in the aqueous phase produced the corresponding neutralization. The polytransesterification approach was limited to those diols possessing a sufficient volatility to be vacuum removed, that is, the two aliphatic diols **4** and **5**.

The polyester from (**1**) and isosorbide 6 (**PDASF**), polyester from **1** and isoidide 7 (**PDAIF**), and **PHMBF** were prepared from monomer **1** and diols **6**, **7**, and **9** using a conventional solution polycondensation protocol at low temperature, as shown in Scheme 3.

The interfacial polycondensation between **1** and **10** (see Scheme 4) was carried out at room temperature using a sodium hydroxide water solution/dichloromethane system and tetrabutylammonium bromide as the phase transfer catalyst. These specific conditions were selected on the basis of



SCHEME 3 Solution polyesterification.



SCHEME 4 Interfacial polycondensation for the synthesis of PHQF.

a previously reported systematic study,[7(d)] which showed that they gave the best results for the interfacial polycondensation of furan monomers.

This synthetic approach was also selected for the preparation of the fully furan-based polyester, poly(2,5-furandimethylene 2,5-furandicarboxylate) (**PBHMF**; Fig. 1), because of the low thermal stability of bis-(2,5-hydroxymethyl)furan.

Poly(ethylene 2,5-furandicarboxylate) (**PEF**) was prepared by the polytransesterification of monomer **2**. After an investigation aimed at optimizing the process, the best results, in terms of molecular weights for this polyester, were obtained with the synthetic approach described in Experimental section (Scheme 5), which was also applied to monomer **3** to prepare the homolog polyester, poly(3-propylene 2,5-furandicarboxylate) (**PPF**).

The co-polyester PEF-*ran*-PPF was also synthesized in these conditions, with a threefold excess of monomer **3** in the molar feed ratio. The composition of the copolymer was determined by ^{1}H NMR spectroscopy, using the relative integration of the $—CH_2CH_2—$ equivalent protons of the ethylene glycol units and the $—CH_2—CH_2—CH_2$ protons of the propylene glycol units. The respective values indicated 24% of ethylene units and 76% of propylene moieties, in good agreement with the monomer feed compositions, as one would indeed expect from very similar structures, both bearing terminal primary OH functions.

The results of the optimized synthesis, in terms of yields of the isolated polymers and their higher molecular weights, are shown in Table 1. For instance, in the case of PEF, the transesterification of monomer **2** gave much better results when compared with those obtained from its synthesis via the solution polycondensation from monomer **1** and ethylene glycol **4**, as already anticipated in our previous communications.[9,10] Therefore, the transesterification procedure appears to be particularly suited for the synthesis of furan polyesters using aliphatic diols.

Regarding the furan polyesters obtained with nonvolatile diols, solution and interfacial polycondensations were shown to be very good alternatives for the preparation of a wider range of materials from renewable resources with a large spectrum of applications.

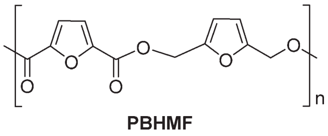
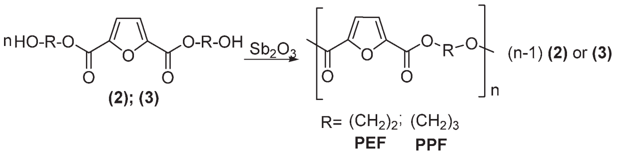


FIGURE 1 The fully furan-based polyester.



SCHEME 5 Synthesis of PEF and PPF via polytransesterification.

The number-average degree of polymerization (**DPn**) of the polyesters prepared by polytransesterification was also assessed by end-group determination. Samples from different syntheses were dissolved in **TFA** and treated with an excess of pentafluorobenzoyl chloride to esterify both terminal groups, as this polymerization technique generated macromolecules bearing a primary OH function at each chain end. After precipitation in methanol and washing several times with it, the modified polymers were submitted to elemental analysis in terms of C, H, O, and F and their **DPn** was calculated, assuming complete end-group modification. These values turned out to be higher than those obtained from the SEC tracings, either because the fluorination had not been complete or, more probably, because of the partial insolubility of the polyesters in the eluent medium used for the SEC analyses (We did not use pure **HFIP** because of its high price!), which excluded the higher molecular weights. Another source of discrepancy could have been the difference in hydrodynamic volume of the polyesters compared with that of the polystyrene standards, which would also account for the fact that some polyesters gave polydispersity index (**PDI**) values lower than two. Cyclic products were not identified and this aspect requires a more thorough investigation.

The lower molecular weight of **PDAIF**, compared with that of **PDASF**, was attributed to a difference in the purity of the corresponding diols, with D-isosorbide being certified as a thoroughly purified compound.

The solubility of the polyesters was examined using different potential solvents. Common organic solvents such as dichloromethane, chloroform, and tetrahydrofuran did not dissolve poly(1,4-phenylbismethylene-2,5-furandicarboxylate) (**PHMBF**), **PEF**, **PPF** and their copolymers, and indeed, the only two compounds that induced total dissolution at room temperature were trifluoroacetic acid and HFIP, with hot TCE as the third candidate. Mixtures of some common solvents containing some 10% of HFIP were successfully used as solvents for low polyester concentrations, as mentioned above in the context of the SEC analyses. **PDASF** was soluble in more manageable solvents like chloroform, whereas poly(1,4-phenylene-2,5-furandicarboxylate) (**PHQF**) was, as expected, the most intractable of all, with acceptable solubility only in hot *m*-cresol.

The FTIR spectra of all the polyesters reported in Table 2 were found to be consistent with the corresponding macromolecular structures. The characteristic bands of the ester carbonyl group appeared in the range of 1713–1739 cm^{-1}, depending on the nature of the group directly attached to it,

TABLE 1 Conditions and Results Related to the Optimized Polyesterifications Carried Out in This Study

Polymer	Monomers	Polycondensation Method	Yield (%)[a]	M_n (g/mol)[b]	M_w (g/mol)[b]	PDI[b]	M_n (g/mol)[c]
PEF	**2**	Transesterification	79	22,400	44,500	1.99	~45,500
PPF	**3**	Transesterification	76	21,600	27,600	1.28	~49,000
PEF	**1** + **4**	Solution	23	2,000	2,500	1.25	
PDASF	**1** + **6**	Solution	91	13,750	23,670	1.72	
PDAIF	**1** + **7**	Solution	80	5,670	7,270	1.28	
PBHMF	**1** + **8**	Interfacial	60	3,880	5,410	1.39	
PHQF	**1** + **10**	Interfacial	77	–	–	–	
PHMBF	**1** + **9**	Solution	75	22,100	47,500	2.15	
PEF-*ran*-PPF	**2** + **3**	Transesterification	58	14,100	32,000	2.27	~48,000

[a] Related to the amount of polymer recovered after reprecipitation.

[b] SEC analysis, PDI = M_w/M_n.

[c] Determined by end-group perfluorination.

and the C—O peak appeared around 1270 cm^{-1}. The typical and characteristic bands of 2,5-disubstituted furan rings were also present as given in the table. No significant absorption in the OH stretching region was detected, suggesting that the polymers had reached a plausibly high molecular weight, thus confirming the SEC data. As an example of these features, Figure 2 displays the typical FTIR spectrum of the furan–aromatic polyester **PHQF**.

The polyesters were also unambiguously characterized by ^{1}H and ^{13}C NMR spectroscopy. The data related to the spectra corresponding to the polyesters prepared by polytransesterification are given in Table 3. In all instances, the spectra were found to be consistent with the expected structure in terms of both chemical shifts and relative integrations. The spectra of **PEF** and **PPF** were very similar in terms of the resonance peaks associated to the furan ring and the methylene moieties directly attached to the ester group. The only difference arose from the extra middle CH$_2$ group in the **PPF** structure. Their integration ratio (1:2) in the **PEF** and **PPF** (1:2:1) spectra reflected the expected behavior, together with the corresponding peak multiplicities.

As a typical example of these spectra, Figure 3 shows the ^{1}H version of the PEF-*ran*-PPF copolyester, together with the chemical shift assignments. A particular feature, observed in both the ^{1}H and ^{13}C NMR spectra of this copolymer, was a slight split in all furan-related resonances, including that of the carbonyl carbons, pointing to a different chemical environment, as could indeed be anticipated for a random distribution of the two monomer units in its macromolecules.

Similar splits in the chemical shifts were also observed in the ^{1}H and ^{13}C NMR spectra of the PDASF polyester,[6] which was fully derived from renewable resources, namely, in the H3 and H4 of the furan ring (6.61–6.56 ppm), in the C2/C5 and C3/C4 carbons of the furan ring (146.13; 145.99 and 119.41; 119.17 ppm, respectively), as well as in the carbonyl carbon (157.07; 157.02 ppm). In this case, the splits were a consequence of the nonequivalence of the two OH groups of isosorbide.

The other polymer prepared by solution polycondensation, **PHMBF**, also gave NMR spectra, which corroborated its expected structure. The ^{1}H NMR spectrum of its solution in C$_3$F$_6$DOD gave resonances peaks at 7.3 and 7.4 ppm,

TABLE 2 FTIR Data of the Polyesters

	Frequency (cm^{-1})							
Assignment	PEF	PPF	PDASF	PDAIF	PBHMF	PHQF	PHMBF	PEF-*ran*-PPF
=CH Fu	3123	3119	3124	3111	3127	3121	3109	3121
C—H (CH$_2$)	2972	2968, 2906	2979, 2880	2931, 2870	2973	–	2925	2965, 2903
C=O (ester)	1716	1715	1718	1717	1716	1739	1713	1720
C=C Fu	1578	1576	1577	1573	1580	1572	1579	1578
C—O (ester)	1264	1267	1267	1266	1267	1269	1267	1269
Fu breathing	1015	1024	1017	1019	1024	Superposition with aromatic bands	1014	1017
2,5-Disubstituted Fu	960, 834, 761	966, 825, 763	976, 826, 761	976, 822, 762	960, 821, 764		967, 810, 761	967, 826, 764

Fu: furan ring.

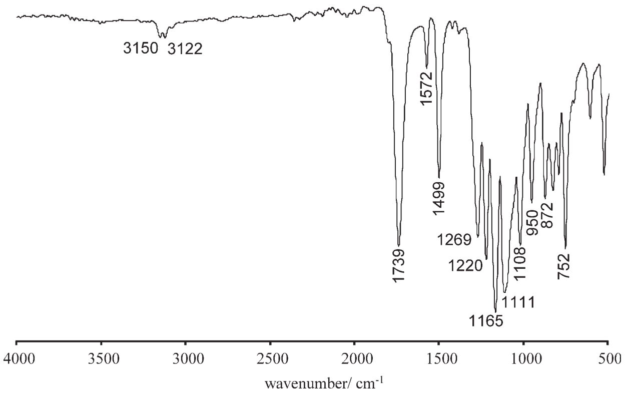


FIGURE 2 FTIR spectrum of PHQF.

respectively, for the furan H3/H4 and aromatic protons, with the methylene protons between the two rings resonating at 5.4 ppm. In the same solvent, the ^{13}C NMR spectrum showed the corresponding assignments of the carbon from the carbonyl moieties at 160.7 ppm, the C2/C5 furan carbons at 147.1 ppm and C3/C4 at 120.4 ppm. The peaks assigned to the aromatic ring carbons appeared at 128.9 ppm (unsubstituted carbons) and 135.7 ppm (p-substituted carbons) and those of the methylene carbon at 66.4 ppm.

As stated earlier, the furanic–aromatic polyester **PHQF** was insoluble in all common solvents and consequently its structural characterization was conducted by solid-state ^{13}CP-MAS NMR. This spectrum, shown in Figure 4, gave three intense peaks at 160.0, 147.4, and 122.3 ppm, assigned, respectively, to (i) C═O, (ii) furan C2/C5 and p-substituted aromatic carbons, and (iii) C3/C4 furan and unsubstituted aromatic carbons.

The average values of the elemental analyses of all of the polyesters are given in Table 4. The slightly lower carbon percentages, together with the correspondingly higher hydrogen contents, suggest the presence of residual moisture, a feature which became more pronounced with the isosorbide-based polyester.

Table 5 collects the results related to the thermal properties of the polyesters. The thermal stability in a nitrogen atmosphere was consistently good with an expected higher resistance for the **PHQF**. These features are entirely similar to those associated with the well-known polyesters in which aromatic rings are present instead of furan heterocycles, thus indicating that this structural substitution does not affect the thermal stability of the ensuing polymers. This is particularly relevant in the case of **PEF** and its aromatic counterpart poly(ethylene terephthalate) (**PET**), namely, the most important polyester on the market.

The DSC thermograms, one of which was published in our previous communication,[9,10] showed that the polyesters exhibited glass transition temperatures (T_gs) ranging from 50 to 180 °C, depending on the chain stiffness induced by the structure of the diol used.

The T_g, as well the T_c, of both **PEF** and **PPF** only appeared on the second DSC scan trace after quenching the melted polymers. This observation indicates a very high aptitude to crystallization and, in fact, both polyesters displayed a high degree of crystallinity when examined as pristine materials. The differences in their T_g, T_c, and T_m are clearly related to the increase in macromolecular flexibility associated with the additional methylene group in **PPF**, which results in a substantial reduction in all these thermal transitions. Obviously, their copolymer lost all aptitude to crystallize given its random nature, which was confirmed by the fact that its T_g was intermediate between those of the corresponding homopolymers (Table 5).

PDASF displayed a very high T_g, arising from the particularly rigid isosorbide structure. As expected, this polymer did not display any crystallinity because of its irregular structure, as discussed above. Similar results were obtained for **PDAIF**, with a slightly lower T_g, attributed to its lower molecular weight (see Table 1), but in this case some crystallinity was expected, given its more regular structure. This feature was, however, not detected by X-ray analysis and indeed by the absence of a melting feature in its DSC tracing up to 275 °C, where its thermal decomposition begun. The low molecular weight of this polyester could have been the cause of its failure to crystallize, which indicates the need of further work aimed at improving its synthesis.

TABLE 3 ^{1}H and ^{13}C Chemical Shifts (δ, ppm) from TMS in Different Solvents of the Polyesters Synthesized by Polytransesterification

	^{1}H			^{13}C		
Assignment	PEF C_3F_6DOD	PPF $C_2D_2Cl_4$	PEF-*ran*-PPF C_3F_6DOD	PEF C_3F_6DOD	PPF $C_2D_2Cl_4$	PEF-*ran*-PPF C_3F_6DOD
2/5 Fu	–	–	–	147.1	146.9	147.0
3/4 Fu	7.4 (s)	7.2 (s)	7.2 (s)	121.1	119.3	119.5
2/5-CO	–	–	–	161.0	158.3	158.2
$-\underline{CH_2CH_2}-$	4.8 (s)	–	4.7 (s)	64.7	–	63.5
$-\underline{CH_2}CH_2\underline{CH_2}-$	–	4.5 (t)	4.5 (t)	–	62.6	62.7
$-CH_2\underline{CH_2}CH_2-$		2.3 (q)	2.3 (m)	–	28.4	28.4

Multiplicity—s: singlet; t: triplet; q: quintet; m: multiplet; Fu: furan ring.

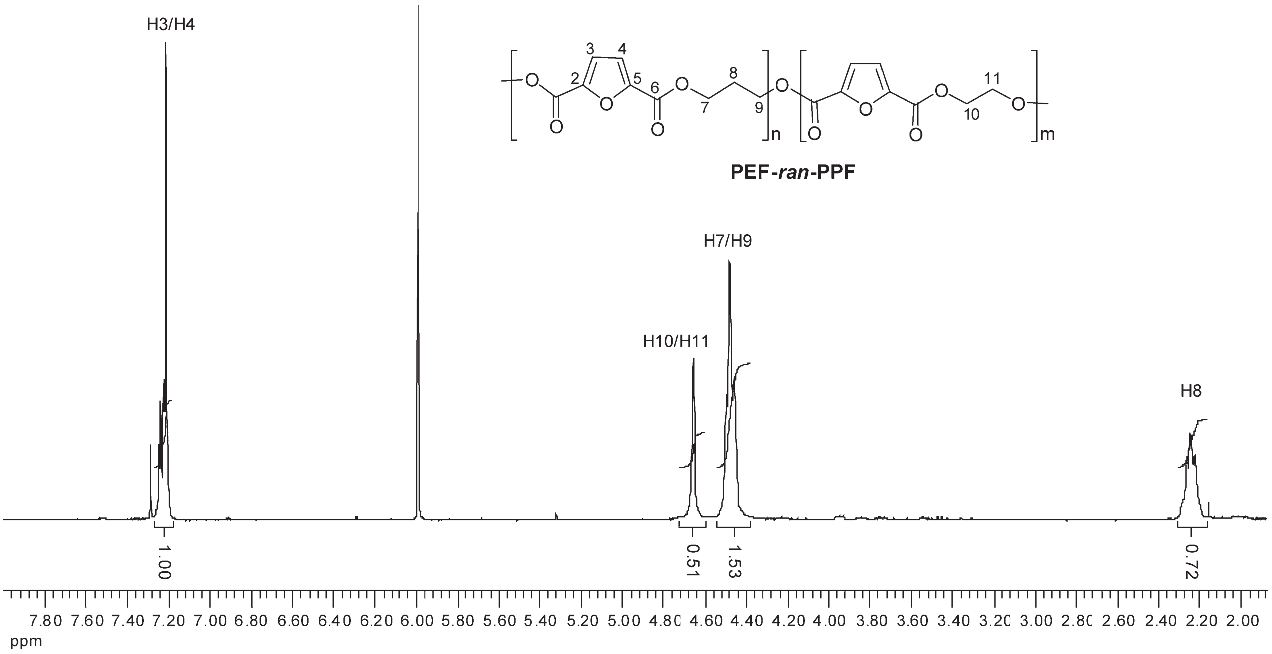


FIGURE 3 ^{1}H NMR spectrum of PEF-*ran*-PPF in TCE*d2*.

The T_g of **PHMBF** was not much higher than that of **PEF** and its lack of pristine or induced crystallinity, confirmed by the X-ray diffractogram, is difficult to rationalize in view of its regular structure. A typical DSC thermogram of this polymer is shown in Figure 5 and its TGA tracing in Figure 6. **PHQF** did not display any thermal transition up to 400 °C, despite its high crystallinity (see below), a feature which is typical of very highly rigid macromolecular structures like those of aromatic polyesters, hence the replacement of a benzene ring by a furan heterocycle did not reduce this stiffness in any detectable way. In other words, the cohesive energy of these polymers places their melting temperature above that of their thermal degradation.

The presence of crystallinity on the pristine polymers was also assessed by XRD. **PEF** diffractograms showed three sharp signals, respectively, at $2\theta = 16.0$, 20.1, and 27.8°. **PPF** showed a similar pattern with $2\theta = 11.0$, 22.5, and 27.8°. The other polyesters did not display any crystallinity pattern, with the exception to **PHQF**, which gave three rather sharp signals at $2\theta = 16.8$, 24.8, and 29.5° (Fig. 7), suggesting a high degree of macromolecular order.

CONCLUSIONS

The first family of furan polyesters described in this study showed structures, molecular weights, and properties which make them thoroughly viable as macromolecular materials,

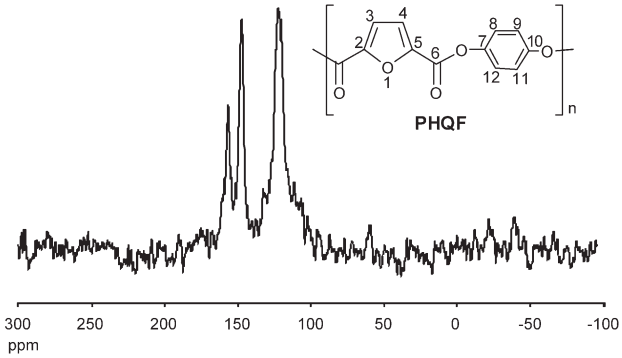


FIGURE 4 Solid-state ^{13}CP-MAS NMR spectrum of PHQF.

TABLE 4 Elemental Analysis Data

	%C	%H
PEF		
Calculated	52.76	3.32
Found	51.88	3.60
PPF		
Calculated	55.10	4.08
Found	54.79	3.88
PDASF		
Calculated	54.14	3.79
Found	52.97	3.80
PHMBF		
Calculated	65.12	3.90
Found	65.18	4.03
PHQF		
Calculated	62.62	2.63
Found	61.90	2.72
PEF-*ran*-PPF		
Calculated[a]	54.50	3.87
Found	54.54	4.02

[a] Calculated on the basis of the copolymer composition.

TABLE 5 Onset of Thermal Decomposition (T_{di}), Maximum Decomposition Temperature (T_d), Glass Transition Temperature (T_g), Crystallization Temperature (T_c), and Melting Temperature (T_m) of the Polyesters

Polymer	T_{di}^{a} (°C)	T_d^{a} (°C)	T_g^{b} (°C)	T_c^{b} (°C)	T_m^{b} (°C)
PEF	300	398	80	165	215
PPF	295	390	50	127	174
PDASF	350	450	180	–	–
PDAIF	275	396	140	–	–
PBHMF	205	345			
PHQF	280	490	nd	nd	nd
PHMBF	300	390	87	–	–
PEF-*ran*-PPF	300	398	80	165	215

[a] TGA measurements.
[b] DSC measurements (nd = not detected below 400 °C).

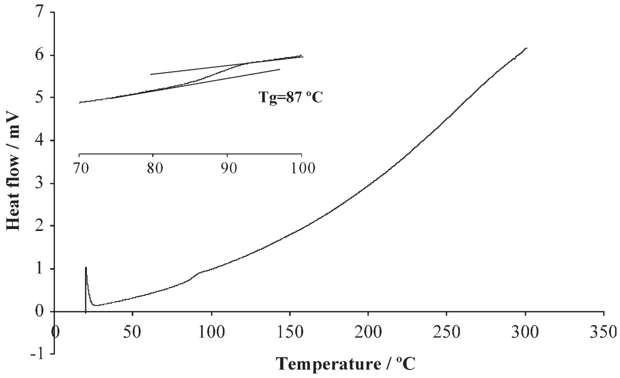


FIGURE 5 Second DSC scan of PHMBF after a rapid cooling of 200 °C/min.

quite comparable with aromatic–aliphatic homologs derived from fossil resources. The most interesting of these comparisons is of course that relating **PEF** to **PET**, because of the enormous relevance of the latter polymer. All the features tested here indicate that **PEF** could successfully replace **PET** and thus constitute a valuable contribution to polymers from renewable resources, considering moreover that ethylene glycol can be prepared from glycerol. Work is in progress, on the one hand, to extend the characterizations of these polyesters to mechanical and other properties, including moisture uptake, and, on the other hand, to synthesize other original furan polyesters.

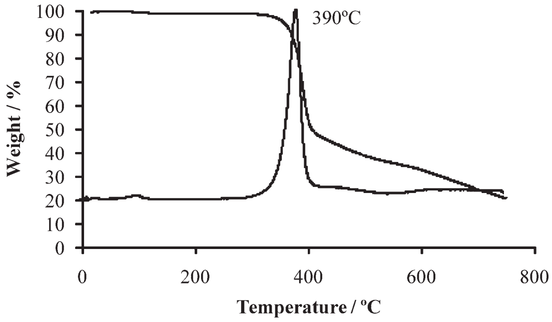


FIGURE 6 TGA of PHMBF in a nitrogen flow.

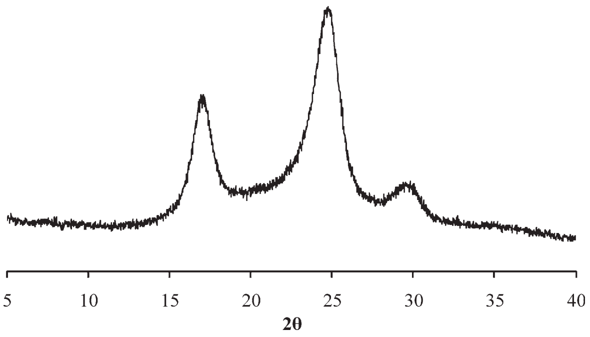


FIGURE 7 X-ray diffractogram of the pristine PHQF.

The authors thank the Portuguese Fundação para a Ciência e a Tecnologia (FCT) for a research grant (PTDC/QUI-QUI/101058/2008) sponsoring this study.

REFERENCES AND NOTES

1 (a) Monomers, Polymers and Composites from Renewable Resources; Belgacem, M. N.; Gandini, A. (Eds.); Elsevier: Amesterdam, 2008; (b) Gandini, A. Macromolecules, 2008, 41, 9491; (c) Gandini, A. Green Chem 2011, 13, 1061.

2 (a) Werpy, T.; Petersen, G. Top Value Added Chemicals from Biomass. Results of Screening for Potential Candidates from Sugars and Synthesis Gas; Pacific Northwest National Laboratory, National Renewable Energy Laboratory for the Office of Biomass Program (US Dept. of Energy): Washington, 2004; Vol. I; (b) Petersen, G.; Bozell, J. Green Chem 2010, 12, 539.

3 (a) Gandini, A. Polym Chem 2010, 8, 245; (b) Belgacem, M. N.; Gandini, A. In Monomers, Polymers and Composites from Renewable Resources; Belgacem, M. N.; Gandini, A.; Eds; Elsevier: Amesterdam, 2008; Chapter 6; (c) Gandini, A.; Belgacem, N. M. Prog Polym Sci 1997, 22, 1203; (d) Gandini, A. In Green Polymerization Methods: Renewable Starting Materials, Catalysis and Waste Reduction; Mathers, R. T.; Meier, M. A., Eds.; Wiley-VCH: Weinheim, 2011; p. 29; (e) Gandini, A. In Films and Coatings from Renewable Resources; Plackett, D., Ed.; Wiley-VCH: Weinheim, 2011; p. 180.

4 Boisen, A.; Christensen, T. B.; Fu, W.; Gorbanev, Y. Y.; Hansen, T. S.; Jensen, J. S.; Klitgaard, S. K.; Pedersen, S.; Riisager, A.; Ståhlberg, T.; Woodley, J. M. Chem Eng Res Des 2009, 87, 1318.

5 (a) Kelly, J. E. Ph.D. Thesis, Rensselear Polytechnic, NY, 1975; (b) Moore, J. A.; Kelly, J. E. Macromolecules 1978, 11, 568; (c) Moore, J. A.; Kelly, J. E. Polymer 1979, 20, 627.

6 Storbeck, R.; Ballauff, M. Polymer 1993, 34, 5003.

7 (a) Khrouf, A.; Boufi, S.; El Gharbi, R.; Belgacem, N. M.; Gandini, A. Polym Bull 1996, 37, 589; (b) Khrouf, A.; Abid, M.; Boufi, S.; El Gharbi, R.; Gandini, A. Macromol Chem Phys

1998, 199, 2755; (c) Khrouf, A.; Boufi, S.; El Gharbi, R.; Gandini, A. Polym Int 1999, 48, 649; (d) Chaabouni, A.; Gharbi, S.; Abid, M.; Boufi, S.; El Gharbi, R.; Gandini, A. J Soc Chim Tunisie 1999, 4, 547; (e) Gharbi, S.; Andreolety, J.-P.; Gandini, A. Eur Polym J 2000, 36, 463; (f) Abid, M.; Kamoun, W.; El Gharbi, R.; Fradet, A. Macromol Mater Eng 2008, 293, 39.

8 (a) Okada, M.; Tachikawa, K.; Aoi, K. J Polym Sci Part A Polym Chem 1997, 35, 2729; (b) Okada, M.; Tachikawa, K; Aoi, K. J Appl Polym Sci 1999, 74, 3342.

9 Gandini, A.; Silvestre, A.; Neto, C. P.; Sousa, A. F.; Gomes, M. J Polym Sci Part A: Polym Chem 2008, 47, 295.

10 Gandini, A.; Coelho, D.; Gomes, M.; Reis, B.; Silvestre, A. J Mater Chem 2009, 19, 8656.

11 Grosshardt, O.; Tübke, B.; Kowollik, K.; Fehrenbacher, U.; Dingenouts, N.; Wilhelm, M. Chem Ing Technik 2009, 81, 1829.

12 Moreau, C.; Belgacem, M. N.; Gandini, A. Topics Catal 2004, 27, 11.