A Facile Method to Synthesize High-Molecular-Weight Biobased Polyesters from 2,5-Furandicarboxylic Acid and Long-Chain Diols

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ABSTRACT: In this study, biobased furan dicarboxylate polyesters have been prepared using 2,5-furandicarboxylic acid (FDCA) and diols with high number of methylene groups (long-chain diols), namely, 8, 9, 10, and 12. Because of the high boiling points of these diols, a modified procedure of the well-known melt polycondensation was applied in this work. According to this, the dimethyl ester of FDCA (DMFD) reacted in the first transesterification stage with the corresponding diols forming bis-hydroxy-alkylene furan dicarboxylates (BHFD). In the second stage, the BHFD reacted with DMFD again at temperatures of 150–170 °C (for 4–5 h), and in the final stage, the temperature was raised to 210–230 °C (vacuum was applied for 2–3 h). The molecular weight of the polyesters and the content of oligomers, as was verified by gel permeation chromatography analysis, depend on the polycondensation time and temperature. The chemical structure of the polyesters was verified from ^{1}H NMR spectroscopy. All the polymers were found to be semicrystalline, with melting temperatures from 69 to 140 °C depending on the diol used. In addition, the mechanical properties also varied with the type of diol. The higher values were observed for poly(octylene 2,5-furanoate), whereas the lowest values were observed for poly(dodecylene 2,5-furanoate) with the higher number of methylene groups in its repeating unit. © 2015 Wiley Periodicals, Inc. J. Polym. Sci., Part A: Polym. Chem. **2015**, *53*, 2617–2632

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INTRODUCTION Biobased polymers have gained high interest in the last decades because of the increased concern to diminish fossil resources and their impacts to the global warming. All these led to the development and growth of new economy known as bioeconomy. According to IUPAC definition, biobased polymer is a polymer derived from the biomass or prepared from monomers derived from the biomass and which, at some stage in its processing into finished products, can be shaped by flow. In 2004, extensive research efforts toward the synthesis of biobased chemicals were triggered when the US Department of Energy published a list of "10 biobased chemicals" of top priority.[1] Among them was 2,5-furandicarboxylic acid (FDCA), which has a large potential as a replacement for terephthalic acid, a widely used component in various polyesters, such as poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT).

The historical progress on FDCA-based polyesters is extensively described in recent reviews.[2,3] However, these new biobased furan dicarboxylate polyesters[4] have not gained any significant interest till recently mainly because of the difficulties to produce sufficient amounts of high-purity FDCA. The most important of these polyesters till today is poly(ethylene-2,5-furanoate) (PEF) because of its ability to formulate in films, fibers, and mostly bottles. When compared with the properties of the newly synthesized PEF bottles relative to PET, the following enhancements are found: six times better O_2 barrier, two times better H_2O barrier, two to four times better CO_2 barrier, 1.6 higher tensile modulus, about 70% lower CO_2 emission, and about 65% lower nonrenewable energy use for PEF production. These better properties of PEF are attributed to the different stiffness and motional processes of the furanic moiety.[5]

One of the major problems of the prepared 2,5-furan dicarboxylate polyesters is their coloration during synthesis. This problem was faced by Moore et al.[6] when 2,5-FDCA and hexamethylenediol were polycondensed with a mixture of calcium acetate and antimony oxide catalysts to synthesize a white fibrous film-forming polyester. The coloration of the FDCA/2,5-dimethylfuran dicarboxylate (DMFD)-based materials can have three origins, namely, sugar-based impurities in the monomer, side reactions (e.g., decarboxylation) taking place during the polymer synthesis, or the presence of various additives.[7] It was also found that catalysts such as manganese, cobalt, and germanium result in a strongly colored PEF product.[8] Furthermore, as was reported by de Jong et al.,[3] there is a clear relationship between the amount of FDCA and the amount of color formed.

Despite the fact that the use of 2,5-FDCA as monomer seems to be associated with colored products, a number of successful attempts have been reported for the preparation of furan dicarboxylate polyesters. To avoid coloration, acid/diol molar ratios ranging from 1/3 to 1/5 have been used in almost all of the published works, whereas when terephthalic acid or aliphatic dicarboxylic acids are used in similar reactions, the ratio is just higher than the equimolecular (1/1.1). In such a work, on the synthesis of poly(butylene 2,5-furandicarboxylate) (PBF), Ma et al.[9] reported a ratio between FDCA and butanediol (BG) of 1/5 mol/mol. Except molar ratios, the effect of polymerization reaction parameters such as the catalyst amount, reaction time, and polycondensation temperature on the molecular weight of the produced PBF was studied extensively.[10]

When high-boiling-point diols like isosorbide and 1,4-benzenedimethanol were used, the procedure for the preparation of the corresponding polyesters of FDCA can be followed only when its dichloride was used.[11] This is because these diols cannot be removed from the reactor during melt polycondensation procedure. In this case, high polycondensation temperatures should be used, in which unfortunately the polyester will decompose. Storbeck and Ballauff[12] proposed earlier a similar procedure to prepare furan dicarboxylate polyesters from three different dianhydrohexitols, namely, 1,4:3,6-dianhydro-D-sorbitol, 1,4:3,6-dianhydro-D-mannitol, and 1,4:3,6-dianhydro-L-iditol, which reacted with 2,5-furandicarbonyldichloride. All these polyesters were amorphous with high glass transition temperatures ranging from 173 to 196 °C and high thermal stability.[13]

The aim of this study is to prepare such biobased alipharomatic polyesters using 2,5-FDCA and diols with 8, 9, 10, and 12 methylene groups with a simple melt polycondensation procedure avoiding the use of acid chloride and the diol excess. These polyesters are named as poly(octylene 2,5-furanoate) (POF), poly(nonylene 2,5-furanoate) (PNF), poly(decylene 2,5-furanoate) (PDeF), and poly(dodecylene 2,5-furanoate) (PDoF), respectively. These diols are crystalline materials with high molecular weight and also have high boiling points. Thus, to remove them during the polycondensation stage, high temperature is needed. However, in our previous attempts to prepare such polyesters using polycondensation temperatures of 260–290 °C, products with dark brown to black color were obtained. This is in accordance to Gruter et al.[8] who reported that with increasing the polymerization temperature from 200 to 240 and 275 °C, the colorization of the final polyester was increased. To avoid this coloration, in our study, a different polymerization strategy was applied using the dimethyl ester of FDCA as raw material and low polycondensation temperatures (<230 °C) and less times (less than 3 h). The polyesters with 9 and 10 methylene groups were prepared for the first time. Besides, although the synthesis of POF and PDoF has been reported in the literature, their physical and mechanical properties have not been studied in such detail as in the current work.

MATERIALS AND METHODS

Materials

2,5-Furan dicarboxylic acid (purum 97%), 1,8-octanediol (98%, m.p. = 57–61 °C and b.p. = 172 °C/20 mmHg), 1,9-nonanediol (98%, m.p. = 45–47 °C and b.p. = 177 °C/15 mmHg), 1,10-decanediol (98%, m.p. = 71–75 °C and b.p. = 297 °C), 1,12-dodecanediol (99%, m.p. = 79–81 °C and b.p. =189 °C/12 mmHg), and tetrabutyl titanate (TBT) catalyst of analytical grade were purchased from Aldrich. All other materials and solvents used were of analytical grade.

Synthesis of 2,5-Dimethylfuran Dicarboxylate

About 15.6 g of FDCA, 200 mL of methanol anhydrite, and 2 mL of concentrated sulfuric acid were transferred into a random flask (500 mL), and the mixture was refluxed for 5 h. The excess of the methanol was distilled, and te solution was filtered through a disposable Teflon membrane filter. During filtration, dimethyl ester was precipitated as white powder, and after cooling, 100 mL of distilled water was added. The dispersion was partially neutralized by adding 5% Na_2CO_3 (w/v) during stirring while pH was measured continuously. The white powder was filtered, and the solid product was washed several times with distilled water and dried. The isolated white dimethyl ester was recrystallized with a mixture of 50/50 (v/v) methanol/water. After cooling, DMFD was precipitated in the form of white needles. The reaction yield was calculated at 83%.

Polyester Synthesis

The polyesters were prepared by applying a variation of the two-stage melt polycondensation method (esterification and polycondensation) in a glass batch reactor. DMFD and the appropriate diols at a molar ratio of diester/diol = 1/2 were charged into the reaction tube of the polyesterification apparatus with 400 ppm TBT. The reaction mixture was heated at 150 °C under argon atmosphere for 2 h, at 160 °C for additional 2 h, and finally at 170 °C for 1 h. This first step (transesterification) is considered to be complete after the collection of almost all the theoretical amount of CH_3OH, which was removed from the reaction mixture by distillation and collected in a graduate cylinder. After this stage, the corresponding bishydroxyalkylene-2,5-furan carboxylate monomers have been formed. In the second stage, these monomers reacted with DMFD in a molar ratio 1/1.05 at 150 °C under argon atmosphere for 2 h, at 160 °C for additional 2 h, and finally at 170 °C for 1 h. During this stage, methanol was also removed as byproduct. After that time, in the third step of polycondensation, a vacuum (5.0 Pa) was applied slowly over a period of time of about 30 min. The temperature was increased to 210 °C, and the polymerization was continued for 1 h at this temperature, at 220 °C for 1 h, and at 230 °C for 0.5 h using a stirring speed of 720 rpm. After the polycondensation reaction was completed, the polyesters were easily removed, milled, and washed with methanol.

Polyester Characterization

Intrinsic Viscosity and Molecular Weight Measurements

Intrinsic viscosity (IV, [η]) measurements of prepared polyesters were performed using an Ubbelohde viscometer at 30 °C in a mixture of phenol/1,1,2,2-tetrachloroethane (60/40 w/w). The sample was maintained in the above mixture of solvents at 90 °C for some time to achieve a complete solution. The solution was then cooled to room temperature and filtered through a disposable membrane filter made from Teflon.

The number–average molecular weight (M_n) was measured by gel permeation chromatography (GPC) using a Waters 150 °C apparatus equipped with differential refractometer as detector and three ultrastyragel (103, 104, and 105 Å) columns in series. Tetrahydrofuran was used as mobile phase at a flow rate 0.5 mL/min at 40 °C. Calibration was performed using polystyrene standards with a narrow molecular weight distribution.

Nuclear Magnetic Resonance

^{1}H NMR spectra of polyesters were obtained with a Bruker spectrometer operating at a frequency of 400 MHz for protons. Deuterated trifluoroacetic acid was used as solvent to prepare solutions of 5% w/v. The number of scans was 10, and the sweep width was 6 kHz.

Wide-Angle X-ray Diffraction Patterns

X-ray diffraction measurements of the samples were performed using a MiniFlex II XRD system from Rigaku, with Cu Kα radiation ($\lambda = 0.154$ nm) in the angle 2θ range from 5° to 60°.

Differential Scanning Calorimetry

A Perkin–Elmer, Pyris Diamond Differential Scanning Calorimeter (DSC), calibrated with pure indium and zinc standards, was used. The system also included an Intracooler 2P cooling accessory, for the DSC apparatus to achieve function at subambient temperatures and high cooling rates. Samples of 10 ± 0.1 mg sealed in aluminum pans were used to test the thermal behavior of the polyesters. The samples were heated from -50 °C to 150 °C in a 20 mL/min flow of N_2 with heating rate of 20 °C/min to observe the melting temperature of as-received polyesters. The samples were held at that temperature for 2 min and cooled with a cooling rate of 10 °C/min to -50 °C.

Polarizing Light Microscopy

A polarizing light microscope (PLM; Nikon, Optiphot-2) equipped with a Linkam THMS 600 heating stage, a Linkam TP 91 control unit, and also a Jenoptic ProgRes C10 Plus camera with the Capture Pro 2.1 software was used for PLM observations.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out with a SETARAM SETSYS TG-DTA 16/18 instrument. Samples (5.0 ± 0.3 mg) were placed in alumina crucibles. An empty alumina crucible was used as reference. The materials were heated from ambient temperature to 600 °C in a 50 mL/min flow of N_2 at heating rate of 20 °C/min. Continuous recordings of sample temperature, sample weight, and heat flow were taken. For decomposition studies of 2,5-FDCA and DMFD, mass loss curves have also been recorded during isothermal heating at different temperatures. For these measurements, 5.0 ± 0.3 mg of each sample has been heated from ambient temperature at heating rate of 10 °C/min to selected temperature, and the sample was remained there for certain time.

Pyrolysis-Gas Chromatography–Mass Spectroscopy

For pyrolysis-gas chromatography–mass spectroscopic (Py-GC/MS) analysis of 2,5-FDCA and DMFD, a very small amount of each material is "dropped" initially into the "Double-Shot" EGA/PY-3030D Pyrolyzer (Frontier Laboratories, Fukushima Japan) using a CGS-1050Ex (Japan) carrier gas selector. For EGA analysis, the furnace temperature is programmed from 50 to 700 °C with a heating rate of 20 °C/min using He as purge gas and air as cooling gas. For pyrolysis analysis (flash pyrolysis), each sample was placed into the sample cup, which afterward fell free into the Pyrolyzer furnace. The sample was retained at 100 °C for 2 min and heated with a rate 200 °C/min to its decomposition temperature. The preselected pyrolysis temperatures for 2,5-FDCA were 260, 330, and 500 °C for DMFD 120, 150, and 200 °C, and the GC oven temperature was programmed from 50 to 300 °C at 20 °C/min. The three temperatures were selected based on the TGA experiments and represent the sample prior, during, and after thermal decomposition. The sample vapors generated in the furnace were split (at a ratio of 1/50), a portion moved to the column at a flow rate of 1 mL/min, pressure 53.6 kPa, and the remaining portion exited the system via the vent.

The pyrolyzates are separated using temperature-programmed capillary column of a Shimadzu QP-2010 Ultra Plus (Japan) gas chromatograph and analyzed by the mass spectrometer MS-QP2010SE of Shimadzu (Japan) use 70 eV. Ultra ALLOY® metal capillary column from Frontier Laboratories was used containing 5% diphenyl and 95% dimethyl polysiloxane stationary phase, column length of 30 m, and column ID of 0.25 mm. For the mass spectrometer, the following conditions were used: ion source heater 200 °C, interface temperature 300 °C, vacuum 10^{-4} to 10^0 Pa, m/z range 10–1000 amu, and scan speed 10,000. The chromatograph and spectra retrieved by each experiment are subject to further interpretation through Shimadzu and Frontier postrun software.

Mechanical Properties

Measurements of tensile mechanical properties of the prepared polyesters were performed on an Instron 3344 dynamometer, in accordance with ASTM D-638, using a crosshead speed of 50 mm/min. Thin films of about 350 ± 25 μm were prepared using an Otto Weber, Type PW 30 hydraulic press, at a temperature of 40 ± 5 °C higher than the melting point of each one polyester. The molds were rapidly cooled by immersing them in water at 20 °C. From these films, dumbbell-shaped tensile test specimens (central portions 5 mm × 0.5 mm thick, 22 mm gauge length) were cut in a Wallace cutting press and conditioned at 25 °C and 55–60% relative humidity for 48 h. From stress–strain curves, the values of tensile strength at yield point and at break, elongation at break, and Young's modulus were determined. At least five specimens were tested for each sample, and the average values, together with the standard deviations, are reported.

RESULTS AND DISCUSSION

Stability Studies of 2,5-FDCA and Its DMFD Diester

In many cases, difficulties were observed in the attempts to prepare colorless and high-molecular-weight furan dicarboxylate polyesters, as 2,5-FDCA decomposed during polycondensation at high temperatures. Thus, in this study, 2,5-FDCA was converted into its dimethyl-2,5-furan dicarboxylate ester (DMFD). One additional advantage of DMFD is that it can be further purified by recrystallization in methanol producing monomer with high purity. Furthermore, transesterification of the diester can be performed under milder conditions than direct Fischer esterification of the diacid.[14] Grosshardt et al.[15] synthesized different polyesters with a polycondensation method using the dimethyl ester of 2,5-furan dicarboxylic acid and four different diols, namely, 1,3-propanediol, 1,6-hexanediol, 1,12-dodecanediol, and 1,18-octadecanediol and a mixture containing 0.13 mol % of calcium acetate and 0.1 mol % of antimony(III) oxide as catalyst. When compared with the other discussed methods for the preparation of such polyesters, the first stage of esterification took place under 0.3 MPa pressure at 140 °C, whereas the polycondensation procedure took place at higher temperatures (242 °C) under reduce pressure for 8 h. This was the first approach to prepare polyesters with direct polycondensation methods using high-molecular-weight diols like 1,12-dodecanediol and 1,18-octadecanediol. However, to achieve molecular weights of 22,000–25,000 g/mol, long polycondensation times were used (8 h). In another study of Gandini et al.,[16] to avoid the decarboxylation of 2,5-FDCA and the high acid/diol molar ratio, the bis-hydroxyethylene-2,5-furanoate was used for the preparation of PEF instead of 2,5-FDCA or its dimethyl ester. Thus, it seems that furan monomers are responsible for the coloration of the prepared polyesters. For this reason, in the current study and before starting the synthesis of polyesters, the thermal decomposition behavior of 2,5-FDCA and its DMFD was studied with TGA.

In Figure 1(a), the TGA curves (remaining mass as a function of temperature) of both 2,5-FDCA and its DMFD diester during dynamic heating are presented. As can be seen, the decomposition of 2,5-FDCA starts above 200 °C, with mass losses 0.1% at 210 °C, 0.22% at 220 °C, 0.35% at 230 °C, 0.5% at 240 °C, and 0.8% at 250 °C, whereas 2,5-FDCA shows its maximum decomposition rate at 350 °C. Furthermore, the 2,5-FDCA decomposition takes place at two stages, and the second stage proceeds above 375 °C, with a maximum decomposition rate at 450 °C. On the other hand, its dimethyl ester seems to be less stable, and its mass loss starts after 90–95 °C with mass losses 0.2% at 100 °C, 0.5% at 110 °C, 0.75% at 120 °C, 1% at 130 °C, 1.5% at 140 °C, and 2.5% at 150 °C, whereas at 230 °C, it shows its maximum decomposition rate. Important information about the decomposition procedure can also be taken from EGA curves recorded during pyrolysis of these monomers [Fig. 1(b)].

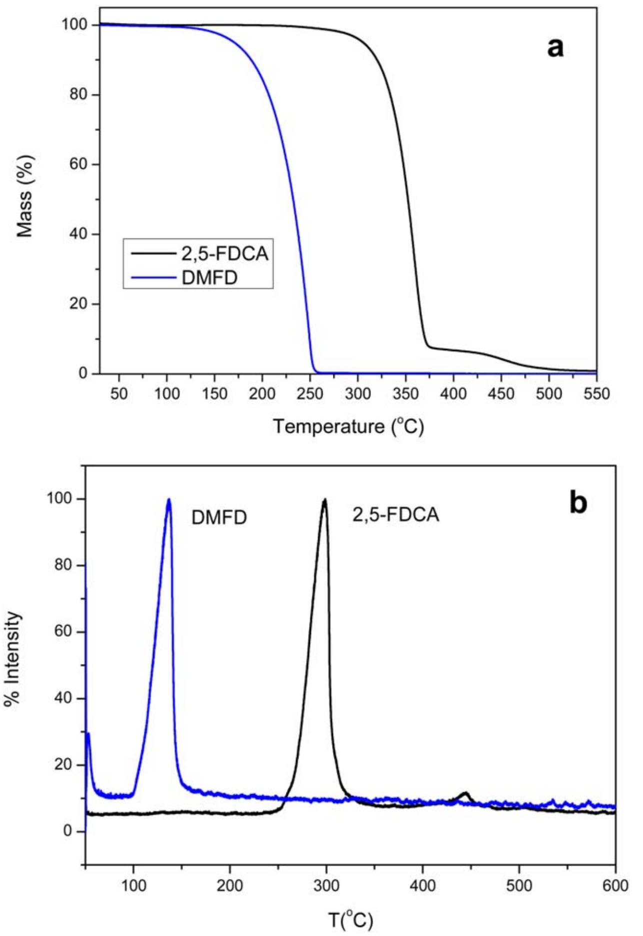


FIGURE 1 (a) Mass loss curves of 2,5-FDCA and its dimethyl ester, and (b) EGA curves recorded from Py-GC/MS. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In case of 2,5-FDCA, two peaks at 300 and 450 °C have been recorded, which is in agreement with TGA curves, as it was verified that its decomposition takes place at two stages. In DMFD, only one peak is recorded at 140–150 °C. Thus, it seems that the gas volatilization in DMFD starts at temperatures slightly higher than its melting point (112 °C) and are completed at temperatures between 190 and 200 °C. However, this temperature is much lower than the temperature

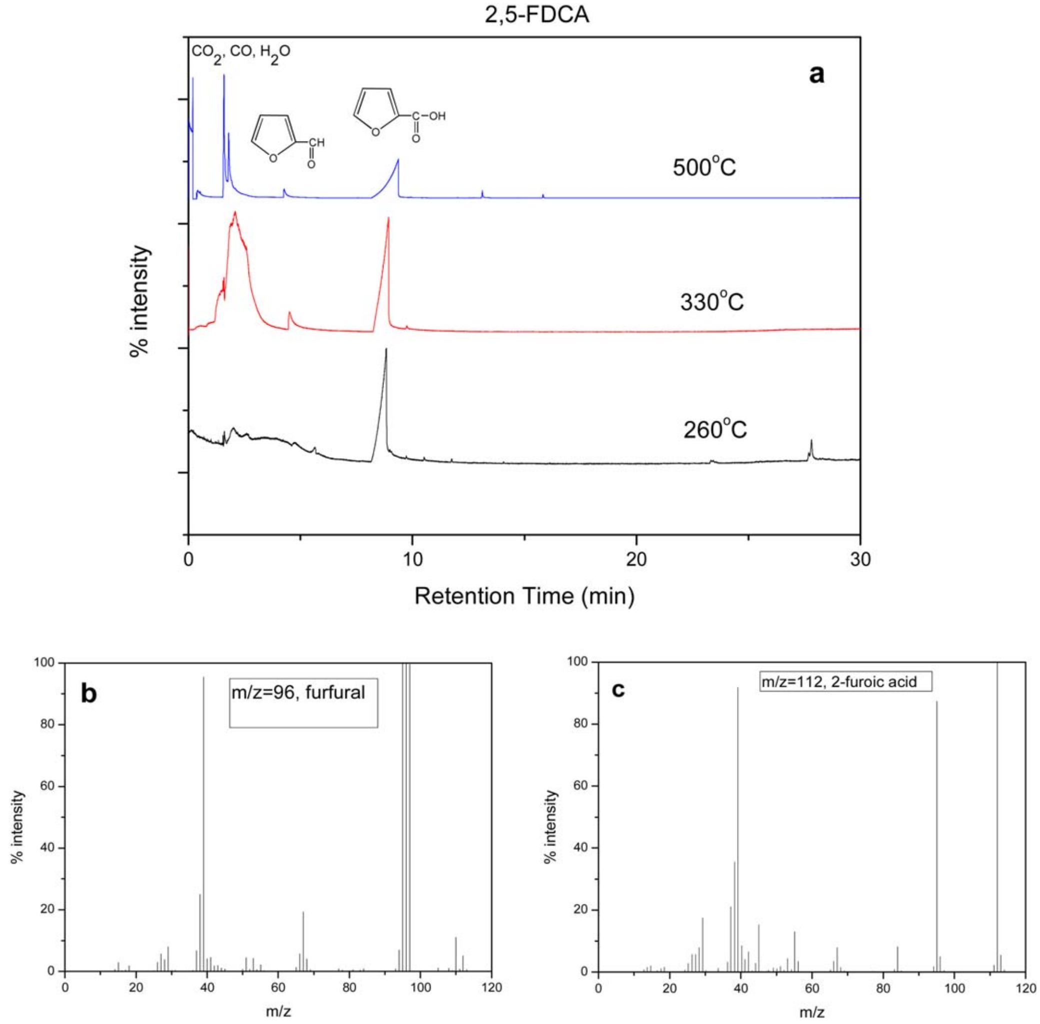


FIGURE 2 (a) Gas chromatographs of 2,5-FDCA decomposition products at different temperatures, and mass spectra (MS) of the main decomposition products, (b) furfural and (c) 2-furoic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that mass loss takes place at TGA [Fig. 1(a)]. For both monomers, Py-GC/MS was used to identify the decomposition procedure and the volatile products at different temperatures. The recorded chromatographs and the mass spectra of the main decomposition products are presented in Figures 2 and 3.

The decomposition of 2,5-FDCA was studied at temperatures 260, 330, and 500 °C, which were chosen from TGA curves and are attributed to the initiation, maximum mass loss rate, and to the end of decomposition. From Figure 2(a), it can be seen that the differences in the recorded chromatographs in all used temperatures are very small, concerning the retention time of the recorded peaks, and some differences can be found only in the intensity and the broadness of the peaks. From mass spectroscopy at each peak at low retention times (1–2 min), high-volatile decomposition byproducts were identified such as H_2O, CO, and CO_2. Formation of these compounds confirm that the decomposition of 2,5-FDCA takes place via decarboxylation, which is in agreement with many studies in the literature. At 4.5 min, a small peak with $m/z = 96$ was recorded, which is attributed to the furfural production [Fig. 2(b)]. At 8.5–9 min, there is a peak with higher intensity corresponding to 2-furoic acid [Fig. 2(c)], which is the main product after the decomposition of the other carboxyl group of 2,5-FDCA. Similar byproducts have also been identified during decomposition of 2,5-furan dicarboxylate polyesters in our previous study using Py-GC/MS.[17]

The gas chromatographs for DMFD have also been recorded for decomposition temperatures 120, 150, and 200 °C. As can be seen from Figure 3(a) in all studied temperatures, the chromatographs have a lot of similarities. For short retention times, till 2 min, CH_3O, CO, and CO_2 are the main decomposition products. At 6.5 min, the methyl ester of 2-furanoic acid [Fig. 3(b)] was identified, but as can be seen from the recorded peak, it is in small amount. The main peak in these chromatographs is recorded at 13 min and as was found from mass spectra [Fig. 3(c)], it is attributed to DMFD. Thus,

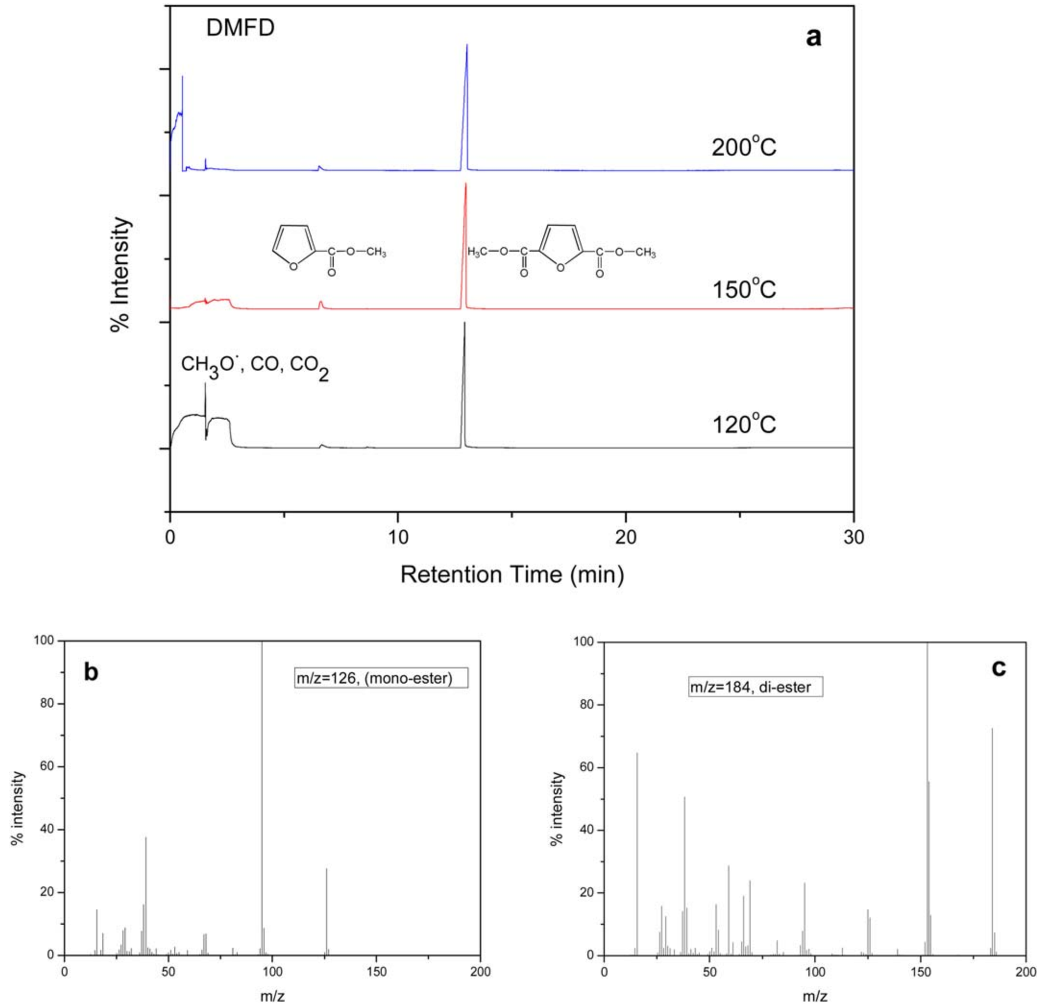


FIGURE 3 (a) Gas chromatographs of DMFD decomposition products at different temperatures, and mass spectra (MS) of the main decomposition products, (b) monoester and (c) diester. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

it seems that the dimethyl ester of 2,5-FDCA is very volatile and can be easily removed during heating even at very low temperatures like 120 and 150 °C, whereas the decomposition products are in low extent. From this study, it was proved that the mass loss of DMFD that was recorded by TGA was mainly due to the DMFD volatilization and not due to its decomposition. This volatilization would be a problem because the transesterification procedure during synthesis of polyesters is taking place at temperatures ranging between 160 and 190 °C. However, the esterification with diols and transesterification procedures are taking place during isothermal reaction of 2,5-FDCA and DMFD, respectively. For this reason, to obtain more information about their decomposition, the isothermal heating in TGA was also studied. The recorded mass loss with time for both materials is shown in Figure 4.

The selected temperatures for isothermal heating of 2,5-FDCA are 160, 170, 180, and 190 °C. The particular temperatures were chosen because such low temperatures have been mentioned in the literature for the preparation of 2,5-furan dicarboxylate polyesters.[9,10] As can be seen from Figure 4(a) for all the tested temperatures, there is a small mass loss which is also time dependent. As was expected, the mass loss is smaller in the temperatures of 160 and 170 °C (about 0.5% after 4 h isothermal heating) and becomes bigger at 180 °C and mainly at 190 °C (close to 2.8%). This is a clear indication that when the 2,5-FDCA is used for the synthesis of polyesters, the esterification temperature should be as low as possible (160–170 °C) prior to avoid the decarboxylation of 2,5-FDCA. Such low temperatures have also been reported in the literature for the synthesis of PBF.[9,10] A similar study was also performed for DMFD, and the diester was isothermally heated at 80, 100, 110, and 120 °C. These temperatures are much lower than the corresponding for 2,5-FDCA, but as was found from dynamic heating in TGA and EGA measurements, DMFD volatizes even at such low temperatures. As can be seen from Figure 4(b), the isothermal study

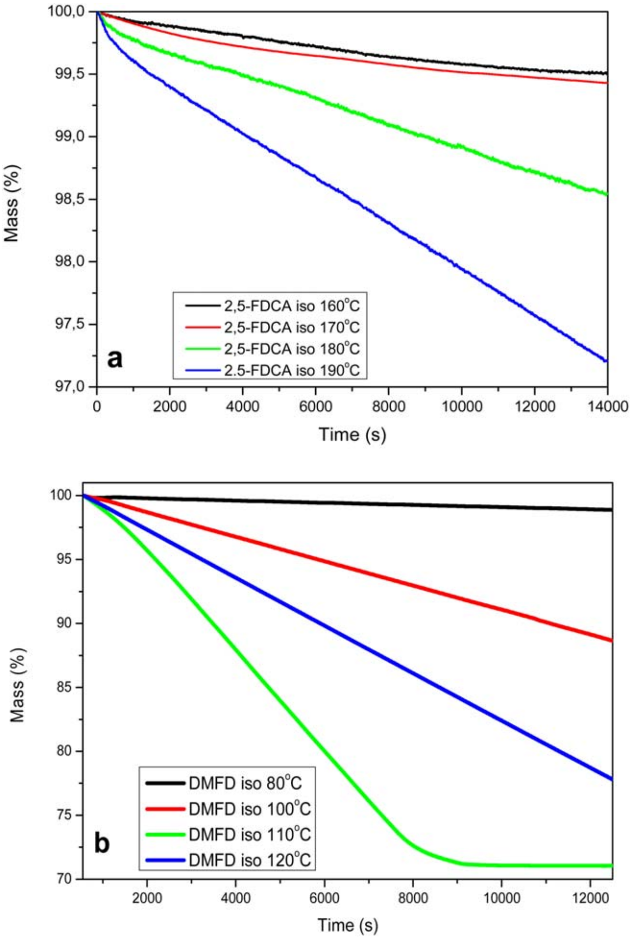


FIGURE 4 Mass loss of (a) 2,5-FDCA and (b) DMFD during isothermal heating at different temperatures. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

confirmed that DMFD loses its mass much easier than 2,5-FDCA. Even at 100 °C, there is a mass loss of about 12% during isothermal holding for 3.5 h and it becomes much higher (about 30%) for holding for 3.5 h at 120 °C. However, as was found from Py-GC/MS, this mass loss is mainly due to the volatilization of DMFD and not due to its decomposition as the decomposition products appeared in low amounts.

Synthesis of Polyesters Using 2,5-FDCA as Monomer

According to the above study, initially for the synthesis of the selected polyesters, 2,5-FDCA was used as monomer, and the diols with FDCA/diol with molar ratios 1/5 were used. For the esterification procedure, the monomers were heated at 150 °C for 2 h, 160 °C for 3 h, and finally at 170 °C for 2 h. After that time, the temperature was increased to 200 °C to remove the excess of diols, and vacuum was applied to start the polycondensation and to increase the molecular weight of polyesters. This temperature, as was found by Zhu et al.,[10] may be the appropriate one for the preparation of furan polyesters. However, because of the low volatilization of the used diols, the viscosity increase was too slow, as was recorded from torque measurements, and thus, the polycondensation temperature had to be increased to 260–280 °C.

After 2-h polycondensation, the color of the prepared polyesters progressively changed slightly from brown to black due to extensive decarboxylation. This was not expected, as in our previous study, it was found that these polyesters are thermally stable materials and their decomposition starts above 300 °C.[17] However, it seems that even though decarboxylation is a slow procedure, as was found from TGA measurements, it results in coloration of the final polyesters. Furthermore, IV measurements showed that after 4 h of polycondensation at 270 °C, low-molecular-weight polyesters are produced, as the IV ranged between 0.2 and 0.3 dL/g. Such IV values are very low and can explain the long polycondensation time (8 h) that Grosshardt et al.[15] selected for the preparation of such polyesters.

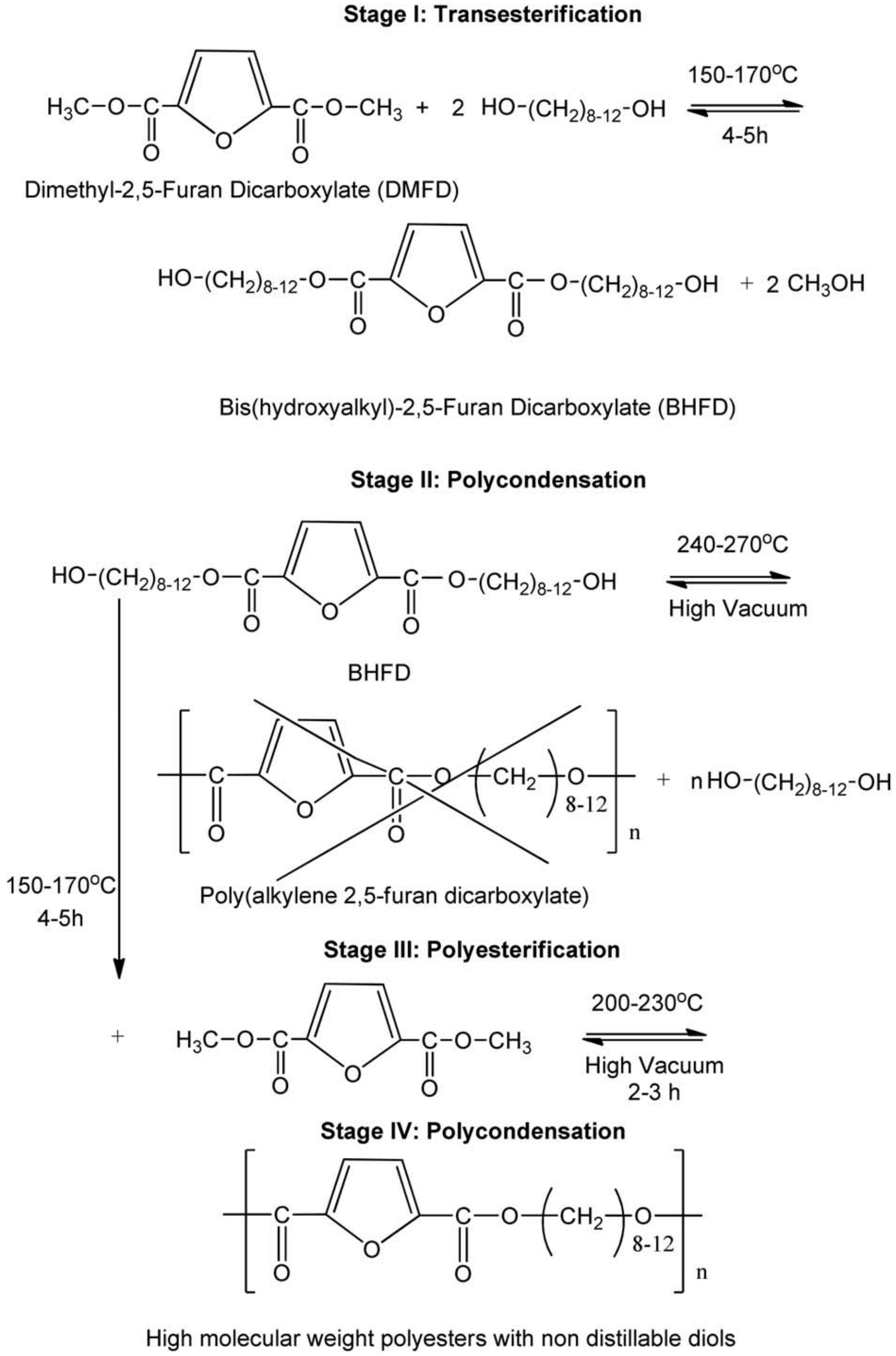
The molecular weight of furanoate polyesters can be increased using solid-state polycondensation (SSP). This procedure was applied by Knoop et al.[14] to low-molecular-weight PEF, which was heated at 195 °C for several hours under reduced pressure. However, in our case, all these polyesters have low melting temperatures and are prepared from diols with high boiling points. Both factors could affect negatively the molecular weight increase during SSP. Furthermore, the coloration of polyesters could not be avoided.

The synthesis of such polyesters could also be performed at room temperature or in even lower temperatures by using a solution method and the chloride of 2,5-FDCA, avoiding the problems of decomposition and decarboxylation.[11] Gomes et al.[18] also used a solution method to prepare such polyesters as well as melt polycondensation and an interfacial polycondensation method. Hirai[19] also applied a solution polycondensation method to prepare macrocyclic and linear oligoesters of 5-hydroxymethyl-2-furancarboxylic acid in high yield, with the aid of 2-chloro-1-methylpyridinium iodide and poly(ethyl phosphate) as polycondensation agents. However, in all these procedures, the dichloride of 2,5-FDCA should be used, which is more difficult to be prepared in high purity.

Furthermore, these procedures are very difficult to be applied in large-scale processes for industrial production. For this reason, in the current study, the dimethyl ester of 2,5-FDCA was used to prepare polyesters with high molecular weights and low coloration using the melt polycondensation technique. DMFD was also used successfully in our previous works for the production of high-molecular-weight furan dicarboxylate polyesters with different diols containing 2–6 methylene groups.[20–22]

Synthesis of Polyesters Using DMFD as Monomer

According to this procedure, DMFD was heated again at low temperatures, particularly at 150 °C for 2 h, 160 °C for 2 h, and 170 °C for 1 h, with diols in a molar ratio DMFD/diol 1/2.2 under N_2 flow, which is the trivial polymerization procedure. These temperatures were selected as it was found from our preliminary



SCHEME 1 The used strategy with reactions that are taking place between DMFD and different long-chain diols and applied conditions for the synthesis of furan dicarboxylate polyesters.

studies that when the temperatures remain at 150–170 °C for 4–5 h, the color of the final polyesters is white to slightly yellow, and when the temperatures are increased to 180–200 °C, the color becomes yellow brown. The first step of transesterification was completed during this time and almost all the theoretical amount of methanol was collected. Even though from Py-GC/MS and TGA studies it was found that DMFD volatizes at lower temperatures than the used for transesterification, it seems that the reaction proceeds without any clear coloration of the solution and bis-hydroxyl-2,5-furan dicarboxylates (BHFD) are formed. This is because the decomposition products of DMFD are in very low quantities. Furthermore, at this stage, it was observed that the volatile DMFD refluxes backward to the reaction tube because of the release of methanol which dissolves DMFD. After that stage, the temperature was increased to 200 °C and vacuum was applied to remove the excess of the used diols and to start the polycondensation of the formed monomers. This temperature was selected to avoid decomposition and coloration of the final

TABLE 1 GPC Analysis and Molecular Weights of Synthesized Poly(nonylene 2,5-furan dicarboxylate) at Different Polycondensation Times at 210 °C

Peak	M_p	M_n	M_w	M_z	$M_z + 1$	M_v	Polydispersity Index	Area (%)
After 30-min polycondensation at 210 °C								
1	39,293	22,669	39,371	58,965	80,245	36,757	1.74	87.2884
2	1,111	1,110	1,116	1,123	1,129	1,115	1.00	3.85214
3	660	649	656	663	670	655	1.01	3.95759
4	335	320	326	332	338	325	1.01	4.90192
After 60-min polycondensation at 210 °C								
1	33,780	25,427	46,639	86,085	141,968	42,428	1.83	97.499
2	879	1046	1144	1258	1379	1128	1.09	2.501

polyesters. However, even in this case, the polycondensation proceeds in a low extent, and the melt viscosity was slightly increased after 2 h of polycondensation at 200 °C. This is because, as was also mentioned previously, the used diols have high molecular weights and boiling points, and thus, their removal is very difficult even with high vacuum application. After 2-h polycondensation at 200 °C, the IV in the case of PDeF was increased to 0.1–0.15 dL/g. In another attempt, the polycondensation temperature was increased at 240 °C for 1 h and 270 °C for additional 1 h, and it was found that IV was increased to 0.19 dL/g. This is also too small; however, the main problem is the intensive coloration of the produced PDeF, which became brown. Thus, according to these findings, it seems that it is very difficult to produce these polyesters from polycondensation of BHFD. The main problem arises from the distillation of high-boiling-point diols, which are very difficult to be removed from the polymerization apparatus. For this reason, to produce polyesters with high molecular weight and low coloration, a slightly varied strategy on the above well-known polycondensation method was applied. The reactions that take place and the conditions are described in Scheme 1.

The proposed procedure is very simple, but its different variations should be clarified to prepare polyesters with high molecular weights. After the end of transesterification stage in which BHFD was produced (Scheme 1, Stage I), DMFD was added in a molar ratio 1/1.05, and the reaction continued for several hours at temperatures 150–170 °C (see “Materials and Methods” section). This is because due to the high boiling point of used diols, these are not volatile and the polycondensation stage (Scheme 1, Stage II) cannot be applied. Thus, after the addition of DMFD, the hydroxyl end groups of BHFD would react easily with the help of TBT catalyst with ester groups of DMFD and methanol will be the byproduct. This stage in Scheme 1 was named as polyesterification (Stage III), as except esterification reactions, the molecular weight of the polyesters would increase simultaneously, even at such low reaction temperatures. According to this strategy, one DMFD molecule could react with one BHFD monomer molecule producing methanol as byproduct and a monomer having hydroxyls in one side and methyl ester groups in the other. As almost equal amounts of DMFD and BHFD were added, this reaction is continuous with other monomers increasing the molecular weight of polyesters.

The advantage of this procedure is that the reaction takes place in low temperatures avoiding coloration, and we do not have to remove diols with high boiling point, as in the case of polycondensation of BHFDs. However, even in this case, as was proved by GPC analysis, together with high-molecular-weight polyesters, a number of oligomers with different molecular weights exist in the reaction mixture (Table 1). For this reason, a final polycondensation step is necessary to be applied to reduce the existence of such oligomers and to further increase the molecular weight of the polyesters (Scheme 1, Stage IV). According to this procedure and due to the high polycondensation time of the final procedure (2–3 h at 230 °C), it is expected the formed polyesters to have both — OH and —COOH groups, which is typical in polyesters. This was also verified from FTIR spectra (data not shown). The ratio of added DMFD, the polycondensation time, and temperatures are the most important parameters that should be studied in this procedure.

The GPC analysis of the formed polyesters after 30 min of polycondensation at 210 °C confirmed that polyesters with number–average molecular weights (higher than 20,000 g/mol) can be prepared in all cases. In Table 1, the calculated molecular weights are presented for PNF as an example. However, as can be seen in Table 1 and also in Figure 5, in GPC traces, there are also some other peaks recorded, corresponding to unreacted monomers or to oligomers. In most cases, there are three to four peaks recorded. These oligomers have molecular weights attributed to 1–6 repeating units. However, from the calculated molecular weights, it seems that each one peak corresponds not to a simple monomer or oligomer but rather to a mixture of these. As can be seen from Scheme 2, the molecular weights of the possible monomers or oligomers in PNF are not the same as these calculated from GPC and are presented in Table 1. Thus, it seems that these are a mixture of oligomers with different molecular weights and cannot be separated during GPC analysis.

Furthermore, as it can be seen from Table 1, the whole area of these oligomers corresponds to about 13% and the macromolecules with high molecular weights to 87%. According to this analysis, even though the molecular weight of the prepared polyester is high enough, the percentage of oligomers is also very high. This was expected as the

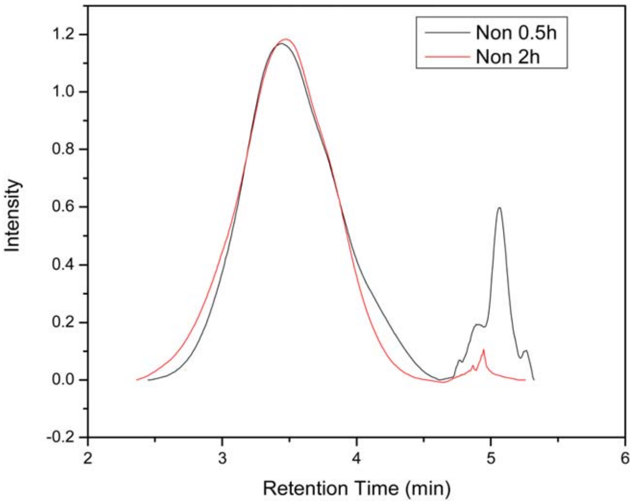


FIGURE 5 GPC curves of PNF produced after 30-min and 60-min polycondensation times at 210 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

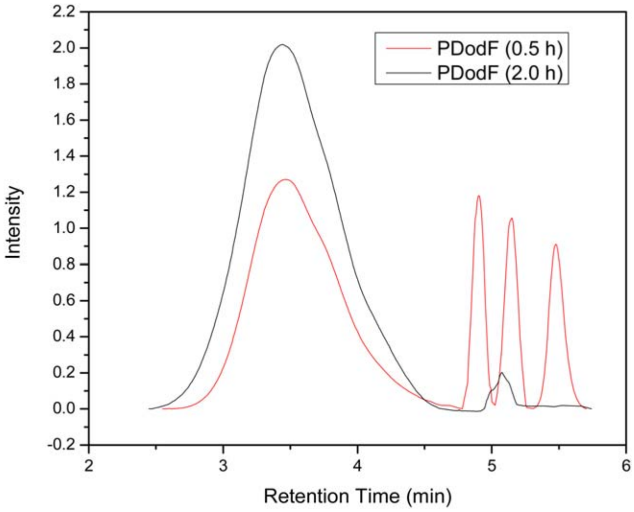
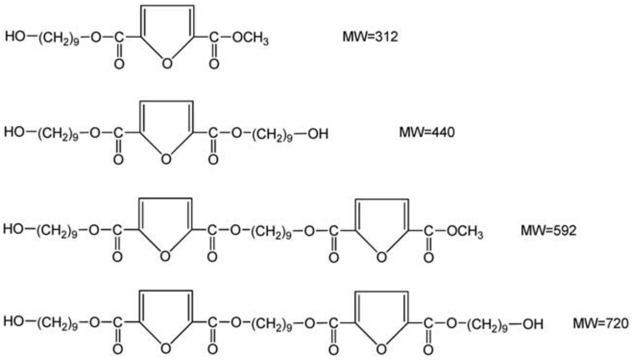


FIGURE 6 GPC curves of PDoF produced after 30-min and 120-min polycondensation times at 220 °C. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

polycondensation time is too small (30 min). When the polycondensation time increased to 60 min, only two peaks were recorded in the corresponding GPC chromatographs. The number–average molecular weight also increased from 22,669 to 25,427 g/mol. The area of high-molecular-weight peak increased from about 87 to 97.5%, whereas the area of the oligomers' peak was reduced to about 2.5%; however, it was still too high.

Polycondensation temperature is another crucial factor. In the case of PDoF after 30-min polycondensation at 220 °C, four peaks were also recorded in GPC (Fig. 6), the three of which correspond to unreacted monomers or formed oligomers and the fourth to the high-molecular-weight prepared polyester (Table 2). However, the whole areas of these are much smaller (about 6%) when compared with the corresponding one that was calculated for PNF. Thus, it seems that at higher temperature, the polycondensation proceeds faster and also as can be seen from Table 2, slightly higher molecular weights were recorded for the produced polymer.



SCHEME 2 Presentation of possible oligomers and their molecular weights during synthesis of PNF.

By increasing the polycondensation time to 120 min, the oligomer amount is clearly reduced (Fig. 6) to about 0.34%. In the same time, the molecular weight of PDoF increased to 49,300 g/mol. Such a molecular weight is very high for polyesters. When compared with the polycondensation times mentioned in the literature for the production of such furan dicarboxylate polyesters, it can be seen that these range between 4 and 8 h.[10,23] Such times are too high and can cause coloration to the final polyester. With the method proposed in the current study, the coloration is limited, as was mentioned in previous studies, and is temperature dependent.[8]

Characterization of the Synthesized Polyesters

According to the established polycondensation procedure previously described in detail, polyesters with IV values ranging from 0.43 to 0.50 dL/g are obtained (Table 3). This is because the used polycondensation time was identical in all polyesters (1 h at 210 °C, 1 h at 220 °C, and 0.5 h at 230 °C). The molecular weights of the prepared polyesters measured by GPC are also presented in Table 3. It can be seen that the number–average molecular weights also ranged from 34,500 to 39,900 g/mol, not depending on the number of methylene groups of the used diols. The polydispersity index is also satisfactory for the polymers. This proves that the used procedure is appropriate for the synthesis of furan polyesters with high molecular weight using high-boiling-point diol monomers.

The structure of the prepared polyesters was verified with ^{1}H NMR. The spectra of POF, PNF, PDeF, and PDoF are shown in Figure 7. As it is known, the protons on and next to the ring are mostly deprotected because of its π-electron shell. As a result, the "a" protons of the composed polymers attributed to the furan ring appear at the highest ppm values, ranging between 7.26 and 7.3 ppm. This is in accordance

TABLE 2 GPC Analysis and Molecular Weights of Synthesized Poly(dodecylene 2,5-furan dicarboxylate) at Different Polycondensation Times

Peak	M_p	M_n	M_w	M_z	$M_z + 1$	M_v	Polydispersity Index	Area (%)
After 30-min polycondensation at 220 °C								
1	33,780	28,130	36,710	47,025	57,995	35,301	1.31	93.987
2	1,384	1,359	1,413	1,473	1,537	1,405	1.04	1.569727
3	695	574	610	645	677	605	1.06	1.982857
4	265	250	257	263	270	256	1.03	2.46946
After 120-min polycondensation at 220 °C								
1	106,044	49,301	130,158	270,735	430,404	114,322	2.64	99.6558
2	863	837	846	855	863	845	1.01	0.3442

with our previous studies.[20–22] The aliphatic segment of the carbon chain of POF, PNF, PDeF, and PDoF contains 16, 18, 20, and 22 protons, respectively. The closest to the ring protons ("b" and "c" protons) are displayed on higher ppm values in comparison with the protons in the middle of the chain ("d" protons). Even the "d" protons are not equivalent due to the fact that they are located far from the molecular groups which attract electrons. They appear at similar ppm values and that differentiation is almost impossible. Thus, the peak integration concerned that the absorption of all "d" protons coincides in each polymer spectrum. The observed absorptions were as follows: POF, "a" protons: 7.32 δ (2H, s), "b" protons: 4.45 δ (4H, t), "c" protons: 1.80 δ (4H, q), "d" protons: 1.45 δ (8H, s); PNF, "a" protons: 7.30 δ (2H, s), "b" protons: 4.40 δ (4H, t), "c" protons: 1.79 δ (4H, q), "d" protons: 1.40 δ (10H, s); PDeF, "a" protons: 7.26 δ (2H, s), "b" protons: 4.38 δ (4H, t), "c" protons: 1.75 δ (4H, q), "d" protons: 1.31 δ (12H, s); and PDoF, "a" protons: 7.31 δ (2H, s), "b" protons: 4.43 δ (4H, t), "c" protons: 1.80 δ (4H, q), "d" protons: 1.37 δ (16H, s). The absence of any other peaks indicates that polyester with high purity have been prepared.

The crystalline phase in the polyesters of the current study was investigated by XRD, and the recorded patterns (Fig. 8) showed a number of characteristic peaks. The POF, PDeF, and PDoF patterns have sharper peaks at the highlighted diffraction angles, whereas the PNF peaks are weaker and broader. POF has characteristic peaks at 2θ 12.6°, 14.8°, 16.4°, 18.1°, 19.5°, 21.5°, and 23.7°, and there exist some similarities with that corresponding to PNF, which has a more complex pattern with eight characteristic peaks at 2θ 6.9°, 10.6°, 14.7°, 16.4°, 19.3°, 21.4°, 22.4°, and 23.6°. PDeF has a much simpler pattern with only four characteristic peaks at 2θ 11.0°, 16.6°, 21.5°, and 23.7°. These last two peaks are almost identical to that recorded for PDoF at 21.6° and 23.8°, whereas its other two peaks appear at 9.8° and 17.9°. This is an indication that the crystal unit cell parameters of these polyesters may also have some similarities. To further investigate the characteristics of the crystal structure, the patterns of the 2,5-furandicarboxylic acid polyesters with even number methylene groups were compared with that of polyethylene [PE; Fig. 8(b)]. It is obvious that furanoates with long sequences of even number (larger than four) of methylene groups crystallize in unit cells with similarities to that of PE, as their dominant reflections appear at the same angles. Thus, the dominant part in this case is the long methylene chains. As a matter of fact, the reflections correspond to the (110) and (200) planes of PE. This means that the *c* axis (usually the longer axis) of the unit cell is the same. A different situation was observed for PEF, with only two methylene groups. In this case, the unit cell parameters are determined by the furanoate moieties and not the short methylene group sequences. Furthermore, the significant intensities of the crystal reflections revealed the significant degree of crystallinity of the samples in this work. Obviously, a lower degree of crystallinity was achieved in case of the PNF, which showed slower crystallization rates as will be discussed below. However, the intensities were always lower than that for the high-density PE (HDPE) sample used for comparison.

TABLE 3 IV and Molecular Weights of POF, PNF, PDeF, and PDoF

Sample	IV (dL/mg)	M_n (g/mol)	M_w (g/mol)	Polydispersity Index (M_w/M_n)
POF	0.43	34,556	62,085	1.80
PNF	0.50	39,956	67,284	1.68
PDeF	0.47	36,710	57,025	1.55
PDoF	0.49	39,371	68,965	1.75

Figure 8(c) shows the patterns of the poly(nonylene furanoate) in comparison with that of poly(propylene furanoate) (PPF). The arrows depict the reflections which were common in these two polyesters with odd number of methylene groups in their repeating units. Thus, the odd number of methylene groups also led to similarities in the crystal unit cells. In conclusion, not only the absolute number of methylene groups but also mainly its odd or even character plays a significant role in the determination of the crystal unit cell.

Thermal Properties

The DSC study showed that the prepared polyesters are semicrystalline materials, as was already found by XRD and

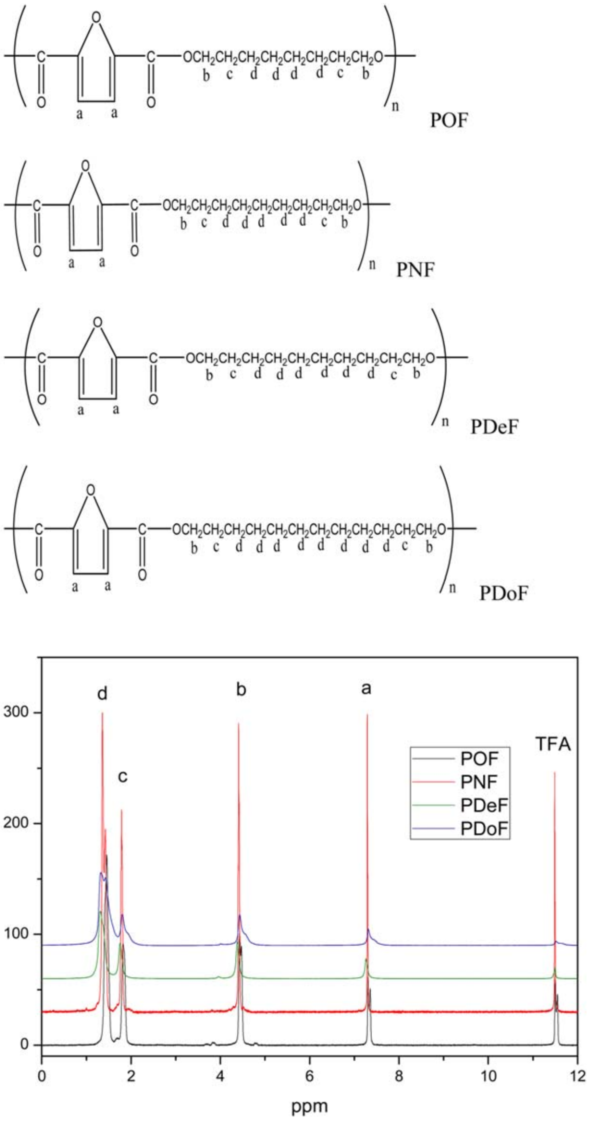


FIGURE 7 Chemical structures and ^{1}H NMR spectra of POF, PNF, PDeF, and PDoF in deuterated trifluoroacetic acid. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

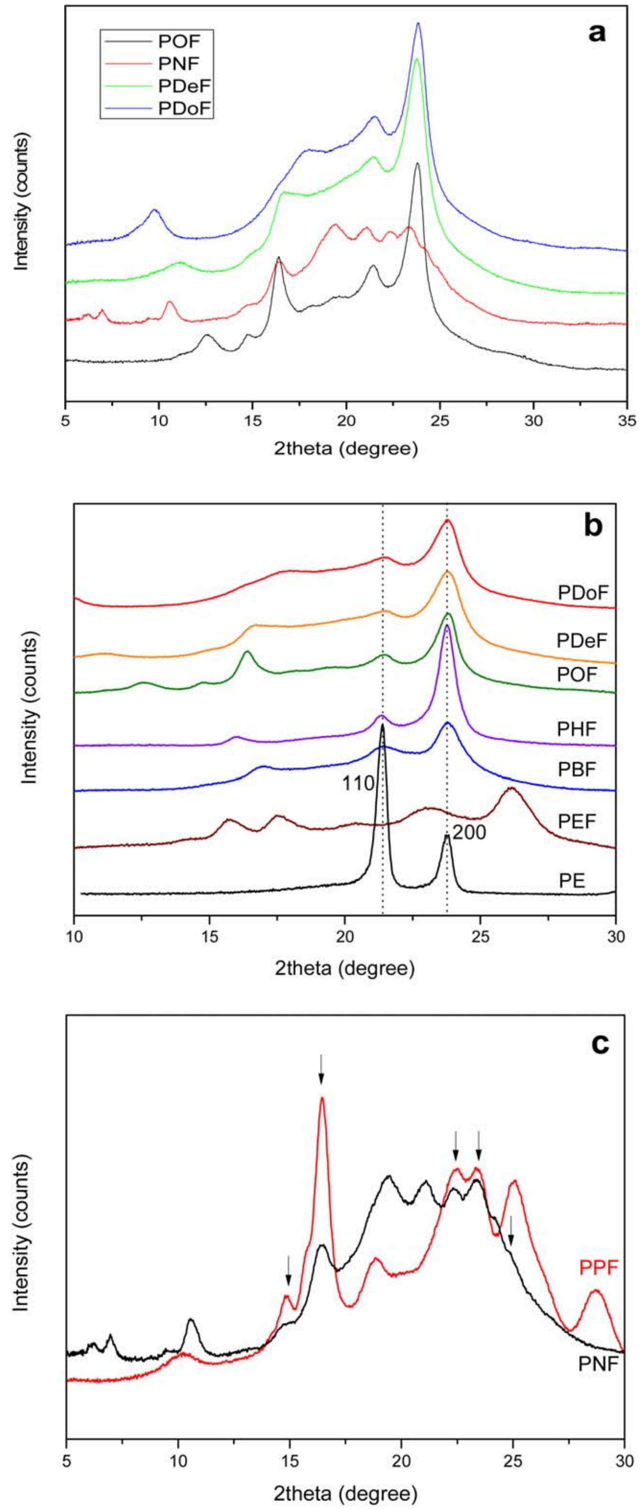


FIGURE 8 Wide-angle X-ray diffraction patterns of (a) POF, PNF, PDeF, and PDoF, (b) furanote polyesters with even number of methylene groups and PE, and (c) PPF and PNF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

can easily crystallize during cooling (Fig. 9), with an exception for the PNF. The latter can be obtained as a glassy material even at slow cooling, in contrast to the other three polymers [Fig. 9(b)]. Furthermore, a significant decrease in the melting temperature was found for PNF ($T_m = 69$ °C). As one can see in Table 4, POF showed a T_m of 140 °C, whereas the T_m values for PDeF and PDoF were 116 and 111 °C, respectively. The recorded T_m for PDoF is very close to that reported from Grosshardt et al.[15] ($T_m = 109.0$ °C), whereas for POF, it is slightly lower than the value reported by Jiang et al.[24] ($T_m = 148.6$ °C). A large value of heat of crystallization (ΔH_c) of about 64 J/g was observed for POF and PDeF on cooling at 10 °C/min, whereas for PDoF, a value of 69.5 J/g was found. The corresponding value for PNF was very low (about 4 J/g). The T_g values for the furanic polyesters of

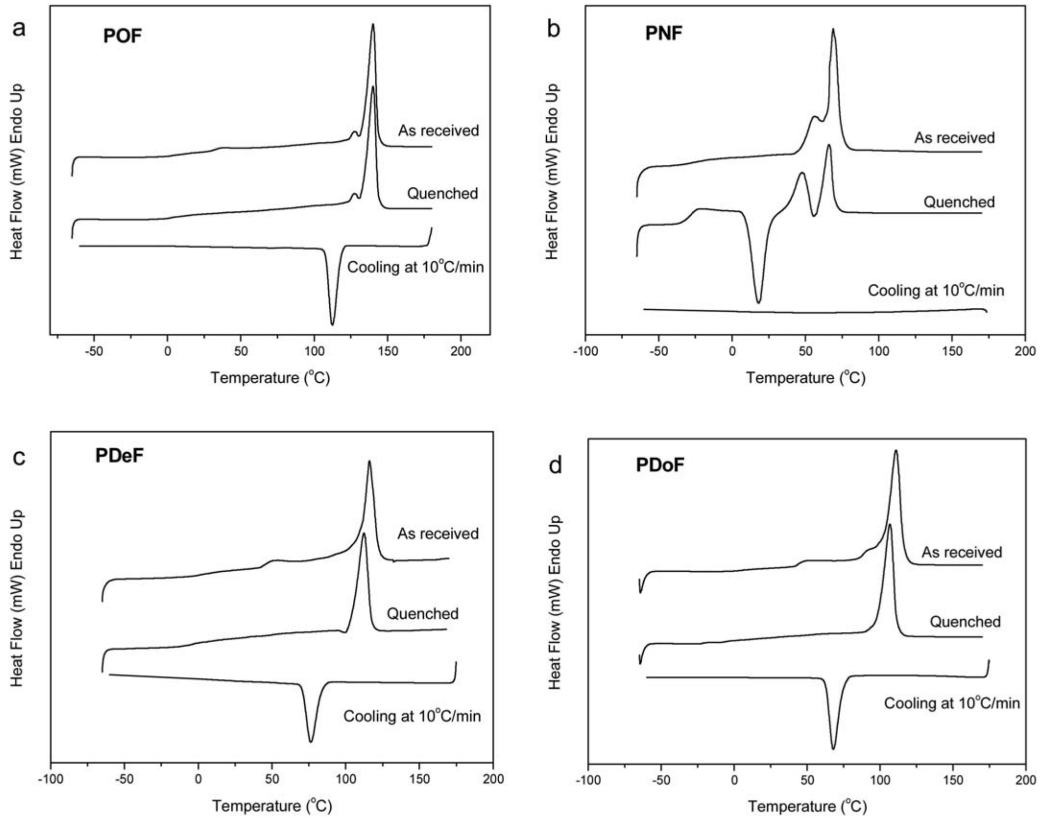


FIGURE 9 DSC scans of (a) POF, (b) PNF, (c) PDeF, and (d) PDoF.

this work were quite below 0 °C, even though in most cases the samples were semicrystalline. The glass transition temperature values are expected to decrease steadily with increasing the number of methylene groups in the polymer repeating unit. The most reliable value for T_g was that for PNF ($T_g = -30$ °C). The reason is that the values for the rest of the polymers correspond to semicrystalline samples, as they might be overestimated. However, even in this case, the recorded T_g for POF is much lower than that reported by Jiang et al.[24] ($T_g = 21.8$ °C). For the other polyesters, there are no reported values in the literature to compare our findings, not only for T_g but also for T_c and T_m. Furthermore, as can be seen from these thermograms and Table 4, after quenching, only PNF can be obtained in the glassy state and then crystallize during heating with a cold crystallization temperature at 18 °C. This is because the other polyesters have a very high crystallization rate and crystallized on cooling.

TABLE 4 Thermal Properties of Synthesized Polyesters Determined from the Heating Scans at 20 °C/min or the Cooling Scan at 10 °C/min

Polymer	T_g (°C)	T_{cc} (°C)	T_c (°C)	T_m (°C)[a]	ΔH_m (J/g)[b]
POF	−5[c]	–	112	140	63.9
PNF	−30	18	43	69	4.3
PDeF	−8[c]	–	77	116	64.2
PDoF	−22[c]	–	68	111	69.6

[a] Measured from the heating scan of the as-received samples.
[b] Measured from the cooling scans at 10 °C/min.
[c] Measured in semicrystalline samples.

The general trends for the variation in the transition temperatures of furanoates can be seen in Figure 10. Although only two polymers with odd number of methylene groups (3 and 9) in their repeating units were studied, it is obvious in the plots of the melting temperature that the odd–even effect holds for the poly(alkylene furanoate)s, which means that the samples with odd number of methylene units show lower melting temperatures. T_g values for the polymers with 2 to 4 methylene groups and that for PNF were directly measured from DSC scans of amorphous samples. For the rest, the use of Fast Scan DSC and cooling rates of the order of 1000 °C/min or faster are needed prior to obtain amorphous samples. In contrast to the melting temperatures, a monotonous decrease was observed in the T_gs. The crystallization temperatures of the polyesters follow, more or less, the trend for the melting temperatures. However, the supercooling that is the difference between the melting temperature (and more correct the equilibrium melting temperature) and the crystallization temperature is larger for the polyesters with small numbers of methylene units in the diol segments. It is obvious that with increasing number of methylene units, the flexibility of the macromolecular chains also increases, as

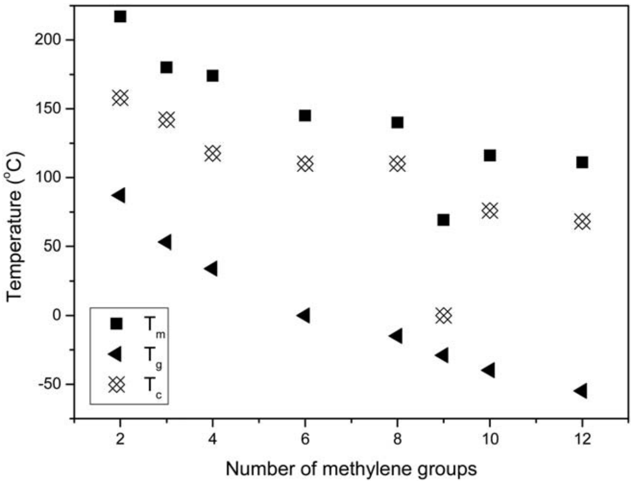


FIGURE 10 Variation of the melting temperature (T_m), glass transition temperature (T_g), and the crystallization temperature (T_c) on cooling at 10 °C/min.

crystallization is favored and lower supercoolings are needed. When compared with the fossil-based polyesters such as PET, poly(propylene terephthalate) (PPT), PBT, poly(ethylene naphthalate) (PEN), poly(propylene naphthalate) (PPN), and poly(butylene naphthalate) (PBN), the furan-based polyesters PEF, PPF, and PBF need larger supercoolings prior to crystallize, as was found in previous works.[20–22,25] In general, furan-based polyesters crystallize slower than the fossil-based polyesters, but show increased nucleation density at given supercooling as was realized from polarized light optical microscopy (PLOM) observations.

To better understand the crystallization behavior of the polyesters, the morphology generated under various crystallization conditions was studied by using PLOM. Figure 11 presents photographs taken during isothermal crystallization of the polymers. As can be seen, PDeF and PDoF formed large numbers of active nuclei even at elevated temperatures and finally gave very small spherulites. The case was a little different for POF and PNF. These last two materials gave slightly larger spherulites due to lower nucleation density. Combining the findings of this work with observations made in previous works on poly(ethylene furanoate) (PEF),[20] poly(butylene furanoate) (PBF),[21] poly(hexamethylene furanoate) (PHF),[22] and PPF,[25] one can conclude that furanoates form smaller spherulites when compared with terephthalates, naphthalates, and aliphatic polyesters like poly(butylene succinate), poly(lactic acid), and poly(ε-caprolactone). In fact the nucleation density of furanic polyesters is even larger when compared with polypropylene but of course less than that of polyethylene as was concluded by parallel tests during this work. This is a result of the chemical structure of the furanoates with a more angular geometry in their repeating units.

Mechanical Properties of Synthesized Polyesters

The detailed mechanical properties of these polyesters have never been mentioned before, even though the synthesis of polyesters with 1,12-dodecanediol and 1,18-decaoctanediol has been reported previously. In the literature, only the tensile

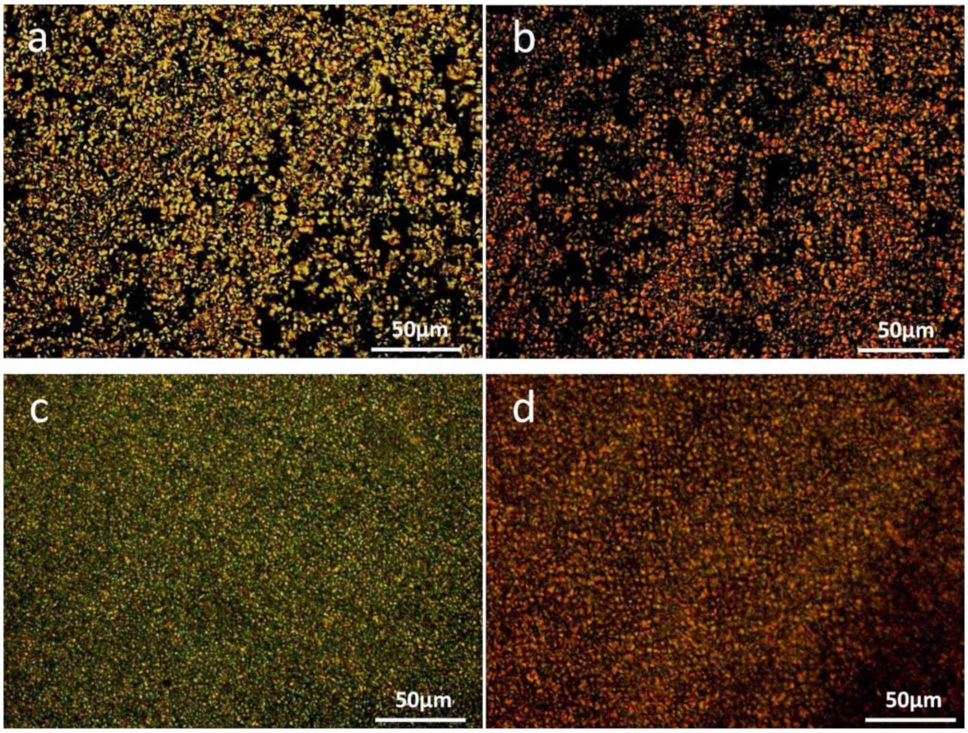


FIGURE 11 POM scans of (a) POF, (b) PNF, (c) PDeF, and (d) PDoF. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

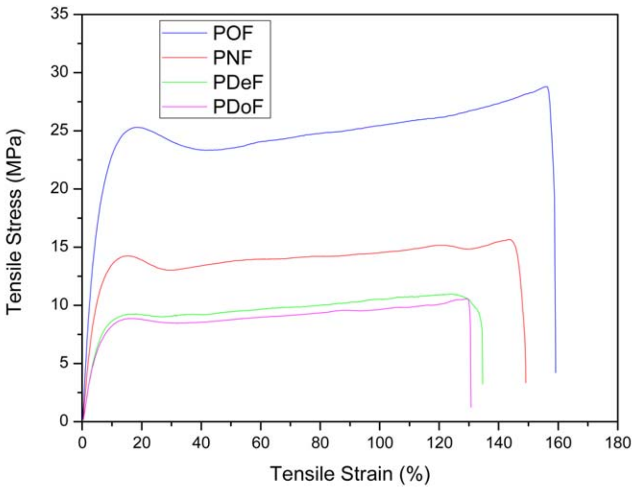


FIGURE 12 Stress–strain curves of synthesized polyesters with crosshead speed of 50 mm/min. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

strength of POF (20.3 MPa) has been reported.[24] In Figure 12, the stress–stain curves of all synthesized polyesters are exhibited. As can be seen, all the polyesters show a clear yield point. However, break occurs before stress hardening. For this reason, low elongation at break values were observed. POF had the highest elongation at break, which progressively shifted to lower values with increasing the number of methylene groups in the used diols. POF also showed the highest stress from all polyesters, whereas PDeF and PDoF had a similar behavior. From these stress–strain curves, tensile strength at yield point and at break, elongation at break, and Young's modulus were calculated and presented in Table 5. Tensile strengths at yield and break points of POF and PNF are comparable with those of HDPE and polypropylene, whereas those of PDeF and PDoF are very close to the corresponding of LDPE. However, all these polyesters have much lower elongation at break than the polyolefins.

From all these results, it is clear that tensile strengths depend on the methylene groups that the used diols have. By increasing the number of methylene groups, all these properties progressively shifted to lower values. Thus, POF has the highest mechanical properties, whereas PDoF, which has the larger number of methylene groups, has the lowest values. Such a trend was also reported by Jiang et al.,[24] who studied the properties of polyesters from 2,5-FDCA and diols with methylene groups 2, 3, 4, 6, and 8. All these polyesters are very strong materials with PEF to have the highest Young's modulus of 2070 MPa and POF the lowest of 330 MPa, which is similar to that calculated in our study (Table 5). Furthermore, as reported by Jiang et al.,[24] all the polyesters, despite their high molecular weights, behave as brittle materials showing elongations at break ranging from 2.8 to 46%. An exception was observed for PHF which has an elongation at break of 210%. PEF and PPF have the highest tensile strength of 66.7 and 68.2 MPa, respectively, followed by PHF (35.5 MPa), whereas PBF and POF have the lowest tensile strength of 19.8 and 20.3 MPa, respectively. These values are smaller than those reported in the literature for PBF samples, for which high mechanical properties were measured such as Young's modulus about 964 ± 37 MPa, elongation at break 1108% ± 108%, and tensile strength at break 32.9 ± 5.2 MPa.[10] Similar properties for PBF like Young's modulus of 875 ± 18 MPa and tensile strength at break of 35 ± 2.6 MPa have also been reported from Zhou et al.,[26] except the elongation at break which was very low, about 55% ± 10%. Wu et al.[27] reported much higher mechanical properties for PBF: Young's modulus 1860 ± 160 MPa, tensile strength at break 55.6 ± 1.6 MPa, and elongation at break 256% ± 19%. These high differences may be due to the different molecular weights of synthesized polyesters, and this is also very common for the other well-studied polyester, PEF. It was reported that the Young's modulus of PEF is 2450 ± 220 MPa and its maximum stress at 35 ± 8 MPa,[14] whereas Zhou et al. found somewhat lower values for the Young's modulus (2070 MPa) but a slightly higher maximum stress at fracture (66.7 MPa).[24] When comparing these values of PEF and PBF with the corresponding of polyesters synthesized in our study, it can be clearly seen that both of these polyesters have higher tensile strength at break and Young's modulus. This could be attributed to the lower number of methylene groups that PEF and PBF have in their repeating units.

TABLE 5 Mechanical Properties of POF, PNF, PDeF, and PDoF Polyesters Calculated from Stress–Strain Curves

Sample	Tensile Strength at Yield (MPa)	Tensile Strength at Break (MPa)	Elongation at Break (%)	Young's Modulus (MPa)
POF	23.9 ± 1.7	26.5 ± 1.5	160 ± 15	310.5 ± 21
PNF	19.0 ± 1.4	21.0 ± 1.6	149 ± 11	251.7 ± 19
PDeF	10.6 ± 1.4	11.4 ± 1.2	135 ± 17	201.9 ± 15
PDoF	9.5 ± 1.1	10.8 ± 0.9	130 ± 10	180.7 ± 16

CONCLUSIONS

Furan dicarboxylate-biobased polyesters have been successfully prepared in this study using the dimethyl ester of 2,5-FDCA and diols with high boiling points using a variation of the melt polycondensation procedure. The advantages of the proposed method are that it is very simple and that polyesters with high molecular weight and low coloration can be produced. Polycondensation time and temperature are among the most critical parameters for the synthesis of high-molecular-weight polyesters. All polyesters are semicrystalline materials with melting temperatures, glass transition, and crystallization temperatures depending on the number of methyl groups of used diols. However, PNF has the lowest values of all the polyesters, which may be due to the odd–even effect. The tensile mechanical properties are also a function of the number of methylene groups of the diol monomers. POF shows the highest values, whereas PDoF has the lowest values.

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