

From Furan to High Quality Bio-based Poly(ethylene furandicarboxylate)

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Abstract 2,5-Furandicarboxylic acid (2,5-FDCA) has been regarded as the ideal bio-based alternative to terephthalic acid (TPA). In recent years, great efforts have been made to synthesize 2,5-FDCA through the following methods: (1) oxidation of 5-hydroxymethylfurfural (HMF) in the presence of complex biocatalyst or metallic catalyst; (2) conversion of 2-furoic acid *via* the well-known Henkel Reaction. Herein, a new strategy for the synthesis of 2,5-FDCA from furan and acetic anhydride under mild condition is reported. The purity of the resulted 2,5-FDCA was above 99.9%. Acetic acid and iodoform generated in the reaction were recyclable and no other harmful by-products were detected. The thus-obtained 2,5-FDCA was applied for the preparation of poly(ethylene furandicarboxylate) (PEF) of high quality in terms of high molecular weight and good appearance.

Keywords 2,5-Furandicarboxylic acid (2,5-FDCA); 2,5-Diacetylfuran (2,5-DAF); Iodoform reaction; Furan; Poly(ethylene furandicarboxylate)

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INTRODUCTION

With the rapid economic development and the depletion of fossil resources, more and more attention has been paid to the conversion of renewable resources into useful chemicals^[1, 2] or polymers^[3, 4]. And the replacement of petroleum-based materials by the bio-based ones has become a hot topic in both academic and industrial communities. As well known, the popular bio-based polymers at present, such as polylactic acid (PLA), poly(butylene succinate) (PBS), polyhydroxyalkanoates (PHAs) and bio-based polyethylene (PE), are all featured by aliphatic or long soft chains, which lead to their relatively low thermal and mechanical properties when compared with common engineering plastics like poly(ethylene terephthalate) (PET) and polycarbonate (PC). The primary reason for the low thermal and mechanical performance might be the lack of aromatic or rigid units in their molecules. Therefore, developing bio-based platform chemicals with unique structures with better properties is always a challenge.

2,5-Furandicarboxylic acid (2,5-FDCA) is a promising bio-based platform chemical with its structure similar to that of terephthalic acid (TPA). As we know, TPA is the key material for the preparation of poly(ethylene terephthalate) (PET)^[5, 6] and poly(butylene terephthalate) (PBT) *etc*^[7, 8]. If

TPA is fully or partially replaced by 2,5-FDCA, and the related polyesters, including poly(ethylene 2,5-furandicarboxylate) (PEF) and poly(butylene 2,5-furandicarboxylate) (PBF), are commercialized, great progress towards the sustainable development of polymer industry will be achieved^[9]. Therefore, both the academic and industrial communities have been making efforts to explore the cost-efficient and environmental friendly strategies to produce 2,5-FDCA and the related polyesters.

To the best of our knowledge, there are two main routes for the synthesis of 2,5-FDCA (Scheme 1). The first one is the catalytic oxidation of 5-hydroxymethylfurfural (HMF): HMF was produced *via* fermentation or chemical reaction from carbohydrates like lignocellulose or fructose^[10] and oxidized into 2,5-FDCA. Up to now, considerable attention has been paid to the preparation of HMF and several international companies, such as Avantium, ADM, Shell and BASF, have also been involved and pilot-plant production has been already realized^[9, 11]. However, there are many problems to be solved. The first is the poor stability of HMF under acidic condition, which is necessary for HMF formation. In addition, the by-products, like levulinic acid (LA), formic acid (FA) and humins, are inevitable and they are difficult to be removed^[12]. Therefore, the efficient isolation or purification method is necessary^[13–15]. The second challenge lies in the oxidation of HMF. In order to obtain a high yield, the metallic catalyst systems, such as the metal bromide catalysts (Co/Mn/Br) in acetic acid^[16], the rare metallic nano-particles based on Pt^[17, 18], Ru^[19] and Au^[20, 21] as well as the bimetallic

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catalysts^[22, 23], have been developed, and harsh reaction condition is required. The enzyme-catalyzed systems have been tried recently^[24–27]. However, the evaluation for its commercial potentiality is necessary. The second strategy for the synthesis of 2,5-FDCA is from furfural (Scheme 1). After furfural oxidation into 2-furoic acid, dicarboxylic acids (FDCA) and unsubstituted compound (furan) are obtained according to the well-known Henkel reaction. However, not only the target product 2,5-FDCA is obtained, but also the isomers, for instances, 2,4-furandicarboxylic acid (2,4-FDCA) and 3,4-furandicarboxylic acid (3,4-FDCA)^[11, 28], which are certainly generated and difficult to be separated from 2,5-FDCA. In addition, this reaction has to be conducted at 300–500 °C under high pressures, usually in the presence of cadmium or other metal catalysts. Most recently, Aanindeeta and co-workers^[29] reported the synthesis of 2,5-FDCA from 2-furoic acid and carbon dioxide *via* carbonate-promoted C–H carboxylation catalyzed by Cs_2CO_3 at 200–260 °C, and further investigation is desired. Obviously, complex catalysts, high temperature and pressure with inevitable by-products as well as high price are common in the reported methods for the preparation of 2,5-FDCA.

In this work, a new strategy for the synthesis of 2,5-FDCA and PEF from furan is reported (Scheme 1, the new route from lignocellulose in the green frame). 2,5-Diacetylfuran (2,5-DAF) was first synthesized from furan and acetic anhydride through a two-step Friedel-Crafts reaction catalyzed by a common acid system under mild condition. Then the iodoform reaction was used to convert 2,5-DAF into 2,5-FDCA. The purity of thus-obtained 2,5-FDCA was 99.9%. With this high purity of 2,5-FDCA, the synthesis of poly(ethylene 2,5-furandicarboxylate) (PEF) was illustrated and its quality was evaluated in terms of thermal and mechanical properties, gas barrier properties and physical appearance. For comparison, HMF-based 2,5-FDCA was also employed as the starting material to prepare PEF. Considering the fact that the reaction is conducted under a mild condition without harmful catalyst, the by-products,

acetic acid and iodoform, are easy to be recycled and no other unmanageable or toxic wastes are detected, and that the raw materials, furan and acetic anhydride, are both bulk chemicals which can be produced from the renewable feedstock^[30], this strategy described here should be a significant progress towards the GREENER synthesis of 2,5-FDCA.

EXPERIMENTAL

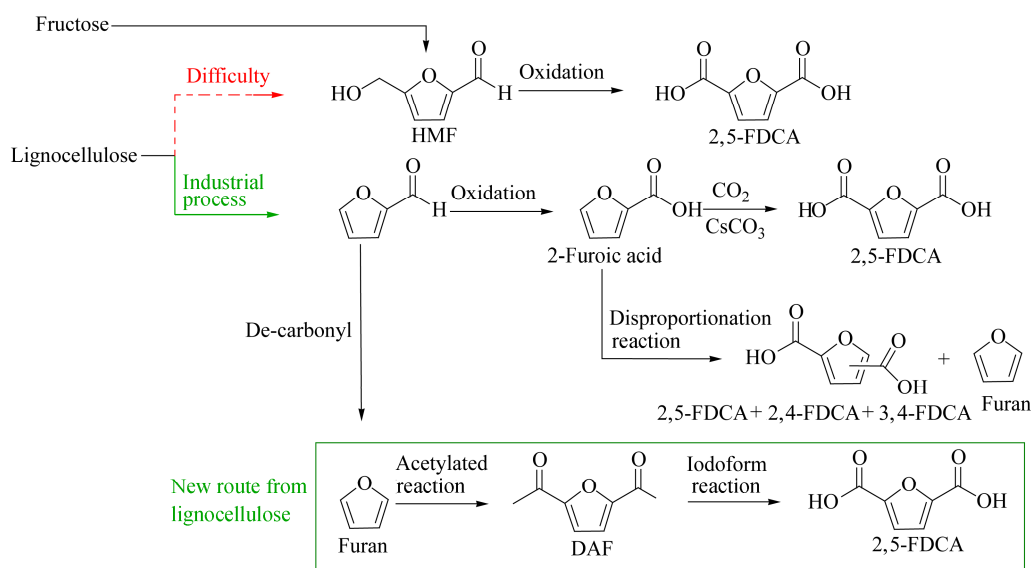
Materials

Furan (99%), acetic anhydride (99%), sodium hydroxide (98%) and ethylene glycol (EG, 99%) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Sulfuric acid (98%), phosphoric acid (86%), methanesulfonic acid (99%), boron trifluoride ether complex (98%), iodine (99.8%), potassium iodide (99%), methanol (HPLC, 99.9%), antimony trioxide (III, 99.9%), zinc acetate (99%), trifluoroacetic acid (99%), phenol (99%) and tetrachloroethane (98%) were obtained from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). 2,5-Furandicarboxylic acid (2,5-FDCA, 99.5% by HPLC) based on HMF was purchased from Suzhou Gaide Fine materials Co., Ltd. (Suzhou China). All the chemicals were used as received.

Characterization

Chemical structures of the synthesized compounds and polyesters were confirmed by ^1H -NMR and ^{13}C -NMR using a Bruker AVIII400 NMR spectrometer at 25 °C. Fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet 6700 spectrometer, scanning from 400 cm^{-1} to 4000 cm^{-1} and 32 scans were collected for each sample.

The concentration of 2-acetylfuran and 2,5-diacetylfuran (2,5-DAF) in reaction system was calculated based on a standard curve obtained with high purity 2-acetylfuran and 2,5-DAF. The 2-acetylfuran and 2,5-DAF were analyzed with an Agilent 1200 HPLC apparatus (Agilent Technologies, Santa Clara, California, USA) equipped with Eclipse XDB-C18 column (150 mm $\times$ 4.6 mm i.d., 5 μm particle size) from Agilent (Palo Alto, CA, USA). The mobile phase was a



Scheme 1 Comparison of different strategies for the synthesis of 2,5-FDCA

mixture of methanol and water (methanol/water = 20/80, *V/V*). The flow rate was 0.5 mL/min and the column temperature was kept at 35 °C. Concentrations of 2-acetylfuran and 2,5-DAF solution were quantified with calibration curves. LC-MS was performed on a Waters XEVO-TQ MS using a Waters ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm i.d., 1.7 μm particle size) and electro spray ionization (ESI).

Viscosity of the synthesized polyesters was measured at 25 °C by Ubbelohde viscometer in a water bath. The diameter of the capillary tube is 0.792 mm. The phenol and tetrachloroethane mixture (1/1, *W/W*) was used as the solvent with the concentration of copolyester at 0.125 g/25mL. The equation $[\eta] = \eta_{sp}/c$ was used to calculate the intrinsic viscosity $[\eta]$, where $\eta_{sp} = (t_1 - t_0)/t_0$, t_0 is the elution time of solvent, and t_1 the elution time of polyesters solution. DSC measurement was performed on a differential scanning calorimeter (Mettler-Toledo DSC I) with nitrogen flow rate of 50 mL/min. It was calibrated with indium and zinc standards before measurement. A sample of about 5–6 mg was placed in an alumina pan and heated from room temperature to 280 °C with a heating rate of 10 K/min. In order to erase thermal history, the sample was maintained at this temperature for 3 min and cooled down to room temperature at a rate of 10 K/min and heated to 280 °C with the same heating rate again. Thermal stability evaluation was conducted using a TGA instrument (Mettler-Toledo TGA/DSC). Sample (6–10 mg) was placed in a ceramic furnace and TGA curve under nitrogen atmosphere was recorded from 50 °C to 800 °C. UV-Vis spectra of the polymer films were recorded on a Lambda 950 UV/Vis/NIR spectrophotometer. Tensile testing was performed on an Instron 5567 tensile machine with a 500 N load cell. The stretching rate was 10 mm/min. Dumbbell-shaped samples with the dimension of 20.0 mm × 2.0 mm × 1.0 mm were prepared by press-molding at 230–240 °C. For the preparation of PET specimen, the hot press-molding temperature was 260–270 °C.

The barrier properties were studied by Labthink VAC-V2 gas permeability tester at 30 °C with the relative humidity (RH) of 50%. Oxygen and carbon dioxide with 99.99% purity were used. Amorphous polyesters films were prepared according to the melt-press/quench procedure. The amorphous round films with a diameter of 97 mm were used and the testing range was 0.05–50000 cm³/(m²·24 h·0.1 MPa).

Synthesis of 2-Acetylfuran

Into a flask equipped with a magnetic stirrer, a solution of methanesulfonic acid (0.48 g, 5 mmol, catalyst) in acetic anhydride (51.05 g, 500 mmol) was first added, followed by dropwise addition of furan (6.81 g, 100 mmol). After the mixture stirred at room temperature for 0.5 h, it was heated to 60 °C and stirred at this temperature for another 10 h. The acetic anhydride in excess was removed through vacuum distillation. The residue was poured into saturated NaCl solution and dried under vacuum at 50 °C to a constant weight. A light yellow liquid product, 2-acetylfuran, was obtained. In order to on-line monitor the reaction and determine the yield of 2-acetylfuran at different time, about 0.25 g of the reaction

mixture was taken from the flask at different reaction time: 1, 2, 4, 6, 8 and 10 h. In this work, boron trifluoride ether complex and concentrated sulfuric acid were also used as catalyst, and the same reaction procedure and stoichiometric ratio were used for different catalyst systems. The chemical structure of 2-acetylfuran was confirmed by FTIR, ¹H-NMR and ¹³C-NMR.

FTIR (KBr, cm⁻¹): 3133, 1680, 1570, 1470, 1395, 1280, 1100, 1024, 957, 765.

¹H-NMR (DMSO, δ): 6.55, 7.19, 7.60 (furan ring, d, 3H); 2.55 (—CH₃, s, 3H).

¹³C-NMR (DMSO, δ): 112.1, 117.2, 146.4, 152.6 (furan ring, 4C), 186.5 (C=O, 1C), 25.8 (—CH₃, 1C).

Synthesis of 2,5-DAF

Into a flask equipped with a magnetic stirrer and containing a mixture of acetic anhydride (20.4 g, 0.2 mol) and predetermined catalyst (*p*-toluenesulfonic acid, phosphoric acid or methanesulfonic acid), 2-acetylfuran (11.0 g, 100 mmol) was added. The mixture was heated to 120 °C and stirred for enough long period of time, and then acetic anhydride was removed through vacuum distillation. The residue was poured into ethanol and stirred at 60 °C for 0.5 h. After cooling down to room temperature, the precipitate was filtered and dried under vacuum to give a pale crystal. At different reaction time, 0.50 g of the reaction mixture was taken from the flask for determination of 2,5-DAF yield. The chemical structure of 2,5-DAF was confirmed by FTIR, ¹H-NMR, ¹³C-NMR and LC-MS.

FTIR (KBr, cm⁻¹): 3133, 1677, 1560, 1421, 1356, 1280, 1112, 1060, 945, 846, 655.

¹H-NMR (DMSO, δ): 7.23 (furan ring, d, 2H); 2.59 (—CH₃, s, 6H).

¹³C-NMR (DMSO, δ): 117.2, 153.6 (furan ring, 4C), 187.5 (C=O, 2C), 26.3 (—CH₃, 2C).

LC-MS (ESI): *m/z* 153.01.

Synthesis of 2,5-FDCA

2,5-Diacetylfuran (5.00 g, 32 mmol) was dissolved in 100 mL of deionized water contained in a 500 mL round-bottomed flask. After dropwise addition of 50 mL of KI-I₂ aqueous solution (2.0 mol/L), the system was stirred at room temperature for 10 min, and NaOH aqueous solution (2 mol/L) was added to adjust the pH of the solution to 6–7. Then the canary yellow precipitate was formed and removed by filtration. After that, the pH value of the filtrate was adjusted to 1–2 by addition of a small amount of hydrochloric acid, and pale white crystalline precipitated out. At last, the precipitate was filtered out and dried under vacuum to a constant weight (4.85 g, yield: 97.1%). The chemical structure of the product was confirmed by FTIR, ¹H-NMR, ¹³C-NMR and LC-MS.

FTIR (cm⁻¹): 3151, 1701, 1572, 1523, 1424, 1276, 1229, 1188, 1041, 962, 851, 763.

¹H-NMR (DMSO, δ): 7.29 (furan ring, d, 2H).

¹³C-NMR (DMSO, δ): 118.8, 147.5 (furan ring, 4C), 159.3 (C=O, 2C).

LC-MS (ESI): *m/z* 154.9.

Synthesis of Dimethyl Furan-2,5-dicarboxylate (DMFD)

2,5-FDCA (7.8 g) together with 0.5 mL of concentrated sulfuric acid as the catalyst was added into a flask containing 32 g of methanol and equipped with a mechanical stirrer. The mixture was refluxed at 90 °C for 5 h. Excess methanol was distilled out and dimethyl ester precipitated out as white powder after cooling to room temperature. The precipitate was collected *via* filtration, washed with water for several times and dried in a vacuum oven. The yield was calculated to be 89.0%. The melting point of the resulted DMFD was 109–110 °C, and its chemical structure was confirmed by ¹H-NMR and ¹³C-NMR. For comparison, a commercial 2,5-FDCA, the oxidation product of HMF (named as FDCA-HMF, with the purity above 99%), was also used to prepare DMFD following the same synthetic procedure.

¹H-NMR (DMSO, δ): 7.40 (furan ring, s, 2H), 3.86 (–CH₃, s, 6H).

¹³C-NMR (DMSO, δ): 119.4, 146.5 (furan ring, 4C), 158.3 (C=O, 2C), 52.8 (–CH₃, 2C).

Synthesis of PEF and PET

Two-stage melt polycondensation was used to prepare PEF and PET (with the synthesis of PET as the control) from EG, DMFD or dimethyl terephthalate (DMT) with molar ratio of diol/diester of 1.6. All the reactions were conducted in a three-necked round bottom flask of 500 mL equipped with a mechanical stirrer with torque indicator. The predetermined EG, DMFD or DMT and the catalyst (zinc acetate, 0.2 mol% based on DMFD or DMT) were added into the flask. The reaction was conducted at 180 °C for 4 h under the protection of nitrogen. A second portion of the catalyst (antimony trioxide(III), 0.15 mol% based on DMFD or DMT) was added subsequently. After that, the reaction temperature was increased to 240–280 °C with the pressure of the reaction system gradually reduced to 10–30 Pa for a certain time until the torque value of the stirrer reached a fixed value to ensure the similar viscosity for all the products. Finally, the reaction system was returned to the normal atmospheric pressure by introduction of N₂ and the target product was obtained. The samples were denoted as PET, PEF-HMF and PEF-Furan, respectively. PEF-HMF stands for PEF synthesized from HMF-based 2,5-FDCA (commercial) and PEF-Furan stands for PEF synthesized from 2,5-FDCA prepared in this work. The chemical structure of the prepared PEF was confirmed by ¹H-NMR and ¹³C-NMR.

¹H-NMR (TFA, δ): 7.20 (furan ring, s, 2H), 4.63 (–CH₂, s, 4H).

¹³C-NMR (TFA, δ): 119.8, 145.9 (furan ring, 4C), 159.8 (C=O, 2C).

RESULTS AND DISCUSSION

Synthesis of 2-Acetylfuran

For the synthesis of 2-acetylfuran, the reaction was conducted at 60 °C with acetic anhydride as the acylation agent^[31, 32]. In order to gain more insight into the reaction, several different catalytic systems, such as concentrated sulfuric acid, methanesulfonic acid and boron trifluoride ether complex, were used. The yield of 2-acetylfuran catalyzed by different

catalysts along with reaction time was determined by high-performance liquid chromatography (HPLC), and the results are shown in Fig. 1. It was noted that, when the acylation reaction was catalyzed by boron trifluoride ether complex, the yield of 2-acetylfuran was quickly increased up to 92.2% and then decreased dramatically with prolonged reaction time. When the reaction was conducted for 10 h, the yield of 2-acetylfuran was only 61.6%. For the system catalyzed by concentrated sulfuric acid, the similar result was obtained. The reason might be that the furan ring was not stable under strong acidic environment and the ring-opening reaction was easy^[33, 34]. When relatively weak acid, methanesulfonic acid, was taken as the catalyst, the yield of 2-acetylfuran increased gradually along with the reaction time and finally reached 98.3% after 10 h reaction. In addition, HPLC results were easy to identify the high purity and yield of 2-acetylfuran. Therefore, the relatively weak acids might be the best catalysts for acylation of furan in this work. Methanesulfonic acid was therefore selected as the catalyst for the synthesis of 2-acetylfuran.

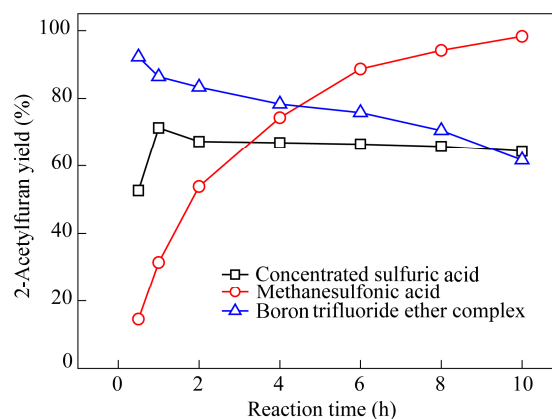


Fig. 1 Yields of 2-acetylfuran along with reaction time catalyzed by concentrated sulfuric acid, methanesulfonic acid and boron trifluoride ether complex at 60 °C

Synthesis of 2,5-DAF

For the synthesis of 2,5-DAF, 2-acetylfuran obtained above was further acylated by acetic anhydride *via* Friedel-Crafts reaction. In order to restrain the ring opening reaction of 2-acetylfuran, relatively weak acids, such as *p*-toluenesulfonic acid, phosphoric acid or methanesulfonic acid, were used as the catalyst. Figure 2 shows the yields of 2,5-DAF as a function of reaction time catalyzed by different catalysts. Obviously, a maximum yield of 2,5-DAF along with reaction time was observed no matter which catalyst was used. The conversion of 2-acetylfuran, the maximum yield of 2,5-DAF and selectivity of this reaction using different catalysts are listed in Table 1. Undoubtedly, methanesulfonic acid was the optimal catalyst for the reaction. It is known that 2,5-DAF is one of the most important furan derivatives and several methods have been tried for its preparation. However, the harsh reaction conditions, including ultra low temperature (–78 °C) and dangerous catalysts (such as *n*-BuLi) are necessary^[35]. Up to now, literature information is hardly available about the synthesis of 2,5-DAF under mild conditions. In this work, the Friedel-Crafts reaction catalyzed

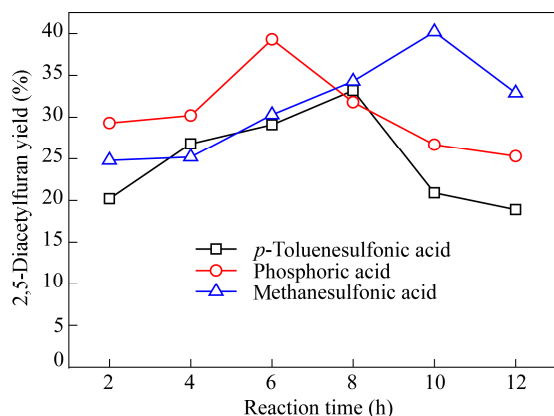


Fig. 2 Yields of 2,5-DAF catalyzed by *p*-toluenesulfonic acid, phosphoric acid and methanesulfonic acid, respectively (Molar ratio of the catalyst to 2-acetylfuran was kept at 1:1.)

Table 1 Effect of catalyst on the acylation of 2-acetylfuran

System	Catalyst ^a	Conversion ^b (%)	Yield ^c (%)	Selectivity ^d (%)
1	Methanesulfonic acid	76.8	40.2	52.3
2	Phosphoric acid	83.0	39.3	47.3
3	<i>p</i> -Toluenesulfonic acid	92.7	33.2	35.8

^a Molar ratio of catalyst to 2-acetylfuran = 1:1; ^b Conversion = 1 – (remained 2-acetylfuran/charged 2-acetylfuran); ^c Maximum yield of 2,5-DAF of the reaction; ^d Selectivity = Yield/Conversion

by methanesulfonic acid was conducted at 120 °C and 2,5-DAF was synthesized successfully, though the yield was only about 40.2%.

In order to optimize the reaction conditions, the effect of methanesulfonic acid dosage on the yield of 2,5-DAF was investigated (Fig. 3). It was noted that a higher ratio of methanesulfonic acid to 2-acetylfuran accelerated the reaction, as indicated by a rapid growth of 2,5-DAF yield along with reaction time. In addition, when the molar ratio of methanesulfonic acid to 2-acetylfuran at 0.3–1.5, no matter how many methanesulfonic acid was used, the yield of 2,5-DAF was increased at first and then decreased subsequently along with the reaction time. When the molar ratio of methanesulfonic acid to 2-acetylfuran was increased

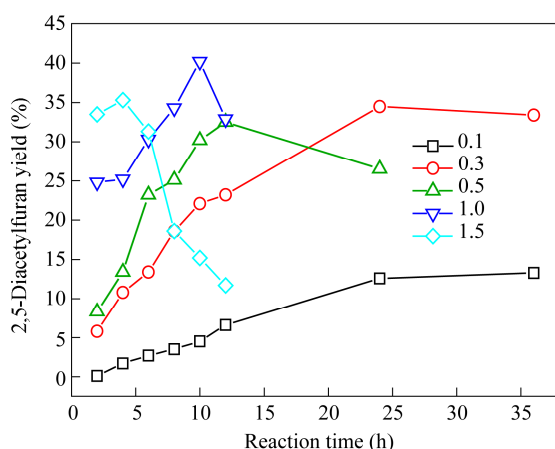


Fig. 3 Yields of 2,5-DAF along with the reaction time under different catalyst dosages (molar ratio of methanesulfonic acid:2-acetylfuran = 0.1, 0.3, 0.5, 1.0, 1.5) at 120 °C

to 1.0, the maximum yield of 40.2% for 2,5-DAF was obtained within 10 h of reaction time.

Synthesis of 2,5-FDCA

The conversion of methyl ketone into carboxylic acid can be realized by the well-known iodoform reaction. This reaction is usually taken to identify the existence of methyl ketone in qualitative organic analysis^[36]. In this work, this reaction was taken to convert 2,5-DAF into 2,5-FDCA and the procedure is illustrated in Fig. 4. KI-I₂ aqueous solution (25 mL, 0.5 mol/L), 2,5-DAF (5.00 g) and deionized water (100 mL) were first mixed and stirred at room temperature for 10 min. By addition of 5–6 mL of NaOH aqueous solution (2 mol/L), the pale-yellow precipitate of iodoform was immediately generated, and it was collected *via* filtration. After that, the pH of the filtrate was adjusted to 1–2 by addition of hydrochloric acid (HCl), and a pale white crystalline precipitate, the target product 2,5-FDCA, was observed. After filtration and vacuum-dried, the final product of 4.85 g was obtained. This gave a yield of 2,5-FDCA of 97.1%. The chemical structure and the purity were confirmed by FTIR, ¹H-NMR, ¹³C-NMR and LC-MS. Obviously, except for the recyclable iodoform, no other waste was generated during the reaction. In addition, this reaction was conducted at room temperature and no complex catalyst was needed.

Based on the above results, the overall yield of 2,5-FDCA starting from furan was calculated to be 38.4% (98.3% × 40.2% × 97.1% = 38.4%), which seems to be relatively low. However, considering the fact that all the reactions were conducted under mild conditions without harmful catalyst, and the by-products (acetic acid and iodoform) were easy to be recycled and no any other toxic wastes were detected, the strategy for the synthesis of 2,5-FDCA described here has significant value. Further investigation will be conducted to increase the overall yield.

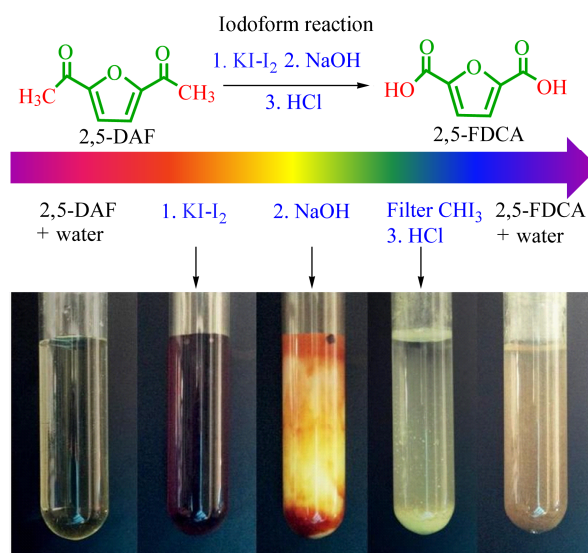


Fig. 4 Illustration for the conversion of 2,5-DAF to 2,5-FDCA (The online version is colorful.)

Synthesis of PEF and Its Property Evaluation

As known, one of the major problems of FDCA-based polyesters is the coloration during the polymerization

reaction^[37, 38]. Sugar-based impurities in FDCA, the side reaction (*e.g.* the decarboxylation of FDCA at high temperature) and the use of catalysts are the main causes for the coloration (brown to black) of resulted polyesters. In this work, in order to restrain or avoid the thermal decarboxylation of FDCA during the polycondensation, it was converted into dimethyl furan-2,5-dicarboxylate (DMFD) *via* esterification with methanol at first. And the transesterification reaction with EG was conducted at 180 °C. Within 4 h of the reaction and after about 95% theoretical methanol distilled out of the system, antimony trioxide(III) (0.15 mol% based on the amount of DMFD) was added as the catalyst for the polycondensation. Using this procedure, the intrinsic viscosity of PEF reached as high as 0.78–0.91 dL/g. For comparison, PET with viscosity of 0.87 dL/g was also synthesized and taken as the control. The appearance of PEF synthesized from different 2,5-FDCA and that of PET are shown in Fig. 5. Obviously, the PET and PEF (PEF-Furan) prepared from furan-based FDCA were more transparent with their transmittance of 91.6% and 89.0% with the film thicknesses of 153 and 156 μm , respectively by radiation with the light at 700 nm wavelength, indicating that the decarboxylation of FDCA might be avoided during the esterification and polycondensation. However, using the similar procedure, the PEF synthesized from HMF-based FDCA was brown and the transmittance was only 69.8% at the same light radiation (700 nm) on a film with the thicknesses of 160 μm . It is widely reported^[39–42] that, during the production of HMF from lignocellulose or fructose, the impurities like humins, soluble in many organic solvents, could co-exist with HMF, and were difficult to be removed even after HMF oxidized into FDCA; they would affect the appearance of the resulted polymers. In this work, the coloration of PEF synthesized from HMF-based FDCA was also attributed to the trace impurity in FDCA, although the purity of FDCA was determined to be 99.5% by HPLC.

In order to evaluate the quality of PEF prepared from different FDCA (PEF-HMF and PEF-Furan, respectively), their thermal properties were investigated by DSC and TGA

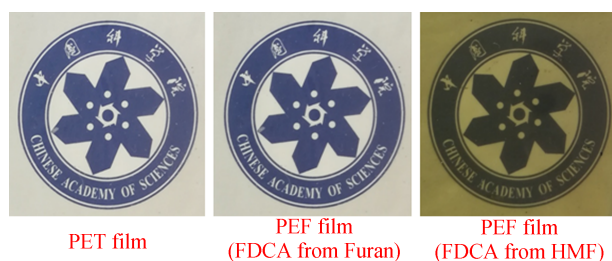


Fig. 5 Appearance and transparency of the synthesized PEF and PET

(Fig. 6 and Table 2). It was noted that all the PEF samples, regardless of the FDCA used as starting material, showed a glass transition temperature of $\sim 87^\circ\text{C}$, a weak melting point at $\sim 214^\circ\text{C}$ and a temperature of 5% weight loss at about 380°C . These results were similar to those reported^[42, 43], and indicated that the thermal properties of PEF were not affected by the origin of FDCA. In another word, the possible trace impurities co-existing with HMF/FDCA did not influence the thermal properties of resulted PEF, though the coloration was observed. With FDCA preparation from furfural by Henkel reaction, not only the target product 2,5-FDCA was formed, but also the isomers, 2,4-FDCA and 3,4-FDCA. Purification of 2,5-FDCA became much difficult and high-costing^[11, 28]. The presence of 2,4-FDCA or 3,4-FDCA will seriously affect the thermal properties of resulted PEF, leading to a much lower glass transition temperature and melting temperature with also a weak crystallization^[44].

One of the most attractive advantages of PEF is its excellent barrier property (6–11 times better O_2 barrier and 13–19 times better CO_2 barrier)^[6, 45] and high glass transition temperature ($\sim 87^\circ\text{C}$) when compared with its petroleum-based counterpart PET. In Table 3, the gas barrier property and tensile property of the synthesized PEF-Furan are listed.

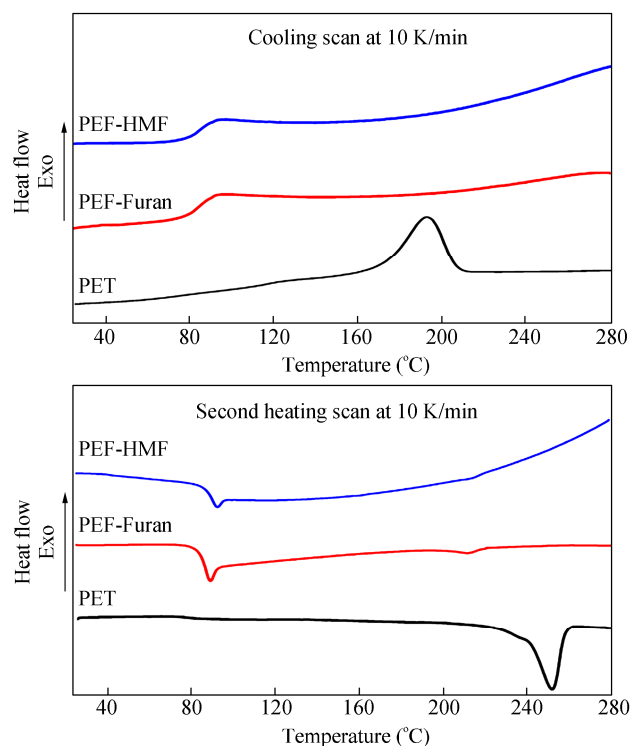


Fig. 6 DSC curves of PEF synthesized from different FDCA (N_2 , heating rate 10 K/min, 25–280 °C)

Table 2 Thermal properties of PEF synthesized from furan route compared with HMF route

Sample	Intrinsic viscosity $[\eta]^a$ (dL/g)	DSC ^b					TGA ^c		
		T_g (°C)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)	R_{600} (wt%)
PET	0.87	69.5	177.3	27.6	249.6	29.7	407	445	15.7
PEF-HMF	0.78	87.0	nd	nd	214.0	0.2	376	411	11.3
PEF-Furan	0.91	87.6	nd	nd	212.9	0.9	381	413	10.4

^a Intrinsic viscosity obtained with an Ubbelohde viscometer; ^b N_2 , the second heating scan at 10 K/min, 25–280 °C; ^c N_2 , heating rate 20 K/min, 50–800 °C

Table 3 Tensile and barrier properties of PEF-Furan and comparison with PET

Sample	Test at 23 °C	PET	PEF-Furan	PEF compared with PET
Barrier properties	CO ₂ (10 ⁻¹⁰ cm ³ ·cm/(cm ² ·s·MPa))	8.25	0.585	Increased ~13.1 times
	O ₂ (10 ⁻¹⁰ cm ³ ·cm/(cm ² ·s·MPa))	3.9	0.578	Increased ~5.8 times
Mechanical properties	Tensile modulus (GPa)	1.9 ± 0.1	2.8 ± 0.2	Increased ~50%
	Tensile strength (MPa)	60 ± 4	85 ± 5	Increased ~40%

^a Thickness of PET and PEF films was 172 and 201 μm, respectively.

For comparison, the synthesized PET was taken as the control with its properties also shown in Table 3. Obviously, compared with those of PET, the barrier to CO₂ and O₂ of PEF was increased by 13.1 and 5.8 times, respectively. These results were in line with those previously reported^[6, 45, 46]. In addition, the tensile modulus and strength of PEF were all much higher than those of PET (50% of increase in modulus and 40% of increase in strength), and slightly higher than some reported results (2450 MPa for modulus and 35 MPa for strength)^[47]. The reason might be the higher viscosity of PEF in this work. Based on above results, it is worth noting that the synthesized FDCA in this work has great potential and advantages for preparation of high performance bio-based polyesters.

CONCLUSIONS

2,5-FDCA was synthesized from furan and acetic anhydride *via* a three-step reaction. Compared with currently known methods (HMF-based route and Henkel reaction from furfural), this strategy in this work showed obvious advantages including: mild reaction condition, common catalysis system, easily recyclable by-products, no harmful wastes, easy purification process and high purity. In addition, the starting materials, furan and acetic anhydride, are both bulk chemicals and can be produced from the renewable feedstock. Using 2,5-FDCA synthesized from furan in this work, high quality PEF with good appearance was obtained. All these results indicate that the strategy for the preparation of 2,5-FDCA from furan is of great advantages and potential. It is a GREENER and novel method for 2,5-FDCA synthesis.

Electronic Supplementary Information

Electronic supplementary information (ESI) includes FTIR, ¹H-NMR and ¹³C-NMR spectra of 2-acetylfuran; FTIR, ¹H-NMR, ¹³C-NMR and LC-MS spectra of 2,5-DAF; FTIR, ¹H-NMR, ¹³C-NMR and LC-MS spectra of 2,5-FDCA; ¹H-NMR and ¹³C-NMR spectra of dimethyl furan-2,5-dicarboxylate; ¹H-NMR and ¹³C-NMR spectra of PEF; UV absorption of 2-acetylfuran along with the reaction time; TGA thermograms of PEF synthesized from different FDCA samples, which is available free of charge in the online version of this article at <http://dx.doi.org/10.1007/s10118-018-2092-0>.

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