

Progress in the Synthesis and Properties of 2,5-Furan Dicarboxylate based Polyesters

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Biomass is a class of abundant renewable resource. Its efficient use in the field of biobased materials is one of the important ways for implementation of sustainable development strategies. 2,5-Furandicarboxylic acid (FDCA) as a potential alternative of terephthalic acid (PTA) to make aliphatic polyesters, can be obtained in mass amount from cellulose *via* bio- or chemical process. For this reason, FDCA-based polyesters have gained high interest recently. This review systematically summarizes recent progress in the making of FDCA-based polyesters (including poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), poly(butylene 2,5-furandicarboxylate) (PBF), poly(hexylene 2,5-furandicarboxylate) (PHF), and their copolyesters), especially highlighting the progress and fundamental aspects for their synthesis and properties. Significant advantages (and also disadvantages) of the FDCA-based polyesters are clearly indicated relative to price, performance, and sustainable development, in reference to traditional petroleum-based polyesters in industrial application. The goal of this review is to provide useful information regarding the synthesis and properties of FDCA-based polyesters.

Keywords: FDCA; FDCA-based polyesters; Copolyesters; Synthesis; Polycondensation

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INTRODUCTION

Plastics are closely related to the development of human society. Terephthalic acid (PTA) based polyester, as one of the most important plastics, has been widely used in food packaging, plastic toys, plastic furniture, and engineering plastics. In recent years, due to the excessive consumption of fossil resources and environmental problems, the search for new materials with environment friendly and unique properties to synthesize biobased polymers has attracted extensive attention. Simultaneously, European countries and the United States have begun to support the development and use of biomass-based products to reduce the excessive reliance on oil-based products. Against this background, a large number of monomers derived from renewable resources, such as dodecanedioic acid (Green *et al.* 2000; Zou *et al.* 2018; Firoozi and Kang 2019; Zhang *et al.* 2019a;), lactic acid (Duo *et al.* 2016; Herran *et al.* 2019; Montava-Jorda *et al.* 2019; Wu *et al.* 2019), levulinic acid (Hartweg and Becer 2016; Pileidis and Titirici 2016; Amarasekara *et al.* 2018; Sinisi *et al.* 2019), isosorbide (Sousa *et al.* 2016a; Chebbi *et al.* 2019; Hu *et al.* 2019a; Kieber *et al.* 2019), ethylene diol (Haernvall *et al.* 2017; Li *et al.* 2017; Lu *et al.* 2017; Sukhawipat *et al.* 2018), and succinic acid (Rizescu *et al.* 2017; Landim *et al.* 2018; Garcia-Campo *et al.* 2019; Hu *et al.* 2019b; Pasma *et al.* 2019) have been continuously developed and promoted the synthesis and widespread use of a large number of new biobased polymers products.

Among them, 2,5-furandicarboxylic acid (FDCA) is deemed as a promising platform chemical to prepare biobased polyesters.

FDCA has two carboxylic acid groups, and this implies that there is good potential as a replacement for PTA due to similarities between PTA and FDCA (Moreau *et al.* 2004). This aromatic diacid has been considered as a potential replacement and also as a renewable resource-based equivalent of PTA, which is a monomer in poly(ethylene terephthalate) (PET) plastics. The market for PTA exceeds 50,000 kt per year, demonstrating the large potential of FDCA for the preparation of polyethylene furanoate (PEF) as a replacement for PET (Eerhart *et al.* 2012; Amarasekara *et al.* 2017). For this reason, the biobased FDCA has attracted extensive attention from academy and industry, including the preparation of FDCA and its precursor, 5-hydroxymethylfurfural (HMF), together with varieties of FDCA-based materials that can be used in the domain of packaging, textile and coating. There have some related publications reviewing the progress and critical aspects in the synthesis and properties of FDCA-based polyesters a few years ago (van Es 2013; Sousa *et al.* 2015; Papageorgiou *et al.* 2016). Now, ongoing research and industrial production of FDCA-based polyesters, especially for poly(ethylene 2,5-furandicarboxylate) (PEF), poly(propylene 2,5-furandicarboxylate) (PPF), poly(butylene 2,5-furandicarboxylate) (PBF), poly(hexylene 2,5-furandicarboxylate) (PHF) and their copolyesters, has progressed in a new stage due to the increasing attention paid by researchers in recent years. In order to gain a deeper understanding of the current status of the synthesis and properties of FDCA-based polyesters, this mini review paper summarizes and discusses the recent progress, hoping to help readers to have a deeper understanding and cognition in this field, and to make a greater breakthroughs in this exciting research area.

SYNTHESIS OF POLY(ETHYLENE 2,5-FURANDICARBOXYLATE) (PEF)

Poly(ethylene 2,5-furandicarboxylate) (PEF) is the most eye-catching member of the FDCA-based polyesters family, which is considered a furan counterpart of the engineering polyester, PET (Gandini *et al.* 2009b; Sousa *et al.* 2015; Banella *et al.* 2019). Although fully renewable-based PET has been foreseen, and several routes are under development today, attempts to amplify the process have been limited due to the low yields (Tavener *et al.* 2003; Collias *et al.* 2014; Jerpdal *et al.* 2019). By contrast, PEF is totally based on renewable resources, as its two monomers, ethylene glycol (EG) and FDCA can be obtained from cellulose (Zhang *et al.* 2015; Zhou *et al.* 2019). It is expected that PEF will create its own market niche toward its full penetration in existing polyester market and be widely used in all works of life due to its high performance in high barrier, thermal, and mechanical properties (Sousa *et al.* 2015).

The synthesis of PEF dates back to the middle of the previous century; however, the literature on PEF is scanty after the research about the X-ray study of the FDCA-based polyester's structure in 1968 (Sousa *et al.* 2015). Until the last decade, as people have been paying more and more attention to building a sustainable society, a revival of interest in the synthesis and characterization of PEF and related polyesters can be observed (Ji *et al.* 2008; Gandini *et al.* 2009a,b; Gomes *et al.* 2011). For example, Ji *et al.* (2008) developed a two-stage method for the preparation of PEF from cellulose (Fig. 1). In the first stage, dihydroxyethyl furanate monomers or oligomers can be obtained through the esterification or reverse transesterification between FDCA and EG. Next, the polycondensation reaction allows the polymerization product to reach the corresponding molecular weight. In the

process of polycondensation, the excessive and generated EG is removed by raising the temperature and vacuum degree to promote the polycondensation reaction in the direction of PEF formation.

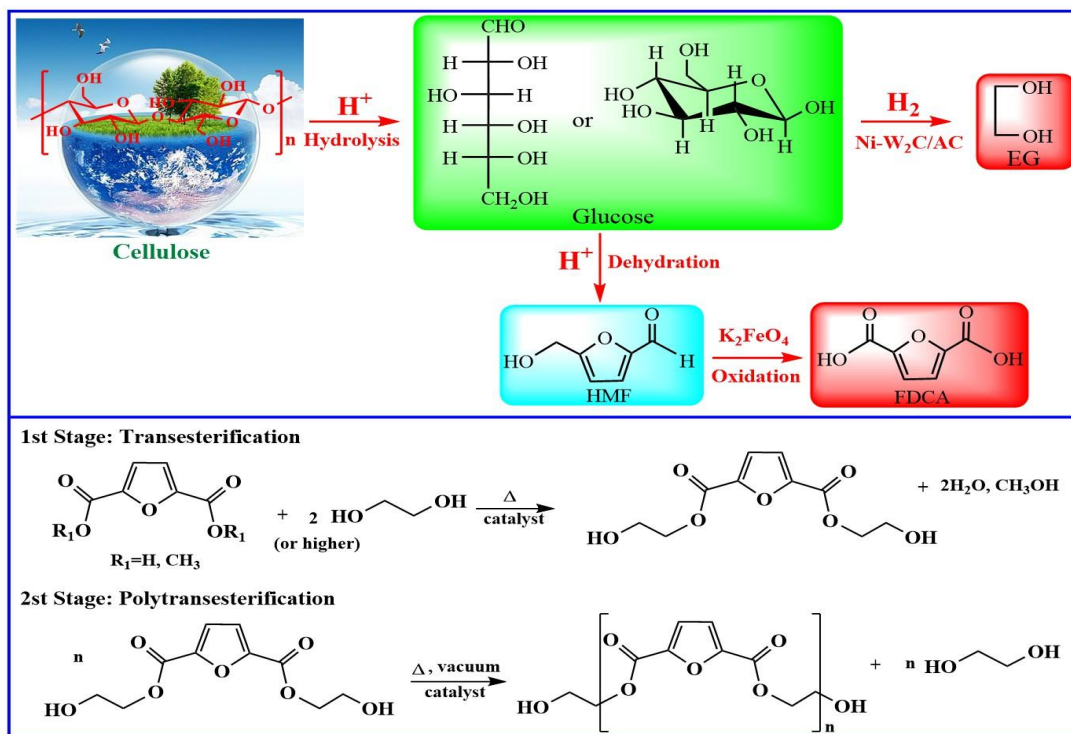


Fig. 1. Typical route for the synthesis of EG and FDCA from cellulose and the two-stage approach for the synthesis of PEF

Gandini *et al.* (2009a,b) developed two methods for the synthesis of PEF from FDCA and EG. They used a small amount of hydrochloric acid to catalyze the esterification of FDCA with EG, then antimony trioxide (Sb_2O_3) was used as the catalyst for condensation polymerization to obtain some white PEFs with DP_n values of 250 to 300. It was determined that the PEFs exhibited good chemical stability, which was only soluble in strong acid (trifluoroacetic acid, TFA) and strong polar organic solvents (hot tetrachloroethane, TCE), and was thermally stable (around 300°C) by TGA analysis. Further analysis of the differential scanning calorimetry (DSC) and X-ray diffraction (XRD) showed that the PEFs exhibited a high degree of crystallinity, and the melting temperature (T_m) was 210 to 215 °C. Furthermore, the glass transition temperature (T_g) was 75 to 80 °C (Gandini *et al.* 2009b). In the same year, they developed another method to obtain PEF, which had similar properties to their prepared PEFs. The product was soluble in TFA and 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) but insoluble in TCE; however, the difference was that the DP_n was very low (about 70) (Gandini *et al.* 2009a).

Gomes *et al.* (2011) used a similar method to get PEF with a number-average molecular weight (M_n) of 22400, weight-average molecular weight (M_w) of 44500 and polydispersity index (PDI) of 1.99. The peak value of X-ray diffraction was obtained at $2\theta=16.0, 20.1, \text{ and } 27.8^\circ$. In addition, the thermogravimetric analysis (TGA) and DSC measurements revealed that the thermal decomposition (T_{di}), maximum decomposition temperature (T_d), T_g , crystallization temperature (T_c), and T_m was 300, 398, 80, 165, and 215

°C. The T_g as well as the T_c only appeared on the second DSC scan trace after quenching the melted polymer, indicating that the obtained PEF had a high degree of crystallinity.

In addition to the two-step method, direct esterification is also an important method to prepare PEF. For example, Jiang *et al.* (2012) prepared the PEF *via* direct esterification method. The obtained PEF had a specific viscosity (η_{sp}) of 1.20 dL/g, and its M_n , M_w , and PDI values were 105300, 252000, and 2.39. In addition, the tensile test of PEF samples showed that PEF was a thermoplastic polyester material. Its tensile modulus, tensile strength, and elongation at break of PEF were 2070 MPa, 66.7 MPa, and 4.2%, respectively. Codou *et al.* (2014) also obtained some melt-crystallized and glass-crystallized PEF samples *via* the direct esterification method. The products exhibited similar crystallinities and unit cell structures with those reported for PEF obtained by transesterification (Gandini *et al.* 2009b; Papageorgiou *et al.* 2014). In addition, the non-isothermal data analysis of PEF was carried out by DSC, and a new calculation method was used to evaluate the Hoffman-Lauritzen theory. The evaluation equation of the method showed that the effective activation energy of the growth rate depended on the melting temperature (T_m) and the assumed temperature (T_∞), and results showed the growth kinetics of the crystals were different during the two crystallization processes. Nevertheless, PEF crystals from the glass temperature and melting temperature had a similar structure. Furthermore, compared with melt crystallization rate of PEF, the experimental data of glass crystallization was in good agreement with the predicted value of Hoffman-Lauritzen rate equation (Codou *et al.* 2014). The main reason for the deviation of melt crystallization was that the secondary nucleation limited the transverse growth rate (Codou *et al.* 2014).

In order to further understand the unique characteristics of the PEF, its crystal structure, dynamics, structure-property correlations, and penetrant transport have attracted much attention (Burgess *et al.* 2014, 2015; Tsanaktsis *et al.* 2015a; Mao *et al.* 2016; Burgess *et al.* 2016; Araujo *et al.* 2018; Rosenboom *et al.* 2018). For example, Mao *et al.* (2016) determined the crystal structure of PEF with X-ray fiber diffraction (XRFD) and molecular model, which was composed of monoclinic unit cell with a space group of $P2_1$, whose cell parameter was $a=5.784 \text{ \AA}$, $b=6.780 \text{ \AA}$, $c=20.296 \text{ \AA}$, and $\gamma=103.3^\circ$, and the density of this crystalline structure was 1.562 g/cm^3 . Araujo *et al.* (2018) revealed that the PEF presented strained $\text{syn}^{\text{FDCA}}\text{-trans}^{\text{EG}}$ extended zigzag conformation in the crystalline region, which was favorable in the crystal but was not feasible for single chain due to the formation of a large array of $\text{C-H}\cdots\text{O}$ bonds. In the amorphous regions, PEF chains tended to the $\text{anti}^{\text{FDCA}}\text{-gauche}^{\text{EG}}$ helical conformation. Compared with PET, PEF with a high energy difference among the amorphous and crystalline chains resulted in a higher crystallization temperature, while strain-induced crystallization required a higher tensile ratio. The use of novel inelastic neutron scattering (INS) spectroscopy further indicated that the PEF chains of several low frequency vibration modes was less flexible than that of PET, so that the gas barrier properties were higher.

What's more, a preliminary experiment and analysis of uniaxial stretching of PEF were carried out by Menager *et al.* (2018). It turned out that strain-induced crystallization (SIC) can develop under appropriate stretching conditions with PEF and controlled in a manner comparable to that of PET to promote strain hardening. According to the tensile conditions of PEF, the crystals with different morphologies were formed. On the other hand, the three-phase models can be well applied to the stretched PEF. The mobile amorphous content was between 0.50 and 0.65, and the rigid amorphous content was between 0.15 and 0.30. In addition, when the tensile condition was at the most rubbery state of polyester, the mobile amorphous content in the polymer was much higher, reaching 0.70.

In addition, correlations between molecular weight and solution viscosity for PEF in comparison to PET were studied by van Berkel *et al.* (2018). Their research revealed that the melt viscosity of PEF was a function of molecular weight, and the temperature-dependence of the melt viscosity showed a higher activation energy for PEF, and the shear rate dependence indicated a lower reputation time. They found that the PEF with sufficient molecular weight displayed ductility but overall a higher tendency to brittleness than PET in the glassy state, which resulted in a significantly higher yield stress combined with a higher strain rate dependence.

However, PEF has some inherent shortcomings in thermomechanical properties, such as slow melt crystallization and brittleness, which may limit the application of PEF. In order to strengthen PEF, some PEF blends or copolymers have been developed. (Sousa *et al.* 2013; Yu *et al.* 2013; Matos *et al.* 2014; Sousa *et al.* 2016a; Wang *et al.* 2017a; Pouloupoulou *et al.* 2019b; Xie *et al.* 2019). For example, Yu *et al.* (2013) prepared some poly(ethylene 2,5-furandicarboxylate-co-ethylene succinate) (PEFS) copolymers with FDCA and succinic acid *via* melt polycondensation in the presence EG. Random copolymers with number-average molecular weights exceeding 25600 and thermal stability exceeding 300°C were obtained.

Sousa *et al.* (2013) prepared a straightforward partial substitution of non-renewable PET by renewable homologous PEF through random copolymerisation of bis(2-hydroxyethyl) terephthalate (BHETP) and bis(hydroxyethyl)-2,5-furandicarboxylate (BHEFDC) (Fig. 2). They found that the isolation yields of all copolyesters were around 80%, quite independent of the stoichiometric ratio of BHETP/BHEFDC used. This was an indication of the successful incorporation of both aromatic and furanic units into the copolyesters backbone.

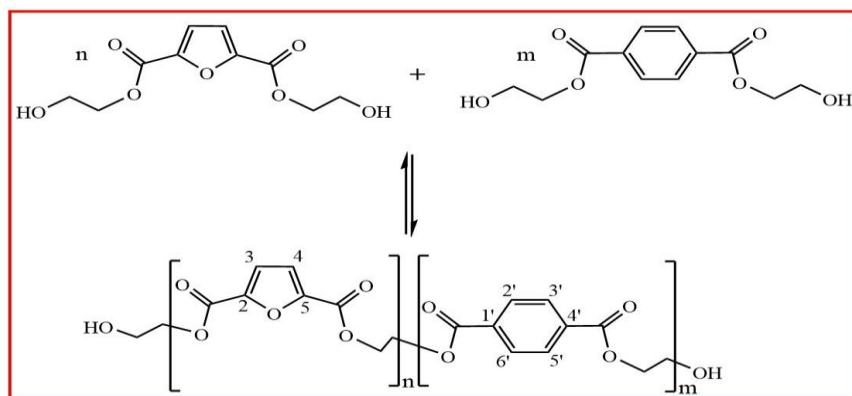


Fig. 2. Polytransesterification reaction of BHEFDC with BHETP

The M_w of these polyesters ranged between 13000 and 47000, and the polydispersity index (M_w/M_n) was close to 2. They found that the most relevant copolyesters corresponded to PET-ran-PEF 4/1, whose chemical structure contained 20% of aromatic and furanic units. Its T_g , T_c and T_m were 62.4, 125.2, and 220.1 °C, respectively, which were very similar to the properties of commercial PET. Furthermore, the thermal stability of the PET-ran-PEF 4/1 was as high as 260°C and the operating temperature determined by dynamic mechanical analyses ranged from -40.9 to 67.5 °C, which were very close to those of PET.

Matos *et al.* (2014) developed some poly(ethylene 2,5-furandicarboxylate)-co-poly(lactic acid) copolyesters based on both PEF and poly(lactic acid) (PLA) to enhance their degradability. They found that the obtained copolyesters were amorphous polymers

with high glass transition temperatures and had improved degradability with compared with PEF homopolyester counterpart.

In addition, Sousa *et al.* (2016a) reported the synthesis of fully renewable-based poly((ether)ester)s (PEEs) from FDCA, poly(ethylene glycol) (PEG), and isosorbide by polycondensation reactions (Fig. 3). Poly((poly(ethylene glycol)) 2,5-furandicarboxylate) (PEGF) polymers were obtained by polycondensation of FDCA with PEG or a mixture of PEG and isosorbide, and the isolation yield was about 65%. Furthermore, the PEGF polymers had a number-average molecular weight (M_n) in the range of 3300 to 17300, and the polydispersity values were close to 1.4, which was determined by size-exclusion chromatography in $\text{CH}_2\text{Cl}_2/\text{CHCl}_3/\text{HFP}$. The properties of PEGF material could be easily adjusted by changing the chain length of PEG and adding isosorbide or not. The product had comparable or better thermal properties than that of the fossil-PEE, and the diluted PEGISF200 chloroform solution can be cast directly on the surface of a Teflon plate to form a film. PEGF series polyesters was found to be a single T_g and below room temperature by DSC thermograms analysis. The crystallization domains were formed by a sufficiently long chain (soft PEG segments) modification so that the T_m of the PEGF200 was about 49 °C. However, due to the enrichment of the second amorphous phase in the stiff isosorbide-furandicarboxylate segments, the existence of PEG2000 and the amorphous domains of PEG soft segments, poly((poly(ethylene glycol)) 2,5-furandicarboxylate)-co-poly(isosorbide 2,5-furandicarboxylate) (PEGISF2000) exhibited different thermal properties, resulting in a T_g value of 168 °C, while T_m and T_g were about 40 °C and -26°C. In addition, the XRD results revealed that the semicrystalline character of PEGF2000 and PEGISF2000 has two sharp signals at $2\theta \approx 19$ and 23°, which was similar to that of PEG2000 polyester. Additionally, XRD analysis of PEGF2000 and PEGISF2000 revealed an amorphous center at about 20°, whereas the more crystalline PEG precursor did not appear.

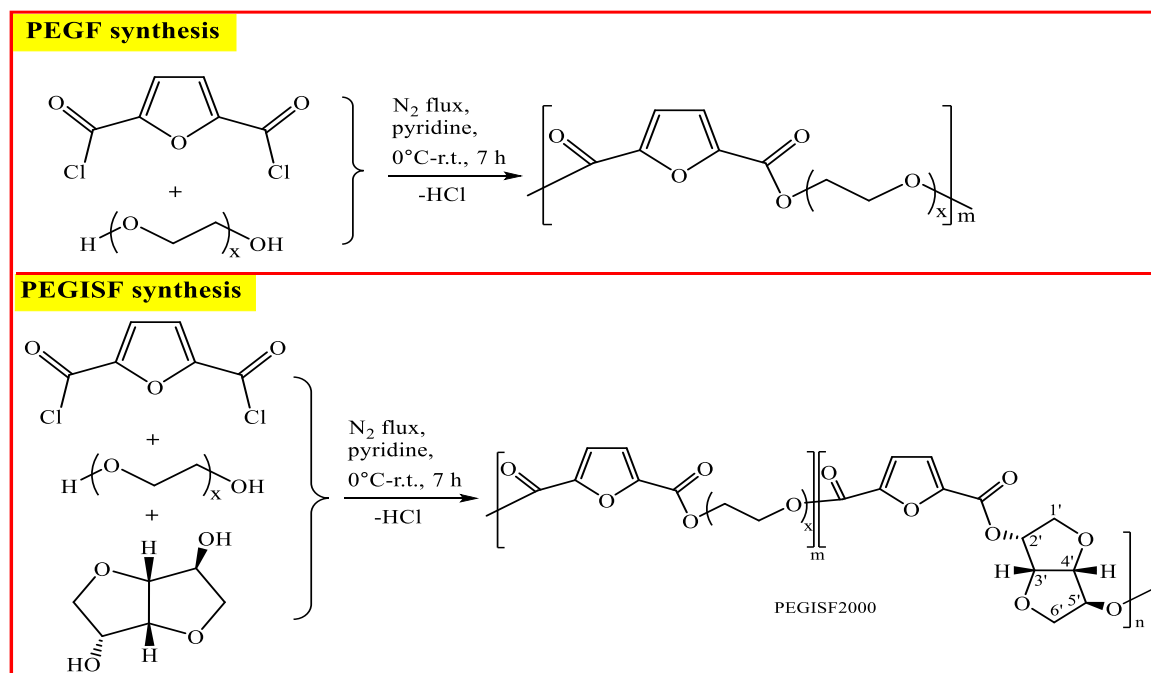


Fig. 3. Synthesis of two series of FDCA-based poly((ether)ester)s (PEGF and PEGISF2000) by polycondensation reaction

Wang *et al.* (2017a) prepared a series of multiblock copolymers poly(ethylene 2,5-furandicarboxylate)-poly(ethylene glycol) (PEFEGs) from FDCA, EG, and PEG through a two-step melt polycondensation method (Fig. 4). TGA analysis showed that PEFEGs had good thermal stability. Additionally, by changing the chain length and content of the PEG, the properties of PEFEGs, including melt crystallization peak, melt peak, and enthalpy of PEG block, were improved. It was also found that the elongation values at break of PEFEGs were significantly higher than PEF, such that they exhibited excellent shape memory properties.

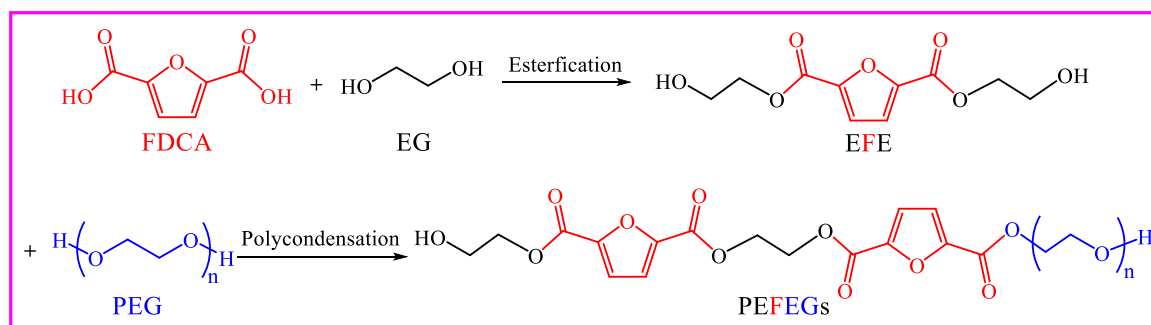


Fig. 4. Synthetic route to PEFEGs copolyesters

More recently, Xie *et al.* (2019) modified PEF with biobased 1,5-pentanediol *via* melt copolycondensation to improve its tensile strength and O₂ barrier property. The obtained poly(ethylene-co-1,5-pentylene 2,5-furandicarboxylate)s (PEPeFs) demonstrated that the amorphous copolyesters had excellent thermal stability. They found that the PEF-rich PEPeFs (ϕ PeF 9-47%) showed greatly improved elongation at break, enhanced impact strength, improved O₂ gas barrier property, high Young's modulus and yielding strength in comparison with PEF. Pouloupoulou *et al.* (2019b) revealed that the PEF-PPF copolyester with the blending of PEF and poly(propylene 2,5-furandicarboxylate) (PPF) showed a single composition-related T_g .

1,4-cyclohexanedimethanol (CHDM) and 1,4-cyclohexanedicarboxylic acid (CHDA) were also selected to be a copolyester monomer for the modification of PEF in recent years (Fig. 5) (Hong *et al.* 2016; Wang *et al.* 2016, 2018c). Wang *et al.* (2016) modified PEFs with CHDM to improve their mechanical and barrier properties. They found that the composition of the resulted poly(ethylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylate)s (PECFs) had the characteristics of random polyester, and the composition of PECFs could be tunable by adjusting the molar amount of CHDM and dimethyl furan-2,5-dicarboxylate (DMFD). Also, the crystallinity, tensile modulus, and strength of the PECFs can be gradually reduced or increased by adjusting the amount of CHDM (0-59% or 76-100%), as revealed by DSC and tensile testing results. Furthermore, PECF-32 and PECF-76 exhibited better properties compared to PEN and PEI by barrier performance studies of O₂ and CO₂ permeability in PEF, which made PECFs more useful as a packaging material. Hong *et al.* (2016) also modified PEF with CHDM to obtain some copolyesters *via* esterification and polycondensation processes. They found that the CHDM had a positive effect on the previously seen drawbacks of furan-based polyesters, and the obtained co-polyester showed a dramatic increase in elongation at break (79±18%) and impact strength (4.0±0.1%). They thought that the cyclohexane ring conformational transition in the co-polyester chains containing CHDM improved the polyester's chain

mobility and resulted in the ductility in the co-polyester. In addition, the results also revealed that the O₂ permeability and amounts of acetaldehyde (AA) content of the co-polyester-containing bottle was considerably lower than that of the PET-containing bottle. Therefore, they deemed that the obtained furan-based co-polyester was superior in both sustainability and performance and showed no limits in applicability for bottles and packaging. In addition, Wang *et al.* (2018c) synthesized a series of poly(ethylene 2,5-furandicarboxylate-co-ethylene 1,4-cyclohexanedicarboxylate)s (PEFCs) from FDCA, EG and CHDA through a two-melt polycondensation. Their results showed that all PEFCs displayed the properties of a random copolymer, and the composition of PEFCs could be tunable by adjusting the molar amount of FDCA and CHDA. The obtained PEFCs were amorphous, and the T_g decreased with the increase of CHDA content, but its thermal stability did not change. Furthermore, it was found that the obtained PEFC-30 was a toughened plastic with tensile modulus and elongation of 801 MPa and 667%, respectively.

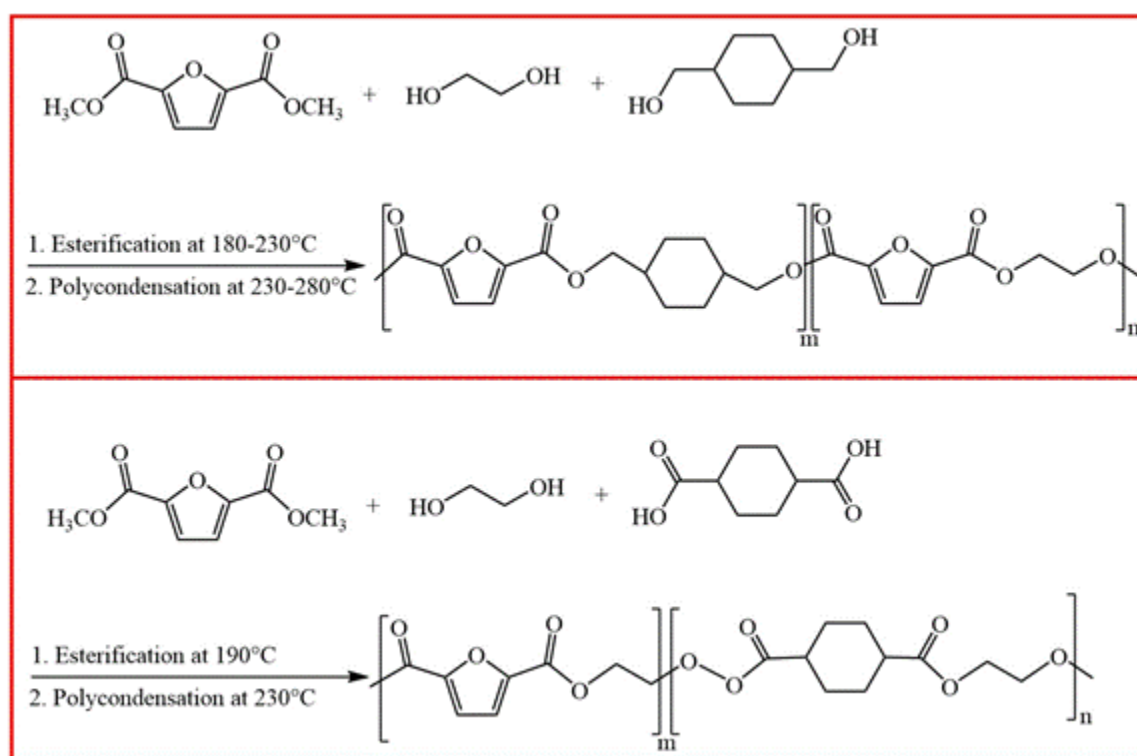


Fig. 5. Step-growth polycondensation of furan-based co-polyesters *via* melt transesterification and polycondensation processes

SYNTHESIS OF POLY(PROPYLENE 2,5-FURANDICARBOXYLATE) (PPF)

Polyesters derived from 1,3-propanediol (PD) were just reported in recent years due to the difficulties in the preparation of PD in sufficient quantities and purity (Bikiaris *et al.* 2008). However, the research of PD polymers has attracted wide attention in academic and industry, as the attractive process for producing PD from renewable resources has been developed (Haas *et al.* 2005; Papageorgiou and Bikiaris 2005; Tsanaktis *et al.* 2015b; Pouloupoulou *et al.* 2018). Poly(propylene 2,5-furan dicarboxylate) (PPF) is a thermoplastic polyester, and its synthesis and structural, thermal, and mechanical properties have been

reported in recent years (Gandini *et al.* 2009a; Gomes *et al.* 2011; Jiang *et al.* 2012; Papageorgiou *et al.* 2015a; Vannini *et al.* 2015; Sousa *et al.* 2016b; Terzopoulou *et al.* 2017b; Guidotti *et al.* 2018; Papadopoulos *et al.* 2018; Wang *et al.* 2019).

Gandini *et al.* (2009a) first reported the synthesis of PPF in 2009. They found that the prepared PPF had similar properties to PEF, except for the characteristic resonance related to the additional intermediate CH₂ groups, which can be obtained by FTIR and NMR spectra analysis of PPF. The T_m and T_g values of PPF were 174°C and 65°C, respectively, which were lower than their PEF homologues. This was attributed to the introduction of methylene groups in each polymer unit, resulting in higher macromolecular flexibility. Gomes *et al.* (2011) also synthesized some PPF polyesters with M_n and M_w values of 21600 and 27600. Analysis of the thermal properties revealed that PPF exhibited high crystallization ability, and its T_g as well as T_c appeared only on the second DSC scan trajectory after molten PPF quenching. In addition, Vannini *et al.* (2015) found that the PPF copolyester displayed excellent barrier properties due to their special crystal phase, which can be used as packaging material due to their properties of exceptionally low oxygen transmission rates and good impermeability to water vapors.

Papageorgiou *et al.* (2015a) reported the synthesis of PPF, and they compared their thermal behavior and solid-state structure with its terephthalate (PPT) and naphthalate (PPN) homologues. Through the structural analysis, they found that the final properties of the prepared samples were affected by different structural rings and ultimate chain stiffness. Compared with PPF and PPT, the PPN with higher rigidity showed higher T_g and thermal stability. The equilibrium melting point of PPF was obtained by the Hoffman-Weeks method at 199 °C, and the heat of fusion of pure crystalline PPF polyester was calculated to be 141.8 J/g or 27.8 KJ/mol. In addition, the spherulites of PPFs at different temperatures were observed by polarized light microscopy (PLM), which revealed that PPF polyester formed small spherulites and had a slow growth rate. With the increase of temperature, the growth rate of PPN was faster and the spherulite was larger, and the band appeared in the spherulite grown above 160 °C. Then the PPT exhibited faster growth rates and banded spherulites, and as the crystallization temperature increased, the band spacing increased.

Recently, Wang *et al.* (2019) studied the effects of various PD on the properties of PPF. In this research, the FDCA polyester with different thermal properties was prepared by using FDCA and different substituent PD as the starting material, which had a similar skeleton structure to the PPF (Fig. 6). They found that the T_g and crystallinity of poly(neopentyl glycol furandicarboxylate) (PNF) was increased compared to PPF, whereas the T_g and crystallinity of poly(2-ethyl-2-butyl-1,3-propylene furandicarboxylate) (PEBF) with more -CH₃ substituted groups decreased compared with PNF. In this study, PNF exhibited high crystallinity with a ΔH_m value of 32.1 J/g, which had the highest T_g (70°C) and T_m (201°C). In contrast, PPF had a low ΔH_m value of 0.9 J/g and T_m of 173°C, while poly(2-methyl-1,3-propylene furandicarboxylate) (PMF) was a non-crystalline polyester. In addition, the gas barrier results revealed that PPF polyester had the best gas barrier property, followed by that of PMF and PNF, mainly due to the introduction of side chain -CH₃ substituents resulting in an increase in β relaxation and fractional free volume.

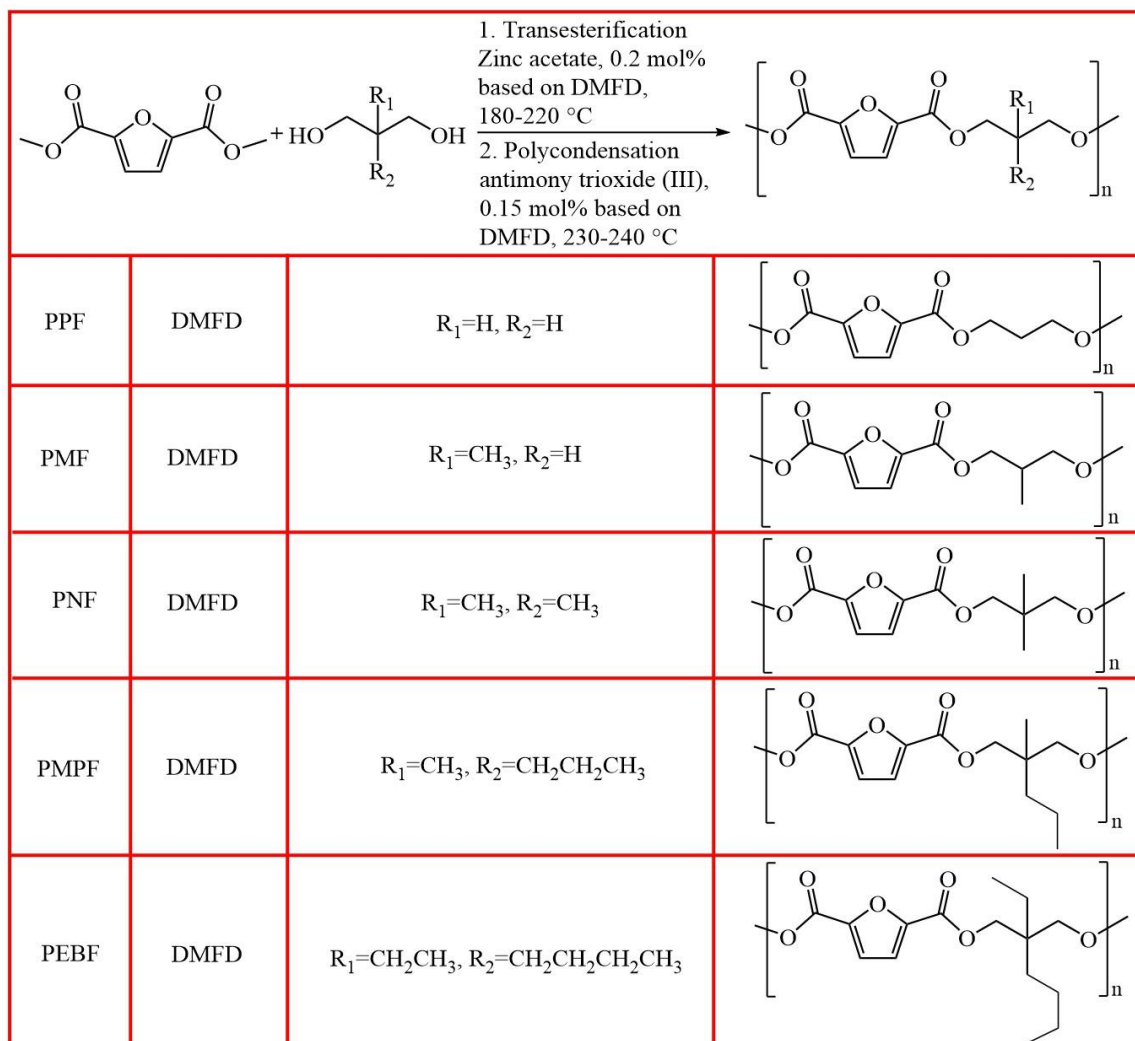


Fig. 6. Illustration for the synthesis of polyesters from FDCA and different diols (Reprinted with permission from Wang *et al.* 2019, American Chemical Society)

In addition, copolyesters based on FDCA and PD were also studied in recent years (Jiang *et al.* 2015; Lomeli-Rodriguez *et al.* 2016; Wang *et al.* 2017b; Jia *et al.* 2019; Righetti *et al.* 2019). For example, Jiang *et al.* (2015) studied the synthesis, structure, and properties of novel copolyesters from TPA, FDCA, and PD *via* direct esterification method by using tetrabutyl titanate (TBT) as catalyst. They found that the obtained copolyester was random copolymers with an average M_w more than 1×10^4 g/mol, which had similar thermal stabilities and higher elongation at break to corresponding homopolyesters. Wang *et al.* (2017b) used 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO) to modify PPF to get the copolyester of PPTF. They found that PPTF had the characteristics of random polyester. On the other hand, the semi-crystalline PPF can be made into a fully crystalline polyester by the addition of 10% CBDO, and it was easily to obtain higher transparency, and the T_g increased from 55.5 °C for PPF to 63.5 °C for PPTF. They also found that the O_2 and CO_2 barrier properties would decrease by the addition of CBDO units, but the modified copolyester still showed good barrier properties.

SYNTHESIS OF POLY(BUTYLENE 2,5-FURANDICARBOXYLATE) (PBF)

In earlier studies, it was found that poly(butylene terephthalate) (PBT) is an important semi-crystalline engineering thermoplastic with the advantages of high rigidity, low humidity, excellent properties, and favorable for processing and production (Tomar and Maiti 2010a; Sharma and Maiti 2013). Moreover, these characteristics were stable in a wide range of temperature and humidity. Compared with PET, PBT had more advantages, mainly depending on its facile crystallinity and easy dyeability, which made it the most commonly used durable product formed by inject molding (Tomar and Maiti 2010b; Sharma and Maiti 2013). However, in the current study, it can be found that the notched Izod impact strength of PBT was very low (Tomar and Maiti 2007, 2008). Therefore, the synthesis of poly(butylene 2,5-furandicarboxylate) (PBF) as PBT counterpart, from FDCA and 1,4-butanediol (BDO) has attracted much attention (Ma *et al.* 2012; Morales-Huerta *et al.* 2016a; Zhu *et al.* 2013).

Ma *et al.* (2012) successfully synthesized furan derivative polyester, PBF, and its crystallization properties was explored. The results of ^1H NMR at 750 MHz showed that chain-end groups were detected in different polymerization stages, which clearly revealed the process of polymerization. By further testing, it is revealed that the polymer had high tendency to form crystalline structured ($T_m=130\text{ }^\circ\text{C}$ and $169\text{ }^\circ\text{C}$; $T_g=32\text{ }^\circ\text{C}$), whose butylene segment is in a folded conformation, which was beneficial to the continuous fiber extraction from the melt of PBF.

Zhu *et al.* (2013) also prepared bio-based polyester PBF with 2,5-furandicarboxylic acid (FDCA) and BDO as raw materials *via* a two-stage polymerization. The obtained PBF had good thermal stability, strength, and ductility. Its melting point was around $172\text{ }^\circ\text{C}$, and a maximum degradation rate occurred at $428\text{ }^\circ\text{C}$. In addition, it was found that the obtained PBF was triclinic ($a=4.78(3)\text{ \AA}$, $b=6.03(5)\text{ \AA}$, $c=12.3(1)\text{ \AA}$, $\alpha=110.1(2)^\circ$, $\beta=121.1(3)^\circ$, $\gamma=100.6(2)^\circ$), which was very similar to the α - and β -forms of PBT.

In addition, Morales-Huerta *et al.* (2016a) prepared cyclic ethylene and butylene 2,5-furandicarboxylate oligoesters and then converted them to furan-based polyesters of PEF and PBF by ring opening polymerization (ROP). High yields of cyclic oligoesters were obtained by both high dilution condensation and thermal cyclodepolymerization methods, and they were found to be crystalline compounds melting within the 140 to $200\text{ }^\circ\text{C}$ range. The obtained PEF and PBF by ROP had weight-average molecular weights between 50000 and 60000 g/mol .

The existing research shows that PBF is a semi-crystalline furanic polyester with T_g near $40\text{ }^\circ\text{C}$, with a high crystallization rate and a similar structure to PBT, which is a good production soft drink bottle or food packaging material. However, one of the main disadvantages of PBF is that the structure of the aliphatic chain of diol leads to its poor thermal performance, which is one of the main disadvantages of the most common aliphatic polyester. In order to extend the application market of polyester materials, the synthesis of a series of copolyesters has attracted the attention of researchers (Zhou *et al.* 2013; Wu *et al.* 2014; Diao *et al.* 2016; Morales-Huerta *et al.* 2016b; Kwiatkowska *et al.* 2017; Hu *et al.* 2018; Matos *et al.* 2018; Morales-Huerta *et al.* 2018; Sousa *et al.* 2018; Hu *et al.* 2019c; Pouloupoulou *et al.* 2019a).

For example, some poly(butylene adipate-co-butylene furandicarboxylate) (PBAFs) copolymers with high molecular weight were synthesized (Zhou *et al.* 2013). They found that all PBAFs presented random structures, and their composition could be adjusted according to the feed molar ratio of the diacid monomers. The crystallization ability and

melting temperature of PBAFs decreased firstly with the increasing of FDCA content, and the trend was reversed when the content of FDCA exceeded 70%. The semicrystalline copolyester with high FDCA content had higher T_g , good tensile modulus, and strength. It was worth noting that the obtained copolyesters with 0 to 50% of FDCA content were biodegradability.

Wu *et al.* (2014) obtained some high molecular weight biobased polyesters of PBF and aliphatic-aromatic copolyesters, including poly(butylene adipate-co-butylene 2,5-furandicarboxylate)s (PBAFs) with adipic acid, BDO and highly purified biobased monomer of 2,5-furandicarboxylic acid (FA) *via* a two-step melt polycondensation reaction. The solubility of PBAF in 5 mg/mL organic solvents was determined, and the results showed that the solubility was related to the composition. In the case where the ϕ_{BF} did not exceed 50%, the PBAFs had high elastic deformation and rebound resilience, and the tensile properties ($E=18$ to 160 MPa, $\sigma_b=9$ to 17 MPa, $\epsilon_b=370$ to 910%) were comparable to those of poly(butylene adipate). When ϕ_{BF} was higher, stress hardening occurred in the tensile test, and PBAFs exhibited a low tensile modulus (42 to 110 MPa), a medium strength (30 to 42 MPa), and a high elongation at break (256%).

Along the same idea, some new PBF-based copolyesters had been synthesized, such as poly(butylene-co-1,4-cyclohexanedimethylene 2,5-furandicarboxylic acid) (PBCFs) and poly(butylene 2,5-furandicarboxylate-co-terephthalate) P(BF-co-BT) (Diao *et al.* 2016; Morales-Huerta *et al.* 2016b). For PECFs, which were synthesized from FDCA, BDO, and CHDM, displayed the characteristics of random polyester with a triad component, and by changing the molar content of BDO and CHDM, the structural properties of PECF will vary, such as the average sequence length and monomer percentage (Fig. 7). It was found that the BDO was easily removed in the process of polycondensation, which was beneficial to the formation of long chain containing CHDM unit. Compared with PBF, the PBCFs modified by CHDM had a significantly change in thermal performance and crystallinity. The DSC results revealed that the T_g , T_m , and decomposition temperature changed from 45.7 to 74.4°C, 140.1 to 251.9 °C, and 380.6 to 388 °C respectively with the molar percent of CHDM unit increased from 20% to 70%. The crystallizability and crystal structure was changed by CHDM incorporation. When the 1,4-cyclohexanedimethylene fragment (CF) unit increased to 31%, the copolyester was non-crystalline due to the difficulty in forming long regular segments, which had no cold crystallization and melting behavior. Nevertheless, the DSC analysis indicated that these copolyesters had multiple melting behavior with increase of CF content, and the shoulder peaks appeared on the main melting point side, mainly due to partial melt recrystallization and final melting (Diao *et al.* 2016). The copolymer P(BF-co-BT), which was prepared from cyclic oligomers of butylene 2,5-furandicarboxylate $c(BF)_n$ and butylene terephthalate $c(BT)_n$ *via* ring opening polymerization (ROP), had an average molecular weight in the range of 55000 and 80000, displaying a good thermal stability (Fig. 8). Although the homopolymer PBF was highly crystalline, the crystallinity of the copolyesters was largely repressed due to the presence of furanoate units. It was found that both T_m and T_g of the copolyesters varied steadily according to the furanoate/terephthalate ratio and the values were comparable to those reported for similar copolyesters prepared by melt polycondensation by other authors (Morales-Huerta *et al.* 2016b).

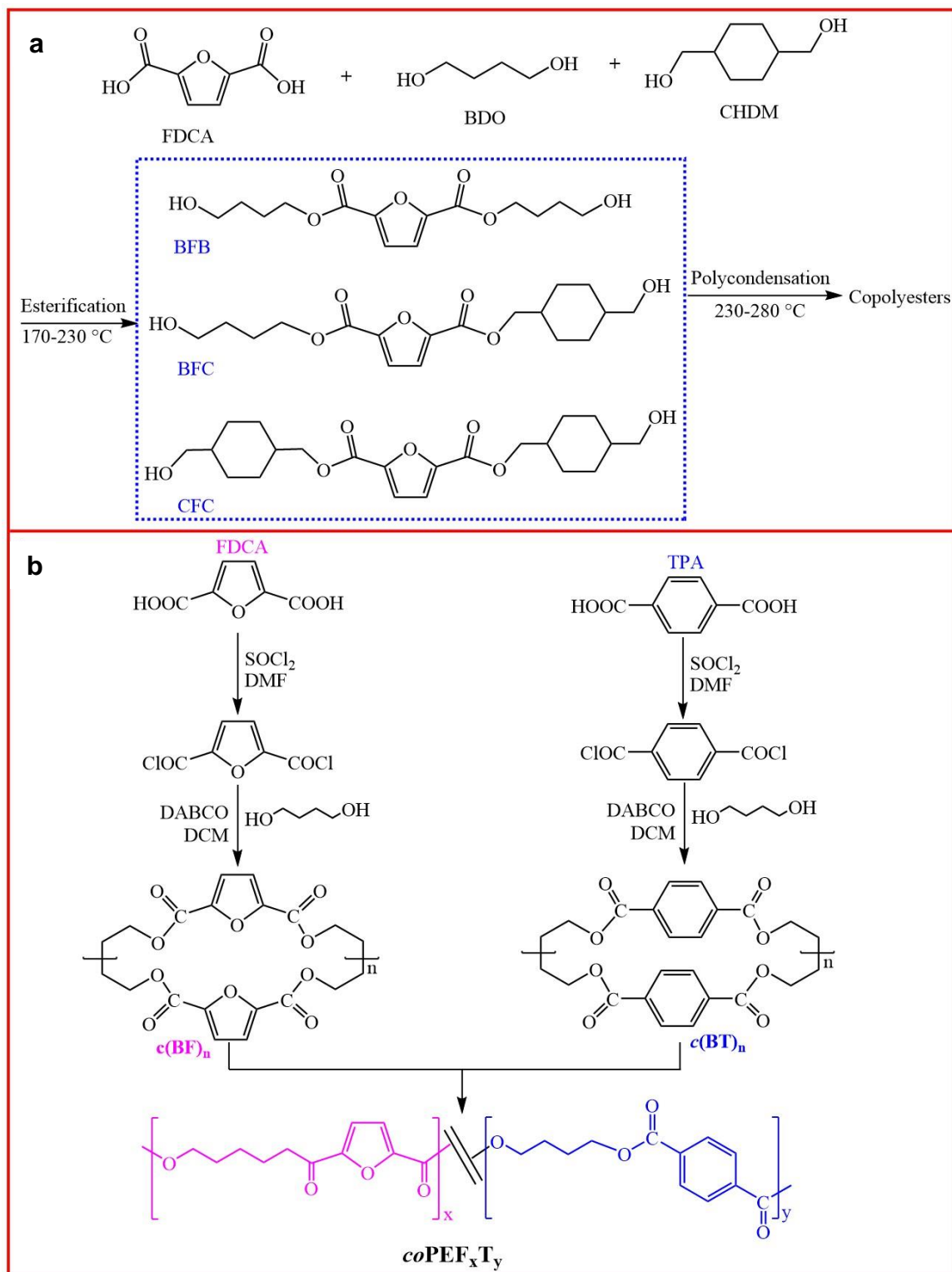


Fig. 7. (a) Polymer synthesis from FDCA, CHDM and BDO; (b) Synthetic route *via* ROP toward aromatic copolyesters containing butylene 2,5-furandicarboxylate and butylene terephthalate units (Reprinted with permission from Diao *et al.* 2016; Morales-Huerta *et al.* 2016b, American Chemical Society)

In a similar vein, Morales-Huerta *et al.* (2018) prepared the cyclic oligo(butylene 2,5-furandicarboxylate) and ϵ -caprolactone copolyester (PCL-PBF) *via* enzymatic ring-

opening polymerization without using organic solvents and metal catalysts, making the polymer greener than conventional polycondensation methods. They found that the PCL-PBF copolyesters with wide and high yield molecular weight were obtained. The copolyesters were semi-crystalline, their monomers were distributed in blocks on the polymer chain, and their T_m and T_g values were between the PCL and PBF polyesters. More importantly, when an appropriate amount of furanoate was added to the chain, the T_g of PCL was significantly increased, which was related to the physical behavior of the polyester. They deemed that the obtained copolyester had the potential use in packaging and biomedicine due to their excellent properties.

Kwiatkowska *et al.* (2017) prepared poly(butylene 2,5-furanoate)-block-(dimerized fatty acid) (PBF-b-FAD) polymers with different properties by polycondensation of FDCA, 1,4-butanediol (1,4-BD), and dimerized fatty acid diol (FAD) under relatively mild and excessive diol conditions. A multi-block structure with ester groups was formed between the PBF blocks by the introduction of FAD and had a randomly distributed crystallizable rigid and non-crystalline flexible segment. It was found that the thermal performance of the PBF-b-FAD polymers was related not only to the molar amount of introduced FAD, but it also was affected by the thermal treatment of material. In addition, the mechanical properties of the macromolecular structure PBF-b-FAD polyesters varied with the molar ratio of PBF to FAD, which had a medium tensile strength and a relatively high deformation and damping at room temperature.

Matos *et al.* (2018), based on the synthesis of polyesters from FDCA, prepared a series of novel nanocomposite materials by introducing bacterial cellulose, such as acetylated bacterial cellulose/poly(butylene 2,5-furandicarboxylate) (Ac-BC/PBF) and acetylated bacterial cellulose/poly(butylene 2,5-furandicarboxylate)-co-(butylene diglycolate)s (Ac-BC/PBF-co-PBDG). The obtained copolyesters had high strength due to the adding of bacterial cellulose fibers. The T_g and T_m of the copolyesters were -25 to 46 °C and 61 to 174 °C, respectively. Furthermore, the nanocomposite copolyesters had better thermal stability (239 to 324 °C), and compared with pure copolyesters, the Young's modulus of nanocomposite copolyesters were as high as 1239 MPa.

In addition, Hu *et al.* (2018) prepared the poly(butylene furandicarboxylate)-b-poly(ethylene glycol), poly(butylene furandicarboxylate-co-glycolate) (PBFGA), and poly(butylene furandicarboxylate)-b-poly(glycolic acid) (PBF-b-GA) copolyesters (Hu *et al.* 2019c), which displayed good thermal, mechanical, barrier and degradable properties.

More recently, the PBF blends were also reported by Sousa *et al.* (2018) and Pouloupoulou *et al.* (2019a), which showed some advantageous processing features as revealed by the lower melting temperature and higher thermal stability as compared with PBF.

SYNTHESIS OF POLY(HEXYLENE 2,5-FURANDICARBOXYLATE) (PHF)

Poly(hexylene 2,5-furandicarboxylate) (PHF) is a furan-type polyester that is synthesized by monomers of renewable resources and has a similar structure to poly(hexamethylene terephthalate) (PHT). PHF was first synthesized as reported by Moore and Kelly (1978), but in recent years, a series of poly(alkylene 2,5-furandicarboxylate)s including PHF have been synthesized and characterized (Jiang *et al.* 2012; Papageorgiou *et al.* 2015b; Terzopoulou *et al.* 2016b; Haernvall *et al.* 2017; Zhang *et al.* 2019b).

For example, Jiang *et al.* (2012) reported the synthesis and characterization of some poly(alkylene 2,5-furandicarboxylate)s including PHF. The obtained PHF with a M_w of 66700 had a tensile modulus, tensile strength, and elongation at break of 493 MPa, 35.5 MPa, and 210%, respectively. The DSC results showed that the T_g and T_m were 28.1 and 148.2 °C, respectively. Papageorgiou *et al.* (2015b) studied the crystallization and thermal degradation behavior of PHF in 2015. They found that the T_m and T_g of the obtained PHF were 145 °C and 7 °C, respectively. Though the DSC analysis, it was revealed that PHF exhibited multiple melting behavior after the crystallization process, which was mainly due to partial melting, recrystallization, and final melting. It was found that the heat of fusion of pure crystalline PHF polyester was 34 kJ/mol, and further calculation gave an equilibrium melting temperature of 157 °C.

More recently, PHF was synthesized from FDCA and 1,6-hexanediol (HDO) *via* direct esterification (Fig. 8) (Zhang *et al.* 2019b). The obtained PHF had typical (110) plane, (010) plane, and (111) plane at $2\theta = 13.78^\circ$ ($d=6.42$ Å), 17.06° ($d=5.19$ Å), and 24.9° ($d=3.58$ Å) with intrinsic viscosity of 0.803 dL/g, average Young's modulus of 479 MPa, and maximum tensile strength of 36.5 MPa. Its elongation at break was 216%, which was significantly higher than that of PET (90%) and PEF (3%). It was found that the high intrinsic viscosity caused the increase in the enthalpy of fusion with respect to as-synthesized PEF, in this case, the melting peak was particularly sharp, and the T_g and T_m was about 48 and 144 °C, which were relatively lower when compared to those of PEF.

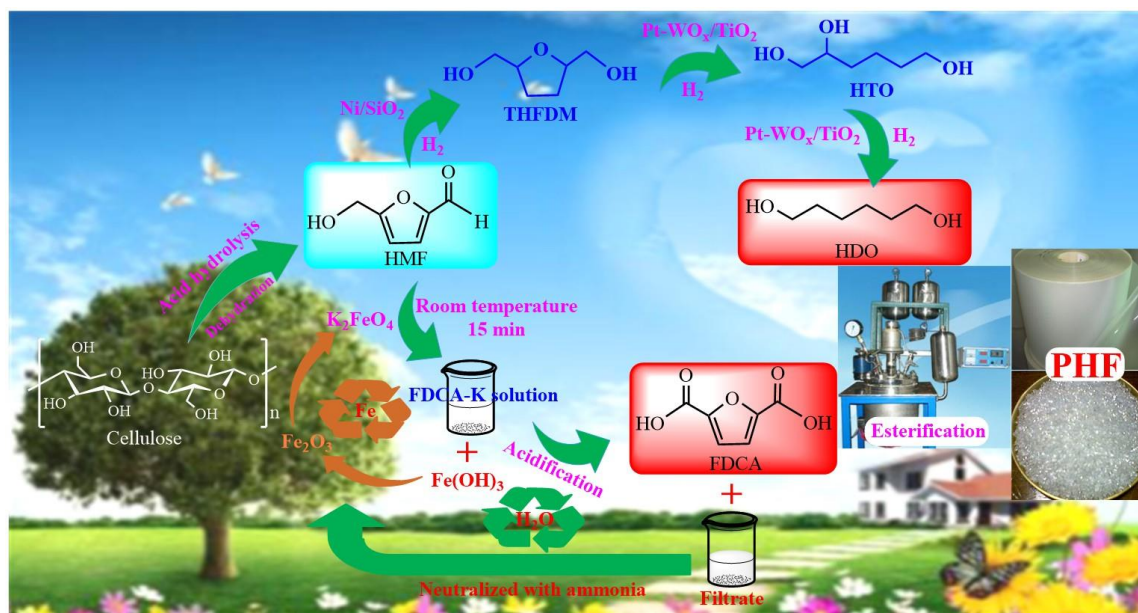


Fig. 8. Typical route for the synthesis of PHF from cellulose (Image from Zhang *et al.* 2019b)

Although the PHFs have been found to exhibit excellent mechanical properties, their applications have been limited due to the flammability. Recently, the synthesis of PHF-based copolyesters also attracted the attention of researchers (Wang *et al.* 2018a, b; Zhang *et al.* 2019b). Wang *et al.* (2018b) reported the use of renewable FDCA, HDO, and 2-carboxyethyl (phenyl)phosphinic acid (CEPPA) to synthesize phosphorus-containing poly(hexamethylene 2,5-furandicarboxylate)s (PHFCs) with different properties. They found that a series of synthetic PHFC showed good thermal performance, and the T_g decreased slightly as the molar content of CEPPA increased. In addition, they also

synthesized the poly(hexamethylene 2,5-furandicarboxylate)-b-poly(ethylene glycol) (PHFEGs) from FDCA, HDO and PEG via a two-step melt polycondensation method. Their results showed that the content of PEG in the prepared PHFEGs polyester was on different from that of the initial addition, and all of the PHFEGs were a dimorphic block copolymers and exhibited the excellent thermal stability with excellent shape-memory ability (Wang *et al.* 2018a). Poly(ethylene-co-hexamethylene 2,5-furandicarboxylate) (PEHF) copolyesters with high intrinsic viscosity were synthesized by two-melt polycondensation using FDCA, EG and HDO as raw materials. They found that when a large amount of hexamethylene 2,5-furandicarboxylate (HF) ($\phi_{HF} \geq 88$ mol%) was introduced, the prepared copolyesters were semi-crystalline, while for the remaining conditions they were amorphous polyesters. The synthesized copolyesters exhibited better thermal properties and had a single T_g which decreased as the amount of HF introduced increased. In addition, as the molar content of HF increased, the tensile modulus and tensile strength of the non-crystalline copolyester decreased, but the elongation at break and impact strength increased. The tensile properties of PEHF copolyesters were similar to those of bottle grade PET (Xie *et al.* 2018).

THE DECOMPOSITION OF FDCA-BASED POLYESTERS

It was known that the start of decomposing of FDCA-based polyesters will happen through the breaking of the polymer chain in the six-member transition stage due to the presence of a β -hydrogen atom, and most of the hetero-cleavage was continued instead of homogenization (Levchik and Weil 2004; Chebbi *et al.* 2019; Lu *et al.* 2019; Terzopoulou *et al.* 2019). Different cleavage methods will form different degradation products, such as -COOH and -CH₂=CH₂ products (Hetero-cleavage) or aldehydes, terminal alkyl, or methoxy terminal molecules (random chain scission).

The decomposition mechanism of FDCA-based polyesters was first studied by applying Py-GC/MS technology (Tsanaktsis *et al.* 2015b; Terzopoulou *et al.* 2016a,b; Terzopoulou *et al.* 2017a; Kasmi *et al.* 2018, 2019). In this research, the thermal degradation mechanism of FDCA-based polyester such as PEF, PPF, and PBF at 340, 390, and 500 °C was investigated, and mass spectrometry was carried out after gas separation in the GC capillary column. It was found that more complex pattern was present at high temperatures of 500 °C, whereas in the case of 340 and 390 °C, the chromatographic peak was less and chromatogram map was simpler. Some volatile substances (CO, CH₃CHO, *etc.*) obtained by decomposition of -COOH and -CH₂=CH₂ products were detected at low retention times. (Tsanaktsis *et al.* 2015b) The results of the Py-GC/MS analysis of PHF, PNF, and some other FDCA-based polyesters showed that the main thermal degradation products were similar to the PEF, PPF, and PBF (Terzopoulou *et al.* 2016a).

CONCLUSIONS AND OUTLOOK

On account of the excessive consumption of fossil resources and environmental issues, renewable biomass materials and sustainable economy have received wide attention in industry and academia. FDCA-based polyesters provide a viable solution to the environmental and economic issues arising from over-reliance on petroleum-based products. As described above, the synthesis of FDCA-based polyesters has made a major breakthrough, and a large number of preparation strategies are being implemented and

improved. Of course, not all these FDCA-based copolyesters will reach industrial application, and their substitution for petroleum-based polymers remains challenging. This arduous task involves obtaining large quantities of biomass raw materials, producing high-performance FDCA-based polyesters, and their cost-effective performance. Academia and industry have devoted a lot of time and effort to the production of FDCA-based polymers and PEF, and there continues to be progress in the right direction. Based on the new trends of rational utilization of renewable biomass resources and the encouraging results, it is exciting to develop valuable products from biomass materials. On the other hand, the global organizations should provide additional funding and incentives to both industry and academia in the field of fully biobased polymers, though large-scale production of fully biobased polymers is still difficult and has a long way to go.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

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