

# Modification of Poly(ethylene 2,5-furandicarboxylate) with Biobased 1,5-Pentanediol: Significantly Toughened Copolyesters Retaining High Tensile Strength and O<sub>2</sub> Barrier Property

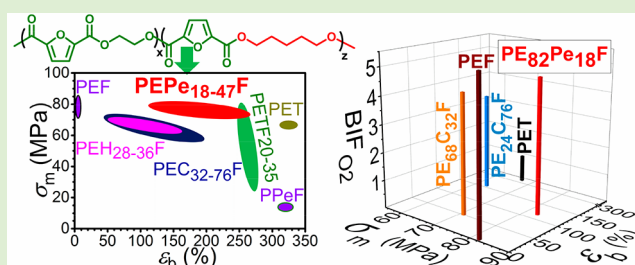
Hongzhou Xie,<sup>†</sup> Linbo Wu,<sup>\*,†</sup> Bo-Geng Li,<sup>†</sup> and Philippe Dubois<sup>\*,‡</sup>

<sup>†</sup>State Key Laboratory of Chemical Engineering at ZJU, Key Laboratory of Biomass Chemical Engineering of Ministry of Education, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

<sup>‡</sup>Laboratory of Polymeric and Composite Materials (LPCM), Center of Innovation and Research in Materials and Polymers (CIRMAP), University of Mons, Mons 7000, Belgium

## Supporting Information

**ABSTRACT:** Poly(ethylene 2,5-furandicarboxylate) (PEF) is a biobased polyester characterized by high gas barrier properties as well as high tensile modulus and strength, but poor toughness. Toughening PEF without sacrificing its modulus, strength and gas barrier performance is a great challenge for PEF modification. In this study, high molecular weight random poly(ethylene-*co*-1,5-pentylene 2,5-furandicarboxylate)s (PEPeFs) were synthesized via melt copolycondensation of 2,5-furandicarboxylic acid (FDCA), ethylene glycol (EG) and 1,5-pentanediol (PeDO), a cheap, biobased and commercially available odd-carbon comonomer. The synthesized PEPeFs were characterized and assessed with intrinsic viscosity, ATR-FTIR, <sup>1</sup>H NMR, DSC, TGA and tensile, impact and O<sub>2</sub> permeation test. Mayo–Lewis equation with “reactivity ratio” of 3.78 for PeDO and 0.75 for EG could be used as an empirical equation to correlate the copolyester composition ( $\phi_{\text{PeF}}$ ) with monomer composition. PEPeFs proved nearly amorphous copolyesters having excellent thermal stability. Brittle–ductile transition was achieved at  $\phi_{\text{PeF}}$  as low as 9 mol %. Increasing  $\phi_{\text{PeF}}$  led to increase in elongation at break and notch impact strength and decrease in  $T_g$ , O<sub>2</sub> barrier performance and tensile modulus and strength. However, in comparison with PEF, PEF-rich PEPeFs ( $\phi_{\text{PeF}}$  9–47%) not only showed greatly improved elongation at break (29–265% vs 4%) and enhanced impact strength (2.2–3.9 kJ/m<sup>2</sup>) but also retained very high Young’s modulus (2.8–3.3 vs 3.3 GPa) and yielding strength (72–83 vs 82 MPa). Particularly, when compared with bottle-grade PET, PE<sub>82</sub>Pe<sub>18</sub>F possesses equal  $T_g$  (ca. 75 °C) and comparable elongation at break (ca. 115%), but greatly improved yielding strength (83 MPa) and O<sub>2</sub> gas barrier property (4.8 times). As modified PEF materials possessing superior thermo-mechanical and O<sub>2</sub> gas barrier properties, these integrally biobased copolyesters may find practical applications in eco-packaging and other fields.



## 1. INTRODUCTION

Poly(ethylene 2,5-furandicarboxylate) (PEF) is a biobased polyester derived from 2,5-furandicarboxylic acid (FDCA) and ethylene glycol (EG). Both FDCA and EG can be synthesized from biomass like starch, cellulose or hemicellulose as starting materials.<sup>1–4</sup> Biobased EG has been industrialized and used in production of bio-PET bottles, and biobased FDCA is also on the way of industrialization. FDCA is the sole aromatic monomer among the 12 top value-added chemicals from biomass launched by the U.S. Department of Energy.<sup>5,6</sup> FDCA has more rigid structure than its petroleum-based counterpart, terephthalate acid (TPA). As a result, FDCA-derived polyesters including PEF and poly(propylene 2,5-furandicarboxylate) (PPF) often possess higher glass transition temperature ( $T_g$ ) than their petroleum-based counterparts, respectively.<sup>7,8</sup> Furthermore, PEF has superior stiffness and strength<sup>9</sup> and notably higher gas barrier properties<sup>10–13</sup> than PET. Its O<sub>2</sub> and CO<sub>2</sub> permeability decreases by 5–11 and 2–19 times with

respect to PET, respectively. Moreover, 45–55% lower greenhouse gas emission and about 40–50% lower non-renewable energy use were predicted for PEF production as compared with PET.<sup>14</sup> Because of excellent sustainability and superior thermo-mechanical and gas barrier performance, PEF is deemed to become another important commodity competing with PET in the future, especially for eco-packaging applications with high gas barrier demand.

PEF has not been industrialized yet though its R&D has attracted extensive interest from both academia and industry. The main challenges include synthesizing FDCA through a highly efficient and cost-effective way and producing high molecular weight (MW) PEF without undesired discoloration. In recent years, great progress has been made in understanding

Received: October 11, 2018

Revised: November 14, 2018

Published: November 15, 2018

PEF discoloration<sup>15,16</sup> and in synthesizing high intrinsic viscosity (1.02 dL/g) PEF via solid state polycondensation (SSP)<sup>17</sup> or bottle-grade PEF through ring-opening polymerization from cyclic PEF oligomers.<sup>18</sup>

On the other hand, there are still some drawbacks of PEF such as brittleness,<sup>9,10,19,20</sup> which must be conquered before its successful industrial application. Very limited elongation at break (1–5%)<sup>10,19–24</sup> and impact strength (3.1 kg·cm/cm of PEF)<sup>19</sup> have been reported in some literature. PEF can be modified by blending,<sup>25,26</sup> copolymerization<sup>10,19,21,22,27–30</sup> and even by biaxial orientation.<sup>31</sup> Very recently, van Berkel et al. reported that PEF showed high elongation at break (35–115%) after biaxial orientation.<sup>31</sup> Pouloupoulou et al. reported the miscibility of the blends of PEF with PET, poly(propylene furandicarboxylate) (PPF) and poly(butylene furandicarboxylate) (PBF), but not the mechanical properties.<sup>26</sup> In the Chen et al. report, highly improved impact strength (15.5 kJ/m<sup>2</sup>) was achieved by blending PEF with 15 wt % PBS, but the elongation at break was still limited (6.6%).<sup>25</sup>

Block<sup>22,27</sup> and random copolymerizations<sup>10,19,21,28–30</sup> are also effective methods for polymer toughening. It was reported that multiblock copolymers poly(ethylene 2,5-furandicarboxylate)-*b*-poly(ethylene glycol) (P(EF-*mb*-PEG)) exhibited improved ductility (elongation at break of 35%) only at high PEG content (60 wt %), at the expense of sharp drop of tensile strength to 15 MPa.<sup>22</sup> In our previous study, we synthesized poly(ethylene 2,5-furandicarboxylate-*mb*-poly(tetramethylene glycol)) (P(EF-*mb*-PTMG)) multiblock copolymers which showed super toughness.<sup>27</sup> The brittle–ductile and brittle–tough transitions occurred at poly(tetramethylene glycol) (PTMG) content of <20 wt % and 30–35 wt %, respectively. At 20 wt % PTMG, the copolymer displayed an elongation at break of 252% while retaining a yielding strength of 74 MPa. At 30–35 wt % PTMG, the impact strength reached 6.4–52.6 kJ/m<sup>2</sup>. Poly(ethylene sebacate-*co*-furandicarboxylate)s (PE-SeFs)<sup>21</sup> showed tensile properties similar to P(EG-*mb*-PEG)s. Synthesis and degradation of poly(ethylene succinate-*co*-furandicarboxylate)s (PESF)s were also reported,<sup>32</sup> but their mechanical properties were not studied. In contrast, poly(ethylene-*co*-2,2,4,4-tetramethyl-1,3-cyclobutylene 2,5-furandicarboxylate) (PETF), a PEF copolyester with a very rigid diol, exhibited higher tensile modulus and strength than PEF, but the ductility was not improved.<sup>23</sup> Interestingly, poly(ethylene-*co*-1,4-cyclohexanedimethylene 2,5-furandicarboxylate)s (PECFs) containing 32–76 mol % CF unit showed improved elongation at break (50–186%) and retained quite good tensile strength (71–59 MPa), modulus (2.2–1.7 GPa) and gas barrier properties.<sup>10</sup> The rigid nonplanar ring structure of the alicyclic diol comonomer 1,4-cyclohexanedimethanol (CHDM) contributes to the high performance. Furthermore, the tensile strength and modulus of PECF can be further enhanced by increasing the trans-isomer content of CHDM.<sup>29</sup> However, the performance improvement was achieved at the expense of having to use a large amount of CHDM, which is an expensive and nonrenewable comonomer, and PECF still showed low impact strength (3.6 kg·cm/cm vs 3.1 kg·cm/cm of PEF) even at 50 mol % CF content.<sup>19</sup> Therefore, exploring PEF-based materials possessing highly improved tensile and/or impact toughness and retaining high tensile strength, rigidity and gas barrier properties at the same time, especially using cheap and biobased comonomers remains a challenge.

In general, the strength and modulus of poly(alkylene 2,5-furandicarboxylate)s (PAFs) decreases but the ductility or tensile toughness increases with the alkylene chain length. In fact, although PEF has poor ductility, much higher elongation at break has been reported for PPF (46%),<sup>24</sup> PBF (256%),<sup>33</sup> poly(hexylene 2,5-furandicarboxylate) (PHF) (210%)<sup>24</sup> and some other PAFs with longer alkylene length.<sup>34</sup> Therefore, modifying PEF by copolymerizing an aliphatic diol with suitable alkylene length may lead to an acceptable property profile, balancing strength and ductility/toughness. However, PEF-based copolyesters with linear aliphatic diols have not been evaluated thoroughly by researchers. Poly(ethylene-*co*-butylene 2,5-furandicarboxylate) (PEBF) is the first example. Ma et al. reported its synthesis, structure and thermal properties, but not the mechanical properties.<sup>35</sup> As PHF possesses reasonably good tensile strength (35.5 MPa) as well as high ductility,<sup>28</sup> and 1,6-hexanediol (HDO) is a potentially biobased monomer, we synthesized poly(ethylene-*co*-hexylene 2,5-furandicarboxylate) (PEHF) copolyesters in a previous study and found that PE<sub>72</sub>H<sub>28</sub>F showed elongation at break of 54% and retained very high tensile modulus (2.6 GPa) and yield strength (71 MPa).

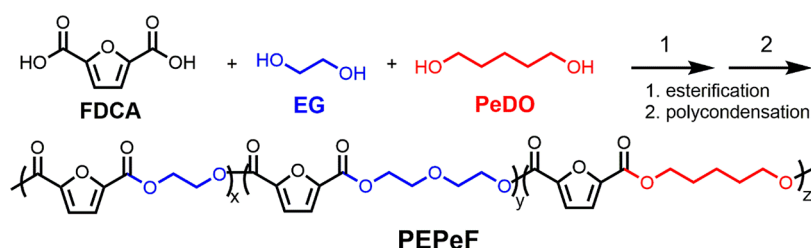
1,5-Pentanediol (PeDO) is also a biobased aliphatic diol. With the R&D in the conversion of furfural into PeDO,<sup>36</sup> its large scale industrial production may be realized in the near future. As an odd carbon diol, it may bring some unique features in PeDO-based (co)polyesters. Synthesis and thermal properties of poly(1,5-pentylene 2,5-furandicarboxylate) (PPEF) have been reported by Tsanaktsis et al.,<sup>37</sup> but no information about the mechanical properties was available. In our previous studies, we found that poly(1,5-pentylene terephthalate) (PPEt)<sup>38</sup> and aliphatic polyesters from PeDO and C<sub>9–12</sub> diacids<sup>39</sup> are all ductile plastics with high elongation at break (450–810%). In fact, these aliphatic polyesters possess thermo-mechanical properties analogous to low density polyethylene. From these results, we have anticipated that PeDO may be a better comonomer than HDO to modify PEF in terms of achieving superior and more balanced properties.

As one of a series of studies on PEF modification by copolymerization,<sup>27,28</sup> poly(ethylene-*co*-pentylene 2,5-furandicarboxylate) (PEPeF) copolyesters spanning a full composition range were synthesized in this study from FDCA, EG and PeDO through melt copolycondensation and characterized with ATR-FTIR, <sup>1</sup>H NMR, DSC and TGA. The thermo-mechanical and O<sub>2</sub> gas barrier properties were assessed and their composition dependences were examined. To the best of our knowledge, this is the first report on the synthesis and structure–property of PEPeF copolyesters. It is encouraging to find that in comparison with PEHF, higher ductility and impact toughness were achieved at lower comonomer content (18 mol %) in PEPeFs, and at the same time, the copolyesters retained higher tensile strength, modulus and O<sub>2</sub> barrier property.

## 2. EXPERIMENTAL SECTION

**2.1. Materials.** 2,5-Furandicarboxylic acid (FDCA) with purity over 99% was purchased from Jiaxing Ruiyuan Biotech Co., Ltd. (China). Ethylene glycol (EG, 99%) was purchased from Sigma-Aldrich. 1,5-Pentanediol (PeDO, 99.5%) was kindly supplied by Yantai Wanhua Co., Ltd. (China). According to the supplier, it was produced via hydrogenation of furfural and then hydrogenolysis of the intermediate, tetrahydrofurfuryl alcohol. Home-made titanium–silica

### Scheme 1. Synthesis of PEPeF Copolyesters from FDCA, EG and PeDO through a Two-Stage Esterification and Polycondensation Process



**Table 1. Synthetic Conditions<sup>a</sup> and Molecular Characterization of PEF, PPeF and PEPeF Copolyesters**

Run	$\phi_{\text{PeDO}}^b$ (mol %)	$C_{\text{es}}^c$ (%)	$t_{\text{mp}}^d$ (h)	$[\eta]^e$ (dL/g)	<sup>1</sup> H NMR				
					$\phi_{\text{PeF}}^f$ (mol %)	$\phi'_{\text{PeF}}^g$ (mol %)	$\phi_{\text{DEGF}}^h$ (mol %)	$\phi'_{\text{DEGF}}^i$ (mol %)	$\phi_{\text{bio}}^j$ (%)
1	0	97	3	0.82	0	0	5.2	5.2	75.0
2	5	97	3	0.78	9.4/10.5	8.9	5.1	5.7	78.2
3	10	97	3	0.84	17.7/17.4	17.1	3.3	4.1	80.9
4	20	98	3	0.83	34.2/33.5	33.4	2.2	3.4	85.2
5	30	98	3	0.92	46.6/44.9	45.8	2.1	4.0	87.4
6	40	98	2	0.93	62.7/61.5	61.7	1.6	4.4	92.5
7	60	99	2	1.01	84.3/82.7	83.7	0.8	5.1	97.0
8	80	99	2	1.03	95.8/94.5	95.3	0.6	14	99.5
9	100	99	2	0.89	100	100	0	0	100

<sup>a</sup>(1) Esterification: Ti@Si, 0.1 wt % based on FDCA was used as catalyst; (EG+PeDO)/FDCA molar ratio was 2; 190 °C for 1 h, and then 200 °C for 3 h. (2) Polycondensation: no additional catalyst was added; 230 °C for 1 h and then at 240 °C for  $t_{\text{mp}}$ . <sup>b</sup>Molar percent of PeDO in two diols (EG+PeDO) feed. <sup>c</sup>Esterification rate, equal to percentage of conversion of carboxyl group. <sup>d</sup>The polycondensation time needed for clear Weissenberg effect emerged at 240 °C and stirring rate less than 50 rpm. <sup>e</sup>Intrinsic viscosity measured at 25 °C using the phenol/1,1,2,2-tetrachloroethane (3/2, w/w) mixed solvent. <sup>f</sup>Molar percent of PeF unit in the PEPeF copolyester, the value “a/b” stand for that a and b were calculated by eqs 3 and 4, respectively. <sup>g</sup>Molar percent of PeF unit in the PEPeF copolyester calibrated with eq 6. <sup>h</sup>Molar percent of DEGF unit in the PEPeF copolyester calculated with eq 2. <sup>i</sup>Selectivity of etherification reaction, equal to the molar percent of DEGF unit in the sum of EF unit and DEGF unit calculated with eq 5. <sup>j</sup>Percent of biobased carbon content in the (co)polyester.

complex (Ti@Si, Ti 1 wt % or 0.21 mmol Ti/g) was used as the catalyst for polyester synthesis. Phenol, 1,1,2,2-tetrachloroethane (TCE) and deuterated trifluoroacetic acid ( $d_1$ -TFA) were all purchased from Sinopharm. A bottle-grade commercial poly(ethylene terephthalate) (PET) resin with intrinsic viscosity  $[\eta]$  of 0.82 dL/g was produced and kindly supplied by Sinopec Yizheng Chemical Fiber Co., Ltd. (China). A commercial PET release film (ca. 50  $\mu\text{m}$ ) was purchased from Shenzhen Ruibiao Packing Materials Co., Ltd. (China) and used as a reference for oxygen permeation test. All the chemicals were used as received.

**2.2. Synthesis of PEPeFs.** As shown in Scheme 1, a two-stage process, esterification and polycondensation, was used to prepare poly(ethylene-co-pentylene furandicarboxylate)s (PEPeFs) from FDCA, EG and PeDO. The molar ratio of diol (EG+PeDO) vs diacid (FDCA) was 2.0. In the first stage, FDCA, EG, PeDO and Ti@Si (0.1 wt % based on FDCA) were charged into a 250 mL four-necked round-bottom reactor equipped with a mechanical stirrer, N<sub>2</sub> inlet and reflux condenser. The molar percentages of PeDO in the diol feed are listed in Table 1. Esterification reaction was conducted at 190–200 °C for 4 h under N<sub>2</sub> atmosphere. The reaction was stopped when the theoretical amount of byproduct, water, was distilled out. Then, the reaction temperature was raised to 230–240 °C and the pressure was reduced to about 100 Pa to carry out melt polycondensation reaction. The reaction lasted for 3–4 h until clear Weissenberg effect emerged at a stirring rate of 50 rpm. Finally, the products were dried at 60 °C in vacuum for characterization. The same procedure was also used to synthesize PEF and poly(1,5-pentylene 2,5-furandicarboxylate) (PPeF).

**2.3. Characterization.** Intrinsic viscosity  $[\eta]$  of the (co)polyesters was measured at 25 °C with an automatic viscosity tester (ZONWON IVS300, China) equipped with an Ubbelohde viscometer. The concentration of the polyesters in a mixed solvent, phenol/1,1,2,2-tetrachloroethane (3/2, w/w), was 5 g/dL.

ATR-FTIR spectra of the (co)polyesters was recorded with a Nicolet 5700 spectrophotometer (Thermo Fisher Scientific, USA) equipped with a germanium crystal ATR accessory in the wavenumber range of 400–4000  $\text{cm}^{-1}$ . Film samples were prepared by hot-pressing molding at 250 °C.

<sup>1</sup>H NMR spectra of the (co)polyesters was recorded on Bruker AC-80 (400 M). Deuterated trifluoroacetic acid ( $d_1$ -TFA) was used as solvent and tetramethylsilane as internal reference.

Thermal transition properties of the (co)polyesters were measured with DSC on a TA-Q200 thermal analyzer (TA Instrument, USA) using the traditional heating–cooling–heating temperature program at a heating/cooling rate of 10 °C/min, and the isothermal time was 5 min.

Thermal stability of the (co)polyesters was assessed with thermogravimetric analysis (TGA) on a TA Q500 analyzer (TA Instrument, USA). All the samples were measured under a nitrogen atmosphere with a heating rate of 10 °C/min from 50 to 600 °C.

Tensile properties of the (co)polyesters were measured with a Zwick Roell Z020 (Zwick, Germany) testing machine at room temperature according to ASTM D638. Dumbbell-shaped specimens with 2 mm in thickness and 4 mm in width were prepared by a HAAKE MiniJet injection molding machine and then conditioned at room temperature for at least 48 h before testing. For each sample, at least five specimens were tested. All the specimens were tested at a crosshead speed of 10 mm/min.

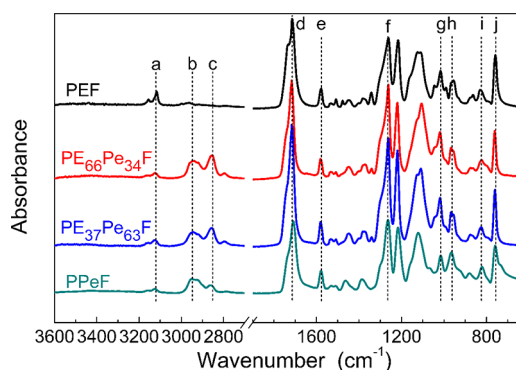
Notched Izod impact testing was done using a CEAST Resil impact tester (CEAST, Italy) with a pendulum of 5.5 J according to ASTM D256. The samples with 80 mm in length, 10 mm in width and 4 mm in thickness were prepared by a HAAKE MiniJet injection molding machine. All samples were notched and conditioned at room temperature for at least 48 h before testing. Five specimens were tested for each sample.

Oxygen permeability of the (co)polyesters was measured at 23 °C and 50% of relative humidity by using Labthink i-Gastra 7100 gas permeability tester based on pressure-difference method using high purity oxygen at 1 atm. Film samples were prepared with a laboratory compression molding machine (Gottech GT-7014-AS0C, Taiwan, China). First, small pieces of samples were sandwiched between two Teflon sheets and melt at 250 °C for 10 min without any pressure. Then, a pressure of about 150 bar was applied for 5 min before immediately quenching to room temperature by cold water. The film thickness was controlled by the stainless steel sheet (200 μm thick) with a 10 cm × 10 cm hole cut for placing sample. All the prepared film samples were measured as ~200 μm by coating thickness gauge (Ruige, Shanghai, RG260). Three films were tested for each sample.

### 3. RESULTS AND DISCUSSION

**3.1. Synthesis and Structure Characterization.** PEF, PPeF and PEPeF copolyesters in full composition range were synthesized via a two-step esterification and polycondensation process, as shown in Scheme 1. The synthetic conditions and results of the (co)polyesters are summarized in Table 1. The intrinsic viscosity ( $[\eta]$ ) of the (co)polyesters ranges 0.78–1.03 dL/g under roughly the same reaction conditions, suggesting high molecular weight (co)polyesters have been successfully synthesized. The  $[\eta]$  of PEPeF copolyesters increases with the PeDO feeding ratio up to 80 mol %, indicating the presence of PeDO contributes to the intrinsic viscosity growth of the copolyesters. The homopolymer PPeF synthesized in this work has a high  $[\eta]$  of 0.89 dL/g, which is much higher than that of PPeF (0.53 dL/g) previously reported.<sup>37</sup> All these results validate the high reactivity of the Ti@Si catalyst. It was also used in synthesizing high intrinsic viscosity P(EF-mb-PTMG)<sup>27</sup> and PEHF<sup>28</sup> copolyesters in our previous work.

The chemical structure of the synthesized (co)polyesters was validated by ATR-FTIR and <sup>1</sup>H NMR spectroscopy. Figure 1 shows the FTIR spectra of PEF, PPeF, PE<sub>66</sub>Pe<sub>34</sub>F and



**Figure 1.** ATR-FTIR spectra of the PEF, PPeF and PEPeF copolyesters.

PE<sub>37</sub>Pe<sub>63</sub>F copolyesters. The characteristic adsorption peaks of furan ring are observed for all the four samples, including the stretching vibrations of C—H at 3123 cm<sup>-1</sup> (a) and C=C at 1580 cm<sup>-1</sup> (e), the furan ring breathing vibration at 1022 cm<sup>-1</sup> (g) and ring bending vibration at 969 cm<sup>-1</sup> (h), 826 cm<sup>-1</sup> (i) and 761 cm<sup>-1</sup> (j). With increasing PeF unit content, the peak intensity of the asymmetric (2939–2951 cm<sup>-1</sup>, (b) and symmetric vibration (2855–2861 cm<sup>-1</sup>, (c) of C—H bonds in CH<sub>2</sub> group increases, and the stretching vibrations of C=O (1714–1705 cm<sup>-1</sup>, (d) and C—O (1261–1259 cm<sup>-1</sup>, (f) in ester bond show slight red shift. In addition, there is no peak of terminal hydroxyl around 3400 cm<sup>-1</sup>. Therefore, the FTIR

results indicate that PeF units have been incorporated into the copolyester chain and high molecular weight copolyesters have been synthesized successfully.

Figure 2 shows the <sup>1</sup>H NMR spectra of PEF, PPeF and PEPeF copolyesters. For PEF, the chemical shifts at 7.44 and 4.86 ppm are attributed to CH (F<sub>1</sub>) in furan ring and CH<sub>2</sub> (a) in EG unit, respectively. Because of etherification side reaction of EG and/or hydroxyethyl ester group, a small quantity of diethylene glycol furandicarboxylate (DEGF) repeat unit was formed as a third repeat unit, as evidenced by the chemical shifts of the outer CH<sub>2</sub> (b) and inner CH<sub>2</sub> (c) in DEGF unit at 4.75 and 4.24 ppm, respectively. For PPeF, the chemical shift of CH in furan ring (F<sub>2</sub>) shifts to 7.40 ppm because of the different chemical environment in PeF unit as compared in EF or DEGF unit. The chemical shifts of outer CH<sub>2</sub> (d), middle CH<sub>2</sub> (e) and inner CH<sub>2</sub> (f) in PeDO unit appear at 4.55, 1.96 and 1.68 ppm, respectively. For PEPeFs, all the proton signals from PEF and PPeF homopolymers are retained; the signal of CH in furan ring splits into two peaks at 7.44 and 7.40 ppm, corresponding to EF and PeF units, respectively. The intensity of the peaks of EF (F<sub>1</sub>, a) and DEGF unit (b, c) decreases while those of PeF (F<sub>2</sub>, d, e, f) increases with increasing PeDO feeding. The results indicate that PEPeF copolyesters composed of three repeat units, namely, EF, DEGF and PeF, have been successfully synthesized.

From the <sup>1</sup>H NMR spectra, the molar percentages of the three repeat units,  $\phi_{EF}$ ,  $\phi_{DEGF}$  and  $\phi_{PeF}$ , are calculated using eqs 1–3, respectively, where  $I_a$ ,  $I_c$  and  $I_e$  are the abbreviations of the integral intensities of chemical shift a, c and e, respectively. The value of  $\phi_{PeF}$  can also be calculated with eq 4. The two series of  $\phi_{PeF}$  results agree well with each other, evidencing the correctness of the chemical shift attribution. The results are listed in Table 1. The  $\phi_{PeF}$  value calculated from eq 3 is used to express the copolyester composition. Therefore, PEPeF copolyester containing  $x = \phi_{PeF}$  mol % of PeF unit is symbolized as PE<sub>100-x</sub>Pe<sub>x</sub>F. From the composition results, the biobased carbon content of these copolyesters is calculated based on the fact that FDCA and PeDO are biobased monomers while EG is petro-based in this study. As shown in Table 1, the biobased carbon content increased from 75% of PEF to 100% of PPeF, indicating that PEPeFs are highly biobased copolyesters. As biobased EG has been industrially produced in large scale, fully biobased PEPeFs are available if biobased EG is used.

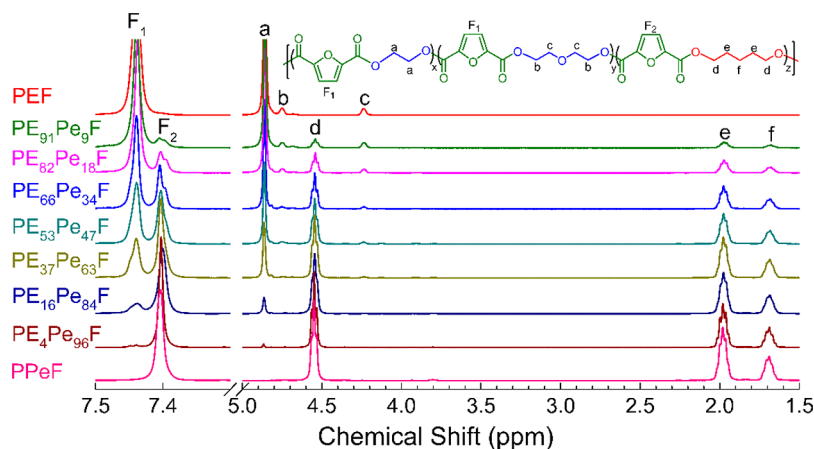
$$\phi_{EF}(\text{mol } \%) = \frac{I_a}{I_a + I_c + I_e} 100\% \quad (1)$$

$$\phi_{DEGF}(\text{mol } \%) = \frac{I_c}{I_a + I_c + I_e} 100\% \quad (2)$$

$$\phi_{PeF}(\text{mol } \%) = \frac{I_e}{I_a + I_c + I_e} 100\% \quad (3)$$

$$\phi_{PeF}(\text{mol } \%) = \frac{I_{F_2}}{I_{F_1} + I_{F_2}} 100\% \quad (4)$$

As the EG monomer contributes to the formation of EF and DEGF units via the main polycondensation reaction and the side etherification reaction, respectively,  $\phi_{DEGF}$  is calibrated with eq 5 to be  $\phi'_{DEGF}$  to express the selectivity of the side reaction. The value of  $\phi'_{DEGF}$  ranges 3.4–5.7 except for the unexpected high value (14) of Run 8, which might result from

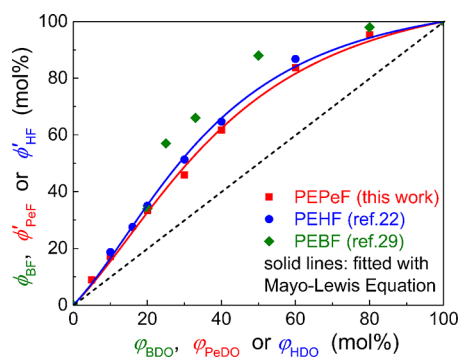


**Figure 2.**  $^1\text{H}$  NMR spectra of PEF, PPeF and PEPeF copolyesters (chemical shift at 11.6 ppm for solvent  $d_1$ -TFA).

the calculation error because of the very tiny signal **c** of this sample. The incorporation of PeDO comonomer seems to be conducive to depress the etherification reaction to some extent, but the reason is not clear yet and needs further study.

$$\phi'_{\text{DEGF}} (\text{mol}\%) = \frac{I_c}{I_a + I_c} 100\% \quad (5)$$

Considering that the DEGF unit contains two EG units,  $\phi_{\text{PeF}}$  is calibrated to be  $\phi'_{\text{PeF}}$  with eq 6. Although  $\phi_{\text{PeF}}$  and  $\phi'_{\text{PeF}}$  differ little from each other as the DEGF unit is the very minor component in PEPeF, the calibrated copolymer composition,  $\phi'_{\text{PeF}}$ , is still used to compare with the comonomer composition in the diol feed ( $\phi_{\text{PeDO}}$ ). The results are shown in Figure 3. It can be seen that the  $\phi'_{\text{PeF}}$  values are clearly



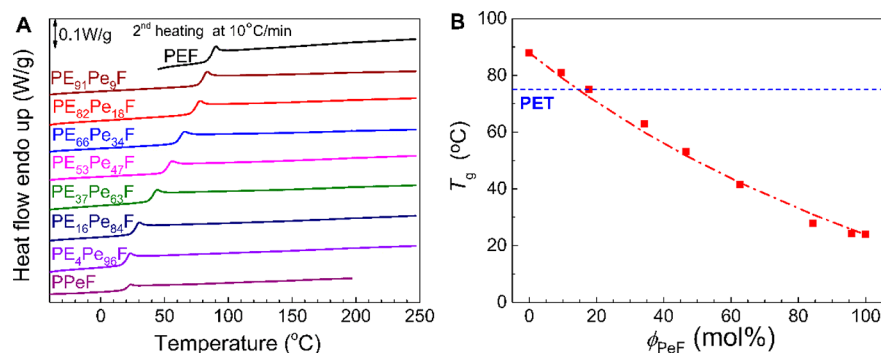
**Figure 3.** Dependence of the copolymer composition of three PEF-based copolyesters,  $\phi_{\text{BF}}$  (not calibrated) of PEBF,  $\phi'_{\text{PeF}}$  (calibrated) of PEPeF and  $\phi'_{\text{HF}}$  (calibrated) of PEHF on the corresponding comonomer composition,  $\phi_{\text{BDO}}$ ,  $\phi_{\text{PeDO}}$  and  $\phi_{\text{HDO}}$ . Solid lines: the curves fitted by Mayo–Lewis equation:  $F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2f_1 f_2 + r_2 f_2^2)$ . For PEPeF,  $F_1 = \phi'_{\text{PeF}}$ ,  $f_1 = \phi_{\text{PeDO}}$ ,  $f_2 = \phi_{\text{EG}} = 1 - \phi_{\text{PeDO}}$ .

higher than the corresponding  $\phi_{\text{PeDO}}$  values because of less volatility of PeDO than EG. Another possible reason may be higher reactivity of PeDO than EG. Similar results have been reported in poly(ethylene-*co*-hexamethylene 2,5-furandicarboxylate)s (PEHFs) by us<sup>28</sup> and poly(ethylene-*co*-butylene 2,5-furandicarboxylate)s (PEBFs) by Ma et al.<sup>35</sup> At the same comonomer composition, it can be seen from Figure 3 that the PeF molar percentage in PEPeF is slightly lower than the HF molar percentage in PEHF, but both of them are clearly less than the BF molar percentage in PEBF. To better

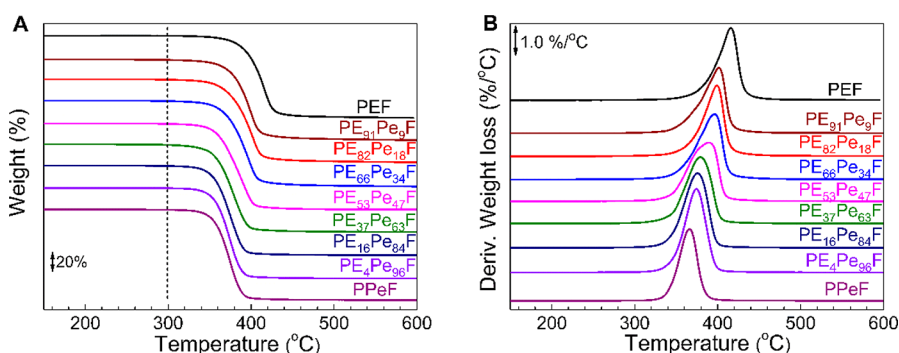
correlate the copolymer composition with the monomer composition, classic Mayo–Lewis equation deduced from free radical copolymerization (FRCP) is borrowed here to fit the corresponding data from the two copolymerization systems though the reaction mechanism of copolycondensation is completely different from FRCP. Mayo–Lewis equation perfectly fits the  $\phi'_{\text{PeF}} - \phi_{\text{PeDO}}$  data from this work, as it did in PEHFs previously.<sup>28</sup> For PEBF, the fitting was not done as there lacked data at  $\phi_{\text{BDO}} < 20$  mol %. The fitted empirical or apparent reactivity ratios of PeDO and EG are 3.78 and 0.75, and their standard error are 0.49 and 0.10, respectively. The results suggest that PeDO has higher “reactivity” than EG. Clearly, such high “reactivity” results from not only possible higher true reactivity but also less volatility of PeDO. Compared with the empirical reactivity ratio of HDO (4.60) and EG (0.74) obtained in PEHFs,<sup>28</sup> EG has similar “reactivity” in both systems, and PeDO has slightly lower “reactivity” than HDO. This result agrees with the conclusion drawn by Ma et al. that reactivity of diols with FDCA increases with the increase in the carbon chain in the range of  $\text{C}_2 - \text{C}_5$ .<sup>35</sup> In fact, the rate constants of EG-FDCA and PeDO-FDCA esterification reactions were reported to be  $3.8 \times 10^{-3}$  and  $0.1 \text{ min}^{-1}$ , respectively.<sup>35</sup> But from the above comparison, BDO seems to have higher “reactivity” than PeDO and HDO.

$$\phi'_{\text{PeF}} (\text{mol}\%) = \frac{I_e}{I_a + 2I_c + I_e} 100\% \quad (6)$$

**3.2. Thermal Transition.** The thermal transition properties of PEF, PPeF and PEPeF copolyesters were determined by DSC. PEF is often reported to be a semicrystalline polyester with weak melt crystallizability,<sup>40</sup> and different crystal structures and polymorphisms of PEF formed under different experimental conditions have been extensively studied by Maini et al.<sup>41</sup> In this study, the PEF sample exhibited a weak melting peak ( $\Delta H_m = 5.9 \text{ J/g}$ ) at  $211.3^\circ\text{C}$  in the first heating scan (Figure S1 and Table S1), but neither crystallization nor melting was observed in the cooling (Figure S1) and second heating scans (Figure 4A). Clearly, the poor crystallizability of PEF is related to its relatively high DEGF content. PPeF was also reported as a weakly crystallizable polyester possibly due to the odd carbon in the pentylene structural unit. Bikiaris et al. synthesized PPeF with TBT catalyst and found that the as-prepared PPeF sample exhibited a large melting peak at  $94^\circ\text{C}$  (no enthalpy reported), but no melting peak was observed after quenching and heating again.<sup>37</sup> In this study, however,



**Figure 4.** (A) Second heating DSC curves of PEF, PPeF and PEPeF copolyesters and (B) composition ( $\phi_{\text{PeF}}$ ) dependence of glass transition temperature ( $T_g$ ) of PEPeF copolyester (dashed line shows the value calculated using the Fox equation).



**Figure 5.** TGA (A) and DTG thermograms (B) of PEF, PPeF and PEPeF copolyesters ( $\text{N}_2$  atmosphere,  $10^\circ\text{C}/\text{min}$ ).

PPeF showed neither crystallization nor melting in all the three scans (1st heating, cooling and second heating), showing its amorphous feature. As a result of the very weak crystallizability of PEF and zero crystallizability of PPeF, the PEPeF copolyesters exhibited neither crystallization nor melting in all the three scans except that a very tiny melting peak ( $\Delta H_m = 1.3 \text{ J/g}$ ) at  $189.7^\circ\text{C}$  was observed in the first heating scan of  $\text{PE}_{91}\text{Pe}_9\text{F}$ . In conclusion, PEPeFs are weakly crystallizable or nearly amorphous polyesters.

The  $T_g$  of PEF is as high as  $88^\circ\text{C}$ . In comparison, PPeF has much lower  $T_g$  of  $24^\circ\text{C}$ . This value is clearly higher than the sole result ( $19^\circ\text{C}$ ) to date reported by Bikiaris et al.,<sup>37</sup> because of higher molecular weight of PPeF in this study ( $[\eta] 0.89$  vs  $0.53 \text{ dL/g}$ <sup>37</sup>). All the PEPeF copolyesters show a single  $T_g$ , and its value decreases with increasing the content of PeF unit (Figure 4A), indicating the random sequence structure of PEPeF copolyesters. The composition dependence of  $T_g$  of PEPeF is plotted in Figure 4B, which agrees well with the Fox equation. Furthermore, it can be seen that the PEPeF copolyester can retain  $T_g$  no less than PET ( $\geq 75^\circ\text{C}$ ) when the content of PeF is no more than 18 mol %. In other words, PEPeF with  $\phi_{\text{PeF}}$  no more than 18 mol % will have heat resistance better than or at least comparable to PET.

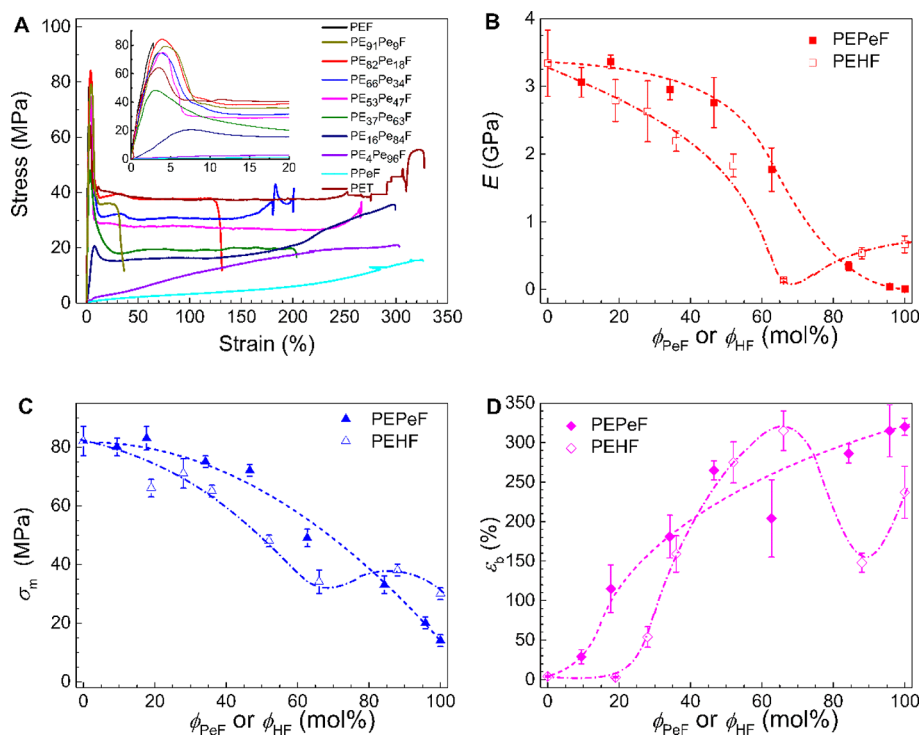
**3.3. Thermal Stability.** The thermal stabilities of PEF, PPeF and PEPeF copolyesters were evaluated by TGA under  $\text{N}_2$  atmosphere. The TGA and DTG curves are shown in Figure 5. The decomposition temperature at 5% weight loss ( $T_{d,5}$ ) and the maximum decomposition rate ( $T_{d,\text{max}}$ ) and the residual mass percentage at  $600^\circ\text{C}$  ( $R_{600}$ ) are listed in Table 2. In comparison, PEF has better thermal stability than PPeF, with higher  $T_{d,5}$  ( $376$  vs  $342^\circ\text{C}$ ),  $T_{d,\text{max}}$  ( $416$  vs  $366^\circ\text{C}$ ) and  $R_{600}$  ( $14.8\%$  vs  $4.7\%$ ). The high  $R_{600}$  of PEF was also reported as  $13.9\%$  by other researchers.<sup>42</sup> It is attributed to

**Table 2.** Thermal Properties of PEF, PPeF and PEPeF Copolyesters

sample	$T_g^a$ ( $^\circ\text{C}$ )	$T_m^b$ ( $^\circ\text{C}$ )	$T_{d,5}^c$ ( $^\circ\text{C}$ )	$T_{d,\text{max}}^d$ ( $^\circ\text{C}$ )	$R_{600}^e$ (wt %)
PEF	88.7	211.3/nd	376	416	14.8
$\text{PE}_{91}\text{Pe}_9\text{F}$	80.6	189.7/nd	359	402	14.5
$\text{PE}_{82}\text{Pe}_{18}\text{F}$	75.2	nd/nd	356	399	12.7
$\text{PE}_{66}\text{Pe}_{34}\text{F}$	62.8	nd/nd	353	396	9.6
$\text{PE}_{53}\text{Pe}_{47}\text{F}$	53.1	nd/nd	349	389	9.2
$\text{PE}_{37}\text{Pe}_{63}\text{F}$	41.6	nd/nd	343	379	7.7
$\text{PE}_{16}\text{Pe}_{84}\text{F}$	27.9	nd/nd	344	376	5.6
$\text{PE}_4\text{Pe}_{96}\text{F}$	24.3	nd/nd	346	374	4.7
PPeF	23.9	nd/nd	342	366	4.7

<sup>a</sup>Glass transition temperature measured from the 2nd DSC heating at  $10^\circ\text{C}/\text{min}$ . <sup>b</sup>Melting temperature measured from 1st/2nd DSC heating at  $10^\circ\text{C}/\text{min}$ . <sup>c</sup>Decomposition temperature at 5% weight loss ( $T_{d,5}$ ) measured with TGA at  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. <sup>d</sup>Maximum decomposition rate ( $T_{d,\text{max}}$ ) measured with TGA at  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. <sup>e</sup>Residual mass percentage at  $600^\circ\text{C}$  ( $R_{600}$ ) measured with TGA at  $10^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere.

graphitization at high temperature.<sup>43</sup> According to the previous reports,<sup>44–46</sup> poly(alkylene 2,5-furandicarboxylate)s with different alkylene units follow identical thermal decomposition mechanism:  $\beta$ -hydrogen bond scission is the main pathway to form carboxyl and vinyl end groups, aldehydes and hydroxyl end groups are also induced by the  $\alpha$ -hydrogen bond and homolytic chain scission. All the copolyesters displayed a single thermal decomposition process, supporting the conclusion of random copolymer structure. Therefore, the  $T_{d,5}$ ,  $T_{d,\text{max}}$  and  $R_{600}$  of PEPeF copolyesters decreased with increasing the content of PeF unit. However, it should be noted that all the



**Figure 6.** Typical stress–strain curves of PEF, PPeF and PEPeF copolyesters (A) and composition dependence of the Young's modulus  $E$  (B), maximum strength  $\sigma_m$  (C), elongation at break  $\epsilon_b$  (D) of PEPeF and PEHF copolyesters.

**Table 3.** Young's Modulus ( $E$ ), Tensile Strength at Yield ( $\sigma_y$ ) and Break ( $\sigma_b$ ), Elongation at Yield ( $\epsilon_y$ ) and Break ( $\epsilon_b$ ), and Notch Impact Strength ( $\sigma_i$ ) of PEF, PEPeF Copolyesters and PPeF

Sample	$[\eta]$ (dL/g)	$E$ (MPa)	$\sigma_y$ (MPa)	$\sigma_b$ (MPa)	$\epsilon_y$ (%)	$\epsilon_b$ (%)	$\sigma_i$ (kJ/m <sup>2</sup> )
PEF	0.82	3.34 ± 0.49	–	82 ± 5	–	4 ± 1	2.1 ± 0.1
PE <sub>91</sub> Pe <sub>9</sub> F	0.78	3.06 ± 0.22	80 ± 3	35 ± 1	4.1 ± 0.2	29 ± 9	2.2 ± 0.3
PE <sub>82</sub> Pe <sub>18</sub> F	0.84	3.27 ± 0.1	83 ± 4	37 ± 2	3.9 ± 0.1	115 ± 30	3.0 ± 0.3
PE <sub>66</sub> Pe <sub>34</sub> F	0.83	2.95 ± 0.15	75 ± 2	33 ± 2	3.8 ± 0.2	181 ± 27	3.4 ± 0.2
PE <sub>53</sub> Pe <sub>47</sub> F	0.92	2.76 ± 0.37	72 ± 2	29 ± 2	3.9 ± 0.3	265 ± 12	3.9 ± 0.2
PE <sub>37</sub> Pe <sub>63</sub> F	0.93	1.77 ± 0.32	49 ± 3	22 ± 2	3.9 ± 0.4	185 ± 18	4.2 ± 0.3
PE <sub>16</sub> Pe <sub>84</sub> F	1.01	0.345 ± 0.07	12 ± 5	33 ± 3	9.1 ± 2.1	286 ± 12	nb <sup>a</sup>
PE <sub>4</sub> Pe <sub>96</sub> F	1.03	0.042 ± 0.003	–	20 ± 2	–	315 ± 33	nb <sup>a</sup>
PPeF	0.89	0.006 ± 0.001	–	14 ± 2	–	320 ± 11	nb <sup>a</sup>
PET	0.82	1.93 ± 0.06	67 ± 3	39 ± 2	3.8 ± 0.2	324 ± 4	2.7 ± 0.3

<sup>a</sup>nb: not broken.

(co)polyesters did not decompose before 300 °C, ensuring excellent thermal stability for melt processing.

**3.4. Mechanical Properties.** Typical tensile stress–strain curves of PEF, PPeF and PEPeF copolyesters are illustrated in Figure 6A. The Young's modulus ( $E$ ), tensile strength at yield ( $\sigma_y$ ) and break ( $\sigma_b$ ), and elongation at yield ( $\epsilon_y$ ) and break ( $\epsilon_b$ ) are listed in Table 3. And the composition dependence of  $E$ , maximum tensile strength ( $\sigma_m$ ) and  $\epsilon_b$  is shown in Figure 6B–D.

In the tensile test, PEF behaved like a typical hard and brittle polymer material, showing high tensile modulus (3.3 GPa) and breaking strength (82 MPa) but very low elongation at break (4%). Different from PEF, the bottle-grade PET with  $[\eta]$  of 0.82 dL/g displayed obvious ductile fracture during the tensile testing, showing much higher elongation at break (324%) than PEF. However, it showed lower tensile modulus (1.93 GPa) and strength (67 MPa) than PEF. In fact, a broad range of elongation at break from 80% to 510% has been reported in

literature for bottle grade PET,<sup>47–51</sup> from amorphous to crystalline.<sup>52,53</sup>

In comparison with PEF, PPeF behaved like an elastomer, showing no yielding/necking but broad rubber plateaus and exhibiting high elongation at break (320%), low tensile modulus (6 MPa) and breaking strength (14 MPa). However, in comparison with common un-cross-linked elastomers or rubbers such as styrene-butadiene rubber (SBR),<sup>54</sup> PPeF has clearly higher tensile strength (14 vs 6 MPa). The tensile strength is even comparable or close to vulcanized rubber. Furthermore, it should be noted that PPeF showed excellent rebound resilience after unloading the stress force. The stretched and then broken specimens recovered almost to their original length. Therefore, PPeF behaves as a high performance elastomer. This makes it a good choice for toughening PEF. To the best of our knowledge, this is the first report on mechanical properties of PPeF. The coexistence of rigid furan ring and flexible pentylene unit in the chain

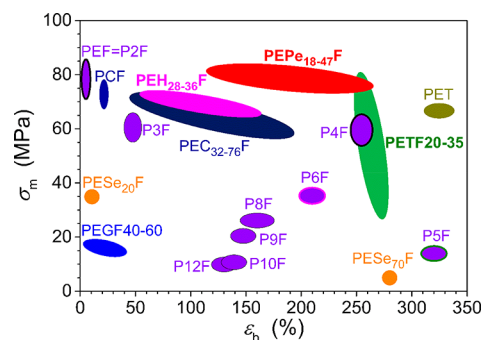
structure and the amorphous feature may contribute to the unique mechanical properties of PEPeF.

Expectedly and encouragingly, incorporating a small amount of PeDO into PEF did result in significant improvement in tensile toughness of PEF. A yielding/necking phenomenon, as an indicator of brittle-ductile transition, occurs at  $\phi_{\text{PeF}}$  as low as 9 mol %. At  $\phi_{\text{PeF}}$  of 9–18 mol %, the elongation at break increases remarkably to 29–115%, and at the same time, the modulus (3.1–3.3 GPa) and yielding strength (80–83 MPa) keep almost unchanged (decreased only by 2–11% and 1–5%, respectively). Obviously, their tensile properties are superior to bottle-grade PET resins.<sup>55</sup> In fact, the PEPeFs with  $\phi_{\text{PeF}}$  of 9–84 mol % show typical tensile behavior of ductile plastics, and PEPeFs with higher  $\phi_{\text{PeF}}$  behave as elastomers with tensile strength superior to PPeF itself. Different composition dependences of the tensile properties of PEPeFs are observed, as shown in Figure 6B–D. Although the breaking strength declines sharply at  $\phi_{\text{PeF}}$  about 9% and then slowly at higher  $\phi_{\text{PeF}}$ , the Young's modulus and yield or maximum strength ( $\sigma_m$ ) decrease slowly up to  $\phi_{\text{PeF}}$  of 47%, and then rapidly at higher  $\phi_{\text{PeF}}$ . Even at a high  $\phi_{\text{PeF}}$  of 63%, the copolyester still retains high modulus of 1.8 GPa and yielding strength of 49 MPa (decreased by 47% and 42%, respectively), which are comparable to the reported tensile properties of PBF.<sup>56</sup> The elongation at break increases progressively despite of some fluctuation, starting from  $\phi_{\text{PeF}}$  as low as 9%.

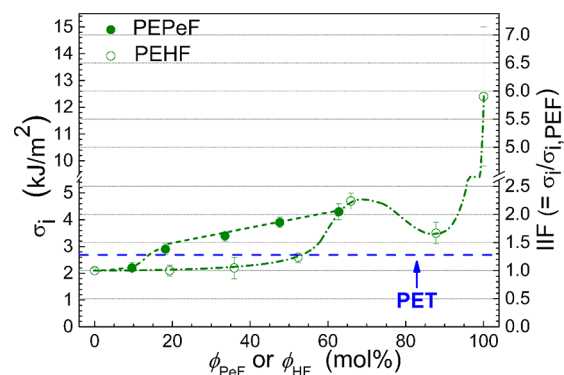
For comparison, the tensile properties of poly(ethylene-co-hexamethylene 2,5-furandicarboxylate) copolyesters (PEHFs) previously reported by us are also plotted in Figure 6B–D. It can be seen that PEF-rich PEPeFs show much higher elongation at break at the same copolymer composition, and furthermore, PEPeFs have clearly higher tensile modulus and yield or maximum strength than PEHFs at the same composition up to  $\phi_{\text{PeF}}$  about 70%. Another obvious difference is that the PHF-rich PEHFs ( $\phi_{\text{HF}}$  about 80–90%) has higher modulus and strength and lower elongation at break than PPeF-rich PEPeFs because of improved crystallinity of PEHFs at this composition range as reported previously.<sup>28</sup> As PEPeFs are amorphous polyester, the tensile properties change with copolymer composition progressively and more smoothly. Clearly, PeDO is a more effective diol comonomer than HDO in terms of tensile toughness modification of PEF though it has shorter carbon chain than HDO. Incorporating small amount of PeDO (9–18%) is enough to achieve high enough tensile toughness and at the same time retains almost unchanged Young's modulus and yielding strength. In addition, it should be noted that the high and well-balanced tensile properties of PEPeFs are achieved by copolymerizing a cheap and biobased monomer with an odd carbon chain. The coexistence of flexible pentylene units and rigid furan rings in PEPeFs may contribute to the unique tensile properties.

The maximum tensile strength and elongation at break of PEF, PCF,<sup>10</sup> some PEF-based copolyesters<sup>10,21,22,27,28</sup> and poly(alkylene 2,5-furandicarboxylate)s (PAFs) with alkylene carbon number of 3–12<sup>24,33,34</sup> are compared in Figure 7. It can be seen that PECFs, PETFs, PEHFs and PEPeFs behave better than other copolyesters in balancing maximum tensile strength and elongation at break. Obviously, PEPeFs give the best results among them.

The notched Izod impact strength ( $\sigma_i$ ) of PEPeFs was also examined, and is compared with that of PEHFs<sup>28</sup> and the bottle-grade PET in Figure 8. The impact strength increases from 2.1 kJ/m<sup>2</sup> of PEF to 3.0 kJ/m<sup>2</sup> of PE<sub>82</sub>Pe<sub>18</sub>F (by about



**Figure 7.** Comparison of the maximum tensile strength ( $\sigma_m$ ) and elongation at break ( $\epsilon_b$ ) in the indicated (co)polyesters. Note: PETF20-35 and PEGF40-60 means P(EF-mb-PTMG)s containing 20–35 wt % PTMG segment and P(EF-mb-PEG)s containing 40–60 wt % PEG segment, respectively; the number A in PAF means the alkylene carbon number of the poly(alkylene 2,5-furandicarboxylate)s; the subscript b in PEX<sub>b</sub>F means the molar percentage of the XF unit in the random copolyester PEXF.

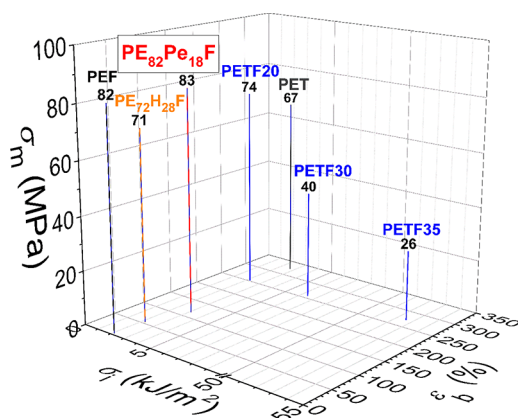


**Figure 8.** Composition dependence of the notched Izod impact strength ( $\sigma_i$ ) and impact improvement factor (IIF, defined as  $\sigma_i/\sigma_{i,\text{PEF}}$ ) of PEPeF and PEHF copolyesters.

50%), which is higher than 2.7 kJ/m<sup>2</sup> of the PET, and then grows slowly and almost linearly with copolyester composition up to 4.2 kJ/m<sup>2</sup> of PE<sub>37</sub>Pe<sub>63</sub>F (2 times of PEF and 1.6 times of PET). At higher PeF content, the PEPeFs and PPeF itself were not broken because they have  $T_g$  values adjacent to room temperature and therefore became a rubbery state at the experimental condition. For PEHF, the increase in impact strength with HF unit content is much slower, and 50% increase is not reached until the HF unit content reaches 58%. The decrease and then increase again in impact strength can be observed at higher composition owing to the increase in crystallinity as reported previously.<sup>28</sup> The above results demonstrate that PeDO is more efficient than HDO to improve impact strength as well as ductility of PEF. As PeDO has a shorter alkylene chain than HDO (5 vs 6), the superior toughening effect is attributed to the unique odd carbon atom number of PeDO.

From the above results, it can be concluded that PeDO behaves better than HDO in improving not only tensile but also impact toughness of PEF. The maximum tensile strength ( $\sigma_m$ ), elongation at break ( $\epsilon_b$ ) and impact strength ( $\sigma_i$ ) of PEF, bottle-grade PET, PE<sub>82</sub>Pe<sub>18</sub>F, PE<sub>72</sub>H<sub>28</sub>F<sup>28</sup> and P(EF-mb-PTMG)s<sup>27</sup> (symbolized as PETF for simplicity) containing 20–35 wt % PTMG are compared in Figure 9. Among them, it can be seen that PE<sub>82</sub>Pe<sub>18</sub>F has tensile strength, ductility and





**Figure 9.** Comparison of the maximum tensile strength ( $\sigma_m$ ), elongation at break ( $\epsilon_b$ ) and notched Izod impact strength ( $\sigma_i$ ) of the indicated (co)polyesters.

impact toughness closer to bottle grade PET. PETF30-35 can reach super impact toughness but the tensile strength sacrificed too much. In contrast, PE<sub>72</sub>H<sub>28</sub>F and PETF20 can retain high enough tensile strength but the impact toughness remains unimproved.

**3.5. Oxygen Barrier Properties.** Finally, the O<sub>2</sub> barrier properties of PEF, PPeF and PEPeF copolyesters were investigated experimentally and theoretically. The O<sub>2</sub> permeability coefficient ( $P_{O_2}$ ) was measured at 23 °C using thermally compressed film samples. The O<sub>2</sub> barrier improvement factor (BIF) defined by Burgess et al.,<sup>12</sup> which stands for the ratio of the  $P_{O_2}$  of PET vs the  $P_{O_2}$  of target polymer, was also calculated. Higher BIF represents higher O<sub>2</sub> barrier property than PET. The composition dependence of  $P_{O_2}$  and BIF is displayed in Table 4 and Figure 10.

Usually, gas permeability in a given polymer can be calculated from Lennard-Jones temperature and collision diameter of the gas and  $T_g$  and crystallinity of the polymer.<sup>57</sup> Salame et al. reported another simpler so-called Permachor method in 1986.<sup>58</sup> In this method, a key physical parameter  $\pi$  related to cohesive energy density and fractional free volume is defined. It is determined by the molar Permachor ( $\Pi$ ), an additive function that can be calculated from group contribution shown in eq 7, where  $N$  is total number of characteristic groups per repeat unit;  $\Pi_i$  and  $N_i$  are the increment or contribution and number of group  $i$ . The permeability of N<sub>2</sub> in a given amorphous polymer can be estimated from eq 8. The permeability of O<sub>2</sub> in the same polymer is 3.8 times that of N<sub>2</sub>. The gas permeability of a crystalline polymer with a volume-based crystallinity of  $x_c$  is  $(1 - x_c)^2$  times of that of the corresponding amorphous one. As the group contribution of furan ring was not reported, it is estimated using the permeability data of fully amorphous PEF at 298 K obtained by extrapolating the data reported by Burgess et al.<sup>12</sup> From the available data (0.0075 barrer), the group contribution of furan ring is calculated to be 149, much higher than 60 of benzene ring.<sup>57</sup> Using this group contribution value of furan ring, the  $\pi$  and  $P_{O_2}$  (298) values of amorphous PEF, PPeF and PEPeFs were calculated, and the results are shown in Table 4 and Figure 10.

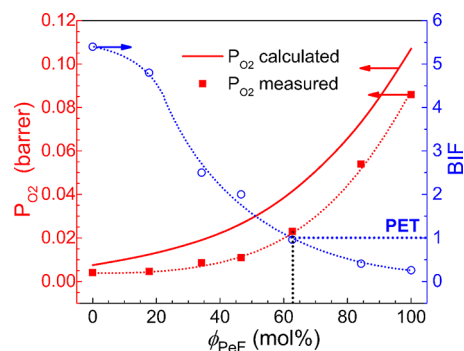
$$N\pi = \Pi = \sum_{i=1} N_i \Pi_i \quad (7)$$

$$\log P(N_2, 298, \text{m}^2/\text{s}\cdot\text{Pa}) = -16 - 0.05\pi \quad (8)$$

**Table 4.** O<sub>2</sub> Barrier Properties of PEF, PPeF, PEPeF Copolyesters and Some Other Related (Co)polyesters

Sample	T (°C)	$P_{O_2}^a$ (barrer)	BIF <sup>b</sup>	$\pi$	$P_{O_2}^c$ (barrer)	Reference
PET	23	0.022	1	58.8	0.058	This work
PEF	23	0.0041	5.4	76.6	0.0075	This work
PE <sub>82</sub> Pe <sub>18</sub> F	23	0.0046	4.8	72.5	0.012	This work
PE <sub>66</sub> Pe <sub>34</sub> F	23	0.0087	2.5	68.7	0.019	This work
PE <sub>53</sub> Pe <sub>47</sub> F	23	0.011	2.0	65.8	0.026	This work
PE <sub>37</sub> Pe <sub>63</sub> F	23	0.023	0.96	62.1	0.040	This work
PE <sub>16</sub> Pe <sub>84</sub> F	23	0.054	0.41	57.1	0.071	This work
PPeF	23	0.086	0.26	53.5	0.11	This work
PET	30	0.06	1			10
PEF	30	0.011	5.5			10
PE <sub>68</sub> C <sub>32</sub> F	30	0.014	4.3			10
PE <sub>24</sub> C <sub>76</sub> F	30	0.017	3.5			10
PET	35	0.114	1			12
PEF	35	0.0107	11			12
PET	30	0.054	1			60
PEN	30	0.019	2.9			60
PEI	30	0.015	3.6			60
PET	35	0.103	1			61
PEN	36	0.037	2.8			61

<sup>a</sup>Measured oxygen permeability coefficient of polymers in the unit "barrer": 1 barrer =  $7.50 \times 10^{-18} \text{ m}^3 \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ . <sup>b</sup>BIF means barrier improvement factor,  $\text{BIF} = P_{O_2, \text{PET}}/P_{O_2}$ . <sup>c</sup>Calculated oxygen permeability coefficient of amorphous polymers at 25 °C.



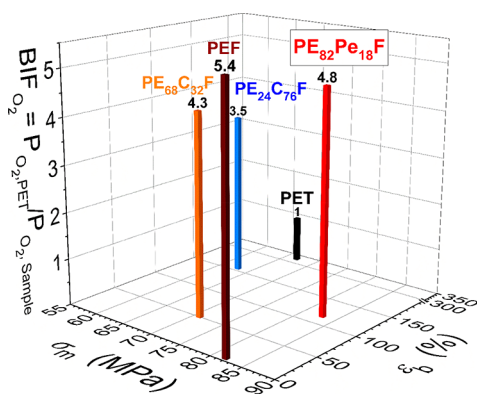
**Figure 10.** Composition dependence of the O<sub>2</sub> permeability coefficient and barrier improvement factor (BIF) of PEPeF copolyesters. The solid line is the oxygen permeability coefficient calculated with the Permachor method.

The PEF sample in this work shows a  $P_{O_2}$  value of 0.0041 barrer and BIF of 5.4. It is lower than the calculated value of amorphous PEF (0.0075 barrer, equal to the extrapolated value at 25 °C from the results of Burgess et al.) due to its weak crystallization. It is also lower than that reported by Wang et al. (0.011 barrer),<sup>10</sup> due to the lower testing temperature (23 vs 30 °C<sup>10</sup>) and possible difference in crystallinity and instrument error. But the relative BIF value agrees well with their result (5.5).<sup>10</sup> In comparison, Burgess et al. reported a double BIF value of 11 of amorphous PEF.<sup>12</sup> Obviously, the PEF sample exhibits greatly improved O<sub>2</sub> barrier property as compared

with PET, which can be attributed to the restricted chain mobility of PEF elucidated by Burgess et al.<sup>59</sup>

In comparison with PEF, PPeF has a much lower  $\pi$  value (53.5 vs 76.6) and therefore much lower O<sub>2</sub> barrier property. It has a 20 times higher  $P_{O_2}$  value (0.086 vs 0.0041 barrer). Its O<sub>2</sub> barrier property is even lower than PET as its BIF value is 0.26. Therefore, for the random PEPeF copolyesters, the  $P_{O_2}$  value increases and the O<sub>2</sub> barrier property decreases with increasing PeF content, the copolyester composition. Although slight differences can be observed, the experimental results basically agree with the calculated ones in the whole composition range and therefore seem to be reliable. On the other hand, it is remarkable that both the experimental and calculated  $P_{O_2}$  values increase slowly at low PeF content and rapidly at high PeF content, as shown in Figure 10. In other words, the negative effect of copolymerization on the O<sub>2</sub> barrier property of PEF is clearly weaker at low PeF content than at high PeF content. In fact, PE<sub>82</sub>Pe<sub>18</sub>F has a  $P_{O_2}$  only slightly higher than PEF by 12% (0.0046 vs 0.0041 barrer), and therefore a high O<sub>2</sub> barrier property (BIF 4.8) is obtained. The O<sub>2</sub> barrier property of PEPeFs remains superior to that of PET until the PeF content reaches 63 mol %. Furthermore, PE<sub>82</sub>Pe<sub>18</sub>F shows superior O<sub>2</sub> barrier property when compared with some other (co)polyesters well-known for high O<sub>2</sub> barrier performance, including poly(ethylene isophthalate) (PEI, BIF 3.6<sup>60</sup>), poly(ethylene naphthalate) (PEN, BIF 2.9<sup>60</sup> or 2.8<sup>61</sup>) and poly(ethylene-*co*-1,4-cyclohexanedimethylene 2,5-furandicarboxylate)s containing 32 and 76 mol % CF unit content (PE<sub>68</sub>C<sub>32</sub>F, BIF 4.3; PE<sub>24</sub>C<sub>76</sub>F, BIF 3.5<sup>10</sup>).

Finally, the values of tensile strength, elongation at break and BIF of PET, PEF, PE<sub>82</sub>Pe<sub>18</sub>F and two PECFs are compared in Figure 11 to evaluate their comprehensive



**Figure 11.** Comparison of maximum tensile strength ( $\sigma_m$ ), elongation at break ( $\epsilon_b$ ), and barrier improvement factor (BIF) of the indicated (co)polyesters.

performance. Obviously, incorporating a small amount (18 mol %) of PeF unit into PEF not only greatly improves the tensile toughness but also retains very high (unchanged) tensile strength and O<sub>2</sub> barrier property (only 12% decrease) at the same time. In comparison with bottle grade PET, the tensile strength and O<sub>2</sub> barrier property of PE<sub>82</sub>Pe<sub>18</sub>F have been greatly improved while having a reasonably good tensile toughness. PE<sub>82</sub>Pe<sub>18</sub>F also has higher tensile toughness, tensile strength and O<sub>2</sub> barrier property than the PECFs. Furthermore, such performance improvements are achieved by copolymerizing small amount of cheap biobased monomer. This unique feature distinguishes PEPeF from other PEF-

based copolyesters reported. Obviously, such a result is very desirable for production and practical application of PEF-based materials.

#### 4. CONCLUSIONS

In this work, poly(ethylene-*co*-1,5-pentylene 2,5-furandicarboxylate) (PEPeF) copolyesters with intrinsic viscosity of 0.78–1.03 dL/g were successfully synthesized via met copolycondensation of FDCA, EG and PeDO, a cheap, biobased and commercially available odd-carbon comonomer. The PeF unit content in PEPeFs is higher than the PeDO content in the diol feed, and their relationship can be correlated empirically with Mayo–Lewis equation with “reactivity ratio” of 3.78 for PeDO and 0.75 for EG. The copolyesters are nearly amorphous polymers with  $T_g$  following Fox equation and excellent thermal stability. Brittle–ductile transition is achieved by incorporating a PeF unit as low as 9 mol % into PEF. In comparison with PEF, PEPeFs containing 9–47 mol % PeF unit show greatly improved tensile toughness (29–265% vs 4%) and enhanced impact toughness (2.2–3.9 vs 2.1 kJ/m<sup>2</sup>), and at the same time retain very high tensile modulus (2.8–3.3 vs 3.3 GPa) and maximum tensile strength (72–83 vs 82 MPa). Particularly, when compared with bottle grade PET, PE<sub>82</sub>Pe<sub>18</sub>F possesses equal  $T_g$  (75 °C) and comparable elongation at break (115%), but greatly improved yielding strength (83 MPa) and O<sub>2</sub> barrier property (BIF 4.8). These unique features highlight PEPeFs as promising modified PEF materials desirable for practical applications in eco-packaging and other fields.

#### ■ ASSOCIATED CONTENT

##### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.biomac.8b01495.

First heating and cooling DSC scans of PEF, PPeF and PEPeF copolyesters; thermal transition properties of PEF, PPeF and PEPeF copolyesters determined from first heating and cooling scans (PDF)

#### ■ AUTHOR INFORMATION

##### Corresponding Authors

\*Linbo Wu. E-mail: [wulinbo@zju.edu.cn](mailto:wulinbo@zju.edu.cn).

\*Philippe Dubois. E-mail: [philippe.dubois@umons.ac.be](mailto:philippe.dubois@umons.ac.be).

##### ORCID

Linbo Wu: 0000-0001-9964-6140

##### Notes

The authors declare no competing financial interest.

#### ■ ACKNOWLEDGMENTS

This work was supported by the National Natural Science Foundation of China (51773177, 51373152), State Key Laboratory of Chemical Engineering (No. SKL-ChE-18D02), the National Key Research and Development Program of China (2016YFB0302402) and 151 Talents Project of Zhejiang Province. The authors are very grateful to Li Xu from College of Chemical and Biological Engineering, Zhejiang University, for her kind help on DSC and TGA measurement, and also acknowledge Labthink Company (China) for O<sub>2</sub> permeation measurement.

## REFERENCES

- (1) Llevot, A.; Grau, E.; Carlotti, S.; Grelier, S.; Cramail, H. From lignin-derived aromatic compounds to novel biobased polymers. *Macromol. Rapid Commun.* **2016**, *37*, 9–28.
- (2) Pereira, B.; Zhang, H.; De Mey, M.; Lim, C. G.; Li, Z. J.; Stephanopoulos, G. Engineering a novel biosynthetic pathway in *Escherichia coli* for production of renewable ethylene glycol. *Biotechnol. Bioeng.* **2016**, *113*, 376–383.
- (3) Liu, H.; Ramos, K. R. M.; Valdehuesa, K. N. G.; Nisola, G. M.; Lee, W. K.; Chung, W. J. Biosynthesis of ethylene glycol in *Escherichia coli*. *Appl. Microbiol. Biotechnol.* **2013**, *97*, 3409–3417.
- (4) Sousa, A. F.; Vilela, C.; Fonseca, A. C.; Matos, M.; Freire, C. S. R.; Gruter, G. J. M.; Coelho, J. F. J.; Silvestre, A. J. D. Bio-based polyesters and other polymers from 2,5-furandicarboxylic acid: a tribute to furan excellency. *Polym. Chem.* **2015**, *6*, 5961–5983.
- (5) Bozell, J. J.; Petersen, G. R. Technology development for the production of bio-based products from biorefinery carbohydrates—the US department of energy's "Top 10" revisited. *Green Chem.* **2010**, *12*, 539–554.
- (6) Werpy, T. A.; Holladay, J. E.; White, J. F. *Top value added chemicals from biomass volume I—Results of screening for potential candidates from sugars and synthesis gas*; U.S. Department of Energy: Washington, DC, 2004; <https://www.nrel.gov/docs/fy04osti/35523.pdf>.
- (7) Papageorgiou, G. Z.; Tsanaktis, V.; Bikiaris, D. N. Synthesis of poly(ethylene furandicarboxylate) polyester using monomers derived from renewable resources: thermal behavior comparison with PET and PEN. *Phys. Chem. Chem. Phys.* **2014**, *16*, 7946–7958.
- (8) Papageorgiou, G. Z.; Papageorgiou, D. G.; Tsanaktis, V.; Bikiaris, D. N. Synthesis of the bio-based polyester poly(propylene 2,5-furandicarboxylate). Comparison of thermal behavior and solid state structure with its terephthalate and naphthalate homologues. *Polymer* **2015**, *62*, 28–38.
- (9) Papageorgiou, G. Z.; Papageorgiou, D. G.; Terzopoulou, Z.; Bikiaris, D. N. Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties. *Eur. Polym. J.* **2016**, *83*, 202–229.
- (10) Wang, J. G.; Liu, X. Q.; Zhang, Y. J.; Liu, F.; Zhu, J. Modification of poly(ethylene 2,5-furandicarboxylate) with 1,4-cyclohexanedimethylene: Influence of composition on mechanical and barrier properties. *Polymer* **2016**, *103*, 1–8.
- (11) Burgess, S. K.; Kriegel, R. M.; Koros, W. J. Carbon dioxide sorption and transport in amorphous poly(ethylene furanoate). *Macromolecules* **2015**, *48*, 2184–2193.
- (12) Burgess, S. K.; Karvan, O.; Johnson, J. R.; Kriegel, R. M.; Koros, W. J. Oxygen sorption and transport in amorphous poly(ethylene furanoate). *Polymer* **2014**, *55*, 4748–4756.
- (13) de Jong, E.; Dam, M. A.; Sipos, L.; Gruter, G. J. M. Furandicarboxylic acid (FDCA), a versatile building block for a very interesting class of polyesters. In *Biobased monomers, polymers, and materials*; Smith, P., Gross, R. A., Eds.; ACS Symposium Series; American Chemical Society: Washington, DC, 2012.
- (14) Eerhart, A. J. J. E.; Faaij, A. P. C.; Patel, M. K. Replacing fossil based PET with bio-based PEF; process analysis, energy and GHG balance. *Energy Environ. Sci.* **2012**, *5*, 6407–6422.
- (15) Gubbels, E.; Jasinska-Walc, L.; Noordover, B. A. J.; Koning, C. E. Linear and branched polyester resins based on dimethyl-2,5-furandicarboxylate for coating applications. *Eur. Polym. J.* **2013**, *49*, 3188–3198.
- (16) Terzopoulou, Z.; Karakatsianopoulou, E.; Kasmi, N.; Tsanaktis, V.; Nikolaidis, N.; Kostoglou, M.; Papageorgiou, G. Z.; Lambropoulou, D. A.; Bikiaris, D. N. Effect of catalyst type on molecular weight increase and coloration of poly(ethylene furanoate) biobased polyester during melt polycondensation. *Polym. Chem.* **2017**, *8*, 6895–6908.
- (17) Kasmi, N.; Papageorgiou, G. Z.; Achilias, D. S.; Bikiaris, D. N. Solid-state polymerization of poly(ethylene furanoate) biobased polyester, II: An efficient and facile method to synthesize high molecular weight polyester appropriate for food packaging applications. *Polymers* **2018**, *10*, 471.
- (18) Rosenboom, J.-G.; Hohl, D. K.; Fleckenstein, P.; Storti, G.; Morbidelli, M. Bottle-grade polyethylene furanoate from ring-opening polymerisation of cyclic oligomers. *Nat. Commun.* **2018**, *9*, 2701.
- (19) Hong, S.; Min, K.-D.; Nam, B.-U.; Park, O. O. High molecular weight bio furan-based co-polyesters for food packaging applications. *Green Chem.* **2016**, *18*, 5142–5150.
- (20) Knoop, R. J. I.; Vogelzang, W.; van Haveren, J.; van Es, D. S. High molecular weight poly(ethylene 2,5-furanoate): critical aspects in synthesis and mechanical property determination. *J. Polym. Sci., Part A: Polym. Chem.* **2013**, *51*, 4191–4199.
- (21) Wang, G. Q.; Jiang, M.; Zhang, Q.; Wang, R.; Zhou, G. Y. Biobased copolyesters: synthesis, crystallization behavior, thermal and mechanical properties of poly(ethylene glycol sebacate-co-ethylene glycol 2,5-furandicarboxylate). *RSC Adv.* **2017**, *7*, 13798–13807.
- (22) Wang, G. Q.; Jiang, M.; Zhang, Q.; Wang, R.; Zhou, G. Y. Bio-based multiblock copolymers: Synthesis, properties and shape memory performance of poly(ethylene 2,5-furandicarboxylate)-b-poly(ethylene glycol). *Polym. Degrad. Stab.* **2017**, *144*, 121–127.
- (23) Wang, J. G.; Liu, X. Q.; Jia, Z.; Liu, Y.; Sun, L. Y.; Zhu, J. Synthesis of bio-based poly(ethylene 2,5-furandicarboxylate) copolyesters: Higher glass transition temperature, better transparency, and good barrier properties. *J. Polym. Sci., Part A: Polym. Chem.* **2017**, *55*, 3298–3307.
- (24) Jiang, M.; Liu, Q.; Zhang, Q.; Ye, C.; Zhou, G. Y. A series of furan-aromatic polyesters synthesized via direct esterification method based on renewable resources. *J. Polym. Sci., Part A: Polym. Chem.* **2012**, *50*, 1026–1036.
- (25) Chen, Y.; Jiang, M.; Sun, C. J.; Zhang, Q.; Fu, Z. P.; Xu, L.; Zhou, G. Y. Preparation and characterization of poly(ethylene 2,5-furandicarboxylate)/poly(butylene succinate) blends. *Chin. J. Appl. Chem.* **2015**, *32*, 1022–1027.
- (26) Pouloupoulou, N.; Kasmi, N.; Bikiaris, D. N.; Papageorgiou, D. G.; Floudas, G.; Papageorgiou, G. Z. Sustainable polymers from renewable resources: polymer blends of furan-based polyesters. *Macromol. Mater. Eng.* **2018**, *303*, 1800153.
- (27) Xie, H. Z.; Wu, L. B.; Li, B. G.; Dubois, P. Poly(ethylene 2,5-furandicarboxylate-*mb*-poly(tetramethylene glycol)) multiblock copolymers: From high tough thermoplastics to elastomers. *Polymer* **2018**, *155*, 89–98.
- (28) Xie, H. Z.; Wu, L. B.; Li, B. G.; Dubois, P. Bio-based poly(ethylene-co-hexamethylene 2,5-furandicarboxylate) (PEHF) copolyesters with superior tensile properties. *Ind. Eng. Chem. Res.* **2018**, *57*, 13094–13102.
- (29) Wang, J. G.; Liu, X. Q.; Jia, Z.; Sun, L. Y.; Zhang, Y. J.; Zhu, J. Modification of poly(ethylene 2,5-furandicarboxylate) (PEF) with 1,4-cyclohexanedimethanol: Influence of stereochemistry of 1,4-cyclohexylene units. *Polymer* **2018**, *137*, 173–185.
- (30) Wang, X. S.; Wang, Q. Y.; Liu, S. Y.; Wang, G. Y. Bio-based copolyesters: Synthesis, structure, thermal and mechanical properties of poly(ethylene 2,5-furandicarboxylate-co-ethylene 1,4-cyclohexanedicarboxylate). *Polym. Degrad. Stab.* **2018**, *154*, 96–102.
- (31) van Berkel, J. G.; Guigo, N.; Kolstad, J. J.; Sbirrazzuoli, N. Biaxial orientation of poly(ethylene 2,5-furandicarboxylate): An Explorative Study. *Macromol. Mater. Eng.* **2018**, *303*, 1700507.
- (32) Terzopoulou, Z.; Tsanaktis, V.; Bikiaris, D. N.; Exarhopoulos, S.; Papageorgiou, D. G.; Papageorgiou, G. Z. Bio-based poly(ethylene furanoate-co-ethylene succinate) copolyesters: solid state structure, melting point depression and biodegradability. *RSC Adv.* **2016**, *6*, 84003–84015.
- (33) Wu, B. S.; Xu, Y. T.; Bu, Z. Y.; Wu, L. B.; Li, B. G.; Dubois, P. Bio-based poly(butylene 2,5-furandicarboxylate) and poly(butylene adipate-co-butylene 2,5-furandicarboxylate): From synthesis using highly purified 2,5-furandicarboxylic acid to thermo-mechanical properties. *Polymer* **2014**, *55*, 3648–3655.
- (34) Tsanaktis, V.; Papageorgiou, G. Z.; Bikiaris, D. N. A facile method to synthesize high-molecular-weight bio-based polyesters

from 2,5-furandicarboxylic acid and long-chain diols. *J. Polym. Sci., Part A: Polym. Chem.* **2015**, *53*, 2617–2632.

(35) Ma, J. P.; Pang, Y.; Wang, M.; Xu, J.; Ma, H.; Nie, X. The copolymerization reactivity of diols with 2,5-furandicarboxylic acid for furan-based copolyester materials. *J. Mater. Chem.* **2012**, *22*, 3457–3461.

(36) Liu, S. B.; Amada, Y.; Tamura, M.; Nakagawa, Y.; Tomishige, K. Performance and characterization of rhenium-modified Rh–Ir alloy catalyst for one-pot conversion of furfural into 1,5-pentanediol. *Catal. Sci. Technol.* **2014**, *4*, 2535–2549.

(37) Tsanakis, V.; Terzopoulou, Z.; Nerantzaki, M.; Papageorgiou, G. Z.; Bikiaris, D. N. New poly(pentylene furanoate) and poly-(heptylene furanoate) sustainable polyesters from diols with odd methylene groups. *Mater. Lett.* **2016**, *178*, 64–67.

(38) Lu, J.; Zhou, L. Z.; Xie, H. Z.; Wu, L. B.; Li, B. G. Bio-based flexible aromatic polyester poly(1,5-pentylene terephthalate) (PPeT): Revisiting melt crystallization behaviors and thermo-mechanical properties. *Eur. Polym. J.* **2019**, *110*, 168–175.

(39) Lu, J.; Wu, L. B.; Li, B. G. High molecular weight polyesters derived from bio-based 1,5-pentanediol and a variety of aliphatic diacids: Synthesis, characterization and thermo-mechanical properties. *ACS Sustainable Chem. Eng.* **2017**, *5*, 6159–6166.

(40) Wu, J. P.; Xie, H. Z.; Wu, L. B.; Li, B. G.; Dubois, P. DBU-catalyzed bio-based poly(ethylene 2,5-furandicarboxylate) polyester with rapid melt crystallization: synthesis, crystallization kinetics and melting behavior. *RSC Adv.* **2016**, *6*, 101578–101586.

(41) Maini, L.; Gigli, M.; Gazzano, M.; Lotti, N.; Bikiaris, D. N.; Papageorgiou, G. Z. Structural investigation of poly(ethylene furanoate) polymorphs. *Polymers* **2018**, *10*, 296.

(42) Jiang, M.; Lu, T. T.; Jiang, G. W.; Zhang, Q.; Zhou, G. Y. Synthesis and characterization of poly(ethylene terephthalate-co-ethylene 2,5-furandicarboxylate). *Acta Polym. Sin.* **2013**, *43*, 1092–1098.

(43) Baek, S.-S.; Kim, M.-J.; Kim, O. Y.; Kang, D. W.; Kang, H.-J.; Jeong, K.-U.; Hwang, S.-H. Synthesis of polyesters based on furan moiety as renewable resource and their thermal and physical properties. *Abstracts of Papers of the American Chemical Society* **2012**, *243*, 379-PMSE.

(44) Terzopoulou, Z.; Tsanakis, V.; Nerantzaki, M.; Papageorgiou, G. Z.; Bikiaris, D. N. Decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and aliphatic diols with medium and long chain methylene groups. *Polym. Degrad. Stab.* **2016**, *132*, 127–136.

(45) Terzopoulou, Z.; Tsanakis, V.; Nerantzaki, M.; Achilias, D. S.; Vaimakis, T.; Papageorgiou, G. Z.; Bikiaris, D. N. Thermal degradation of bio-based polyesters: Kinetics and decomposition mechanism of polyesters from 2,5-furandicarboxylic acid and long-chain aliphatic diols. *J. Anal. Appl. Pyrolysis* **2016**, *117*, 162–175.

(46) Tsanakis, V.; Vouvoudi, E.; Papageorgiou, G. Z.; Papageorgiou, D. G.; Chrissafis, K.; Bikiaris, D. N. Thermal degradation kinetics and decomposition mechanism of polyesters based on 2,5-furandicarboxylic acid and low molecular weight aliphatic diols. *J. Anal. Appl. Pyrolysis* **2015**, *112*, 369–378.

(47) Karayannidis, G. P.; Papachristos, N.; Bikiaris, D. N.; Papageorgiou, G. Z. Synthesis, crystallization and tensile properties of poly(ethylene terephthalate-co-2,6-naphthalate)s with low naphthalate units content. *Polymer* **2003**, *44*, 7801–7808.

(48) Torres, N.; Robin, J. J.; Boutevin, B. Study of thermal and mechanical properties of virgin and recycled poly(ethylene terephthalate) before and after injection molding. *Eur. Polym. J.* **2000**, *36*, 2075–2080.

(49) Hong, S.; Min, K.-D.; Nam, B.-U.; Park, O. O. High molecular weight bio furan-based co-polyesters for food packaging applications. *Green Chem.* **2016**, *18*, 5142–5150.

(50) Tsaiab, Y.; Fan, C.-H.; Hung, C.-Y.; Tsai, F.-J. Synthesis and characterization of amorphous poly(ethylene terephthalate) copolymers containing bis[4-(2-hydroxyethoxy)phenyl]sulfone. *Eur. Polym. J.* **2009**, *45*, 115–122.

(51) Kint, D. P. R.; Alla, A.; Deloret, E.; Campos, J. L.; Muñoz-Guerra, S. Synthesis, characterization, and properties of poly(ethylene terephthalate)/poly(1,4-butylene succinate) block copolymers. *Polymer* **2003**, *44*, 1321–1330.

(52) Bikiaris, D. N.; Karayannidis, G. P. Synthesis and characterisation of branched and partially crosslinked poly(ethylene terephthalate). *Polym. Int.* **2003**, *52*, 1230–1239.

(53) Papageorgiou, G. Z.; Papageorgiou, D. G.; Terzopoulou, Z.; Bikiaris, D. N. Production of bio-based 2,5-furan dicarboxylate polyesters: Recent progress and critical aspects in their synthesis and thermal properties. *Eur. Polym. J.* **2016**, *83*, 202–229.

(54) Chen, J.; Yang, W. Y.; Li, X. Y. The performance modification of SBR with nano calcium carbonate. *J. Gansu Petrochem. Ind.* **2007**, *3*, 25–27.

(55) Huang, Y. H. Study on the Performances of aging on bottle-grade PET. Master's Thesis, Qingdao University of Science and Technology, Qingdao, Shandong, China, 2017.

(56) Wu, L. B.; Mincheva, R.; Xu, Y. T.; Raquez, J. M.; Dubois, P. High molecular weight poly(butylene succinate-co-butylene furandicarboxylate) copolyesters: From catalyzed polycondensation reaction to thermomechanical properties. *Biomacromolecules* **2012**, *13*, 2973–2981.

(57) van Krevelen, D. W.; te Nijenhuis, K. *Properties of Polymers: Their correction with chemical structure, Their numerical estimation and prediction from additive group contribution*, 4th ed.; Elsevier: Amsterdam, The Netherlands, 2009; pp 655–702.

(58) Salame, M. Prediction of gas barrier properties of high polymers. *Polym. Eng. Sci.* **1986**, *26*, 1543–1546.

(59) Burgess, S. K.; Leisen, J. E.; Kraftschik, B. E.; Mubarak, C. R.; Kriegel, R. M.; Koros, W. J. Chain mobility, thermal, and mechanical properties of poly(ethylene furanoate) compared to poly(ethylene terephthalate). *Macromolecules* **2014**, *47*, 1383–1391.

(60) Light, R. R.; Seymour, R. W. Effect of sub-T<sub>g</sub> relaxations on the gas transport properties of polyesters. *Polym. Eng. Sci.* **1982**, *22*, 857–864.

(61) Liu, R. Y. F.; Hiltner, A.; Baer, E. Free volume and oxygen transport in cold-drawn polyesters. *J. Polym. Sci., Part B: Polym. Phys.* **2004**, *42*, 493–504.