

# Chemosynthesis and Characterization of Fully Biomass-Based Copolymers of Ethylene Glycol, 2,5-Furandicarboxylic Acid, and Succinic Acid

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**ABSTRACT:** Poly(ethylene 2,5-furandicarboxylate-co-ethylene succinate) (PEFS) copolymers of 2,5-furandicarboxylic acid (FDCA) and succinic acid with 11.98–91.32 mol % FDCA composition were synthesized via melt polycondensation in the presence of ethylene glycol using tetrabutyl titanate as a catalyst. PEFSs' molecular weight, thermal properties, and molar composition were determined by Fourier transform infrared spectroscopy, gel permeation chromatography, intrinsic viscosity, <sup>1</sup>H NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and wide-angle X-ray diffraction (WAXD) measurements. From experimental conditions, we obtained random copolymers with number-average molecular weights exceeding 25,600, determined by GPC and <sup>1</sup>H NMR analyses. DSC analysis revealed that PEFS copolymers' melting temperatures differed depending on EF units' percentage. TGA studies confirmed that all PEFS copolymers' thermal stability exceeded 300°C. From WAXD analysis, it is observed that the PEFS copolymer crystal structure was similar to that of PES when EF unit was 11.98 mol % and to that of PEF when EF units were 74.35 and 91.32 mol %. These results benefit this novel biodegradable copolymer to be used as a potential biomaterial. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1415–1420, 2013

**KEYWORDS:** 2,5-furan dicarboxylic acid; poly(ethylene 2,5-furan dicarboxylate-co-ethylene succinate); synthesis; characterization; thermal properties

Received 13 February 2013; accepted 30 March 2013; Published online 26 April 2013

DOI: 10.1002/app.39344

## INTRODUCTION

Interest in studying renewable resources and biodegradable materials has arisen owing to the growing emphasis on environmental and sustainability issues concerning petroleum-based feed stocks.<sup>1–4</sup> Poly(ethylene terephthalate) (PET), which is an important material in daily life, is used in textile fibers, films, packaging, and medical applications.<sup>5–7</sup> However, there is a concern regarding the environmental pollution associated with this polymer,<sup>8</sup> because production of the terephthalic acid unit of PET consumes petrochemical resources, and the PET degradation in the natural environment requires several decades.<sup>9</sup> However, the physicochemical properties of PET can be modified by copolymerization, graft, and blend methods.<sup>10–12</sup> These modified PET polymers can be partly or completely degraded in water, acid, alkali, and alcohol media.<sup>13–18</sup> At present, however, the abovementioned methods have not yet been employed in industrial processes<sup>13</sup>; instead, the focus has been on finding the substitutes for PET.

Poly(ethylene 2,5-furandicarboxylate) (PEF) is a novel saturated polyester prepared via the condensation polymerization of ethylene glycol (EG) and 2,5-furandicarboxylic acid (FDCA) or

dimethyl 2,5-furandicarboxylate.<sup>19</sup> The physicochemical properties of PEF are similar to those of PET, and PEF can be derived from natural, biobased sources. For example, lower dihydric alcohols such as EG can be obtained via the fermentation of biomass,<sup>20,21</sup> whereas FDCA can be prepared using several different routes. In one case, 5-hydroxymethylfurfural (HMF) is obtained from monosaccharides or polysaccharides using water, an organic phase, and an ionic liquid.<sup>22–24</sup> Further oxidation transforms HMF into FDCA with 100% of recovery.<sup>25–28</sup> In second method, FDCA is prepared from pyromucic acid via a disproportionation or acyl chloride reaction.<sup>29,30</sup> Dehydration glucaric acid and mucic acid also yield FDCA.<sup>31–33</sup> Finally, FDCA can be manufactured via the fermentation of HMF.<sup>34</sup>

Recently, the physicochemical properties of PEF have been investigated.<sup>35,36</sup> The effect of different catalysts on the polymerization reacting to produce PEF have also been studied.<sup>37</sup> In addition, the reactivity of 1,4-butanediol with EG has been compared to that of FDCA.<sup>38</sup> As to improve the crystallinity and flexibility of PET and poly(butylene terephthalate) with aliphatic dicarboxylic acid,<sup>39,40</sup> this study selected succinic acid (SA) fermented from biomass to modify PEF.<sup>41</sup>

Herein, we report a new poly(ethylene 2,5-furandicarboxylate-co-ethylene succinate) (PEFS) copolymers prepared via the melt condensation reaction of FDCA, EG, and SA. The synthesized copolymers were characterized using gel permeation chromatography (GPC), intrinsic viscosity, FTIR,  $^1\text{H}$  NMR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and wide-angle X-ray diffraction (WAXD) measurements. The solubility of the copolymers was also studied.

## EXPERIMENTAL

### Materials

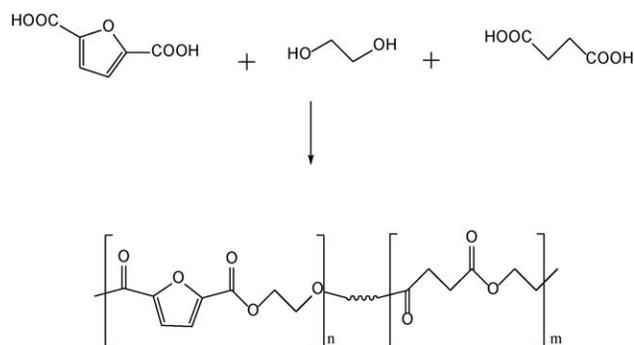
FDCA (99%) was provided by Chemget Chemical (China) and was used after recrystallization from hot water. EG (99%) and SA (99%) were supplied by Sinopharm Chemical Reagent (China). The catalyst tetra-*n*-butyl-titanate ( $\text{Ti}(\text{O}i\text{Bu})_4$ ) (98%) was obtained from Aladdin Reagent (China). All other reagents were used as received unless otherwise indicated.

### Characterization

FTIR spectra were recorded on a Nicolet 380 FTIR spectrometer using solution cast films on KBr disks. The intrinsic viscosity was measured at  $25^\circ\text{C}$  on an Ubbelohde viscometer using 0.1 g/dL of polymer solution in phenol/tetrachloroethane (60/40, w/w). The number-average molecular mass ( $M_n$ ) and the polydispersity ( $M_w/M_n$ ) of the polymers were determined by GPC (Dionex P680 series) on a G3000H<sub>XL</sub> column using a refractive index detector at  $50^\circ\text{C}$  and a calibration curve constructed with linear polystyrene standards (Polymer, Germany). The samples were dissolved in 1 mL of trifluoroacetic acid, and then chloroform was added to obtain a total volume of 10 mL at a concentration of 1 mg/mL. Chloroform was used as the eluent at a flow rate of 1 mL/min, and the samples were filtered using a microporous membrane (pore size, 0.45  $\mu\text{m}$ ) before injection.  $^1\text{H}$  NMR spectra were obtained using an Avance AV-400 instrument at 400 MHz. DSC and TGA were conducted using an STA 449 C at a heating rate of  $10^\circ\text{C}/\text{min}$  under a nitrogen flow. WAXD was recorded on an XRD-6000 X-ray diffractometer (50 kV/180 mA) for the semicrystalline polyester samples. Nickel-filtered Cu K $\alpha$  X-ray beams with a pinhole graphite monochromator were applied as the source ( $\lambda = 0.154$  nm).

### Synthesis of PEFS Copolymers

PEFS copolymers were synthesized via melt polymerization using  $\text{Ti}(\text{O}i\text{Bu})_4$  as a catalyst (Scheme 1). FDCA/SA in different feed ratios (total moles of acid, 0.1M), EG (diacid/dialcohol, 1/2.5), and  $\text{Ti}(\text{O}i\text{Bu})_4$  (FDCA and SA, 0.3 wt %) were added to a four-necked, 150-mL flask with a mechanical stirrer, nitrogen inlet, a thermometer, and a condenser. The PEFS copolymers were coded as PEFS-10, PEFS-30, PEFS-50, PEFS-70, and PEFS-90 for the polymers with ethylene 2,5-furandicarboxylate/ethylene succinate (EF/ES) ratios of 10/90, 30/70, 50/50, 70/30, and 90/10, respectively. Before heating, the flask was evacuated and purged with dry nitrogen three times to ensure a total nitrogen atmosphere. Next, the flask was placed into a temperature-controlled oil bath at  $180^\circ\text{C}$ . The esterification was assumed to be complete when water being produced during the reaction, which was collected in a trap, reached 95% of the theoretical maximum value. In the subsequent polycondensation process, the temperature was rapidly raised to the final reaction



Scheme 1. Synthesis of PEFS.

temperature of  $240^\circ\text{C}$  at a pressure of 100 Pa, and these conditions were maintained for 4 h. The highly viscous products were then cooled in the flask under a nitrogen atmosphere.

The polymer products were then dissolved in  $\text{CHCl}_3$  (or  $\text{CHCl}_3$  with a certain amount of added trifluoroacetic acid in the case of PEFS-70 and PEFS-90), precipitated using excess methanol, filtered, washed with methanol, and then dried to a constant weight.

PEFS copolymers:  $^1\text{H}$  NMR (400 MHz, TFA- $d_3$ ,  $\delta$  ppm): 2.66 (t, 4H,  $\text{OOCCH}_2\text{CH}_2\text{COO}$ ), 4.17–4.42 (t, 4H,  $\text{CH}_2\text{CH}_2$ —SA), 4.53–4.65 (t, 4H,  $\text{CH}_2\text{CH}_2$ —FDCA), 7.26 (d, 2H, Furan). FTIR (KBr,  $\text{cm}^{-1}$ ): 3125 ( $=\text{CH}$ ); 2963 (C—H); 1738 (C=O); 1682, 1582 (C=C); 1279, 1206, 1157, 1049 (C—O); 968, 833, 767 ( $=\text{CH}$ ).

## RESULTS AND DISCUSSION

### Synthesis of PEFS Copolymers

In this study, a series of PEFS copolymers were synthesized with various EF unit compositions using  $\text{Ti}(\text{O}i\text{Bu})_4$  as a catalyst. According to the previous study, we selected nontoxic tetrabutyl titanate as a catalyst to catalyze two-step reaction. In the first step, or the esterification reaction, excess EG was used to accelerate the reaction, and the reaction temperature was maintained at  $180^\circ\text{C}$  for 3–4 h. In the second step, or the polycondensation reaction, the temperature was raised to  $240^\circ\text{C}$  and the reaction was stirred under a slight vacuum for 0.5 h to remove excess EG. The vacuum was then increased and the reaction was stirred for 4 h, during which time the polycondensation reaction produced different copolymers depending on the feeding composition. The reaction sequence for the synthesis of the copolymers is shown in Scheme 1.

Table I summarizes the change in the intrinsic viscosities and molecular weights of the synthesized copolymers with various EF and ES unit compositions. The synthesized copolymers were purified by first dissolving them in chloroform (PEFS-10, PEFS-30, and PEFS-50) or chloroform and a certain amount of trifluoroacetic acid (PEFS-70 and PEFS-90), and then precipitating with methanol to remove the low-molecular-weight components and any traces of catalyst. Copolymers with intrinsic viscosities between 0.84 and 1.26 dL/g were obtained. The number-average molecular weight of the copolymers ranged from 2.56 to  $5.76 \times 10^{-4}$  g/mol, and the polydispersity index ranged from 1.28 to

**Table I.** Physical Properties of the PEFS Copolymers

Sample	(EF/ES)	$M_n (\times 10^{-4})$	$M_w/M_n$	$[\eta]$ (dL/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_d$ (°C)
1	10/90	4.12	1.42	0.84	72.10	42.13	428
2	30/70	5.74	1.28	1.20	21.92	0.477	378
3	50/50	4.25	1.50	1.04	32.36	0.535	386
4	70/30	3.93	1.66	1.26	146.26	37.95	438
5	90/10	2.56	1.40	1.04	172.90	54.15	392

1.66 as summarized in Table I and Figure 1. On the basis of the variation in the  $M_n$  values, it can be concluded that, as the FDCA content increased, the esterification of FDCA became more difficult than that of SA.

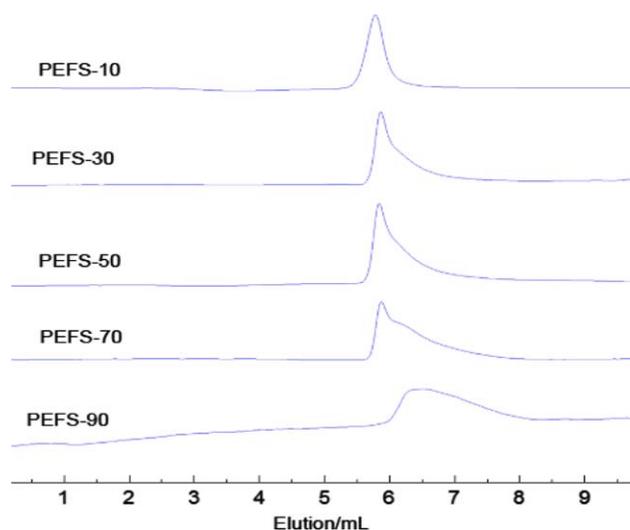
The resulting copolymers were characterized via FTIR. The FTIR spectra shown in Figure 2 provided evidence for the chemical structure of the PEFS copolymers, with the characteristic absorptions of the furan ring at 3128, 1582, 1027, 967, 833, and 766  $\text{cm}^{-1}$ , and that of the ester carbonyl at 1738  $\text{cm}^{-1}$ .<sup>35</sup> The additional ES units in the PEFS copolymers (compared to PEF) are indicated by two strong absorption bands at 1738 and 1682  $\text{cm}^{-1}$ . Notably, as the content of the ES units increased, the intensity of the IR absorption bands for the furan group was decreased, whereas for that of O—C group it was increased at 1280  $\text{cm}^{-1}$ .

The  $^1\text{H}$  NMR spectra of the PEFS copolymers are shown in Figure 3, along with the corresponding assignments. The signals at  $\delta = 7.74$  and 3.22 ppm represent the methine protons of the furan ring and methylene protons of SA, respectively, whereas those signals at  $\delta = 5.15$ –5.05 and 4.95–4.79 ppm represent the methylene protons of EG in EF and ES units, respectively. As the content of the EF units increased, the vibrational intensity of the furan methine protons also increased, whereas that of EG methine proton gradually increased.

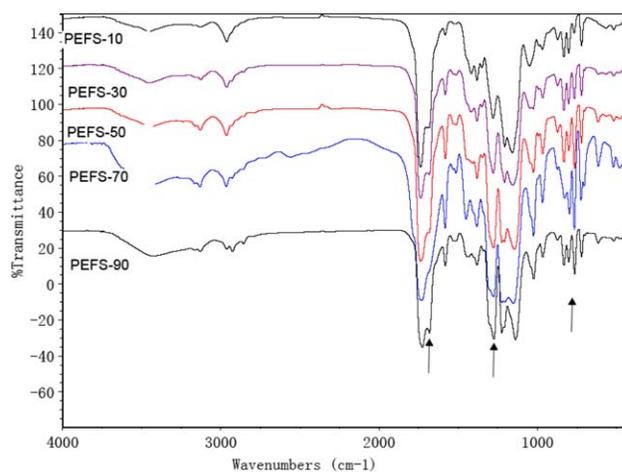
Using the signals of  $^1\text{H}$  NMR spectra, the content of the three possible triad sequences, FEF, FES, and SES, in the PEFS copolymers was calculated from the normalized areas, and the values

are listed in Table II for samples 1–5. The assignment of the triads was conducted according to the previously published literature.<sup>42,43</sup> From these data, it was possible to conclude that the sample PEFS-30 was a random copolymer, as indicated by  $L_B$ ,  $L_S$ , and DR values (Table II), which practically coincide with the theoretically expected values. The distribution of the EF and ES units in these copolyesters can, therefore, be regarded as random.

Figure 4 shows the DSC thermograms for the PEFS copolymers of varying EF contents recorded during the first heating run. The DSC results are also summarized in Table I. The melting points of PES and PEF are approximately 114 and 215°C, respectively.<sup>44,45</sup> The  $T_m$  and  $\Delta H_m$  values for the copolymers have an inevitable relationship with the average sequence length of their chain segments. When the EF content was 10 mol %, the ES segment was a major component, and crystalline regions were primarily formed by the ES segment. When the EF content increased, to the levels contained in the PEFS-30 and PEFS-50 copolymers, the  $T_m$  values were significantly lower than that of PES. As the increased EF content inhibited the formation of crystalline regions by the ES units (Figure 6), no sharp peaks were observed in the WAXD spectra for these polymers. When the EF content increased to 50 mol %, the  $T_m$  of the copolymers increased again, and was between those for PES and PEF. In addition, there was a crystalline phase change temperature observed for PEFS-90. It should be noted that the cold crystallization of the copolymers required an extensive period of time and thus the second heating curves were far from ideal.



**Figure 1.** GPC curves of the PEFS copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 2.** FTIR spectra of the PEFS copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

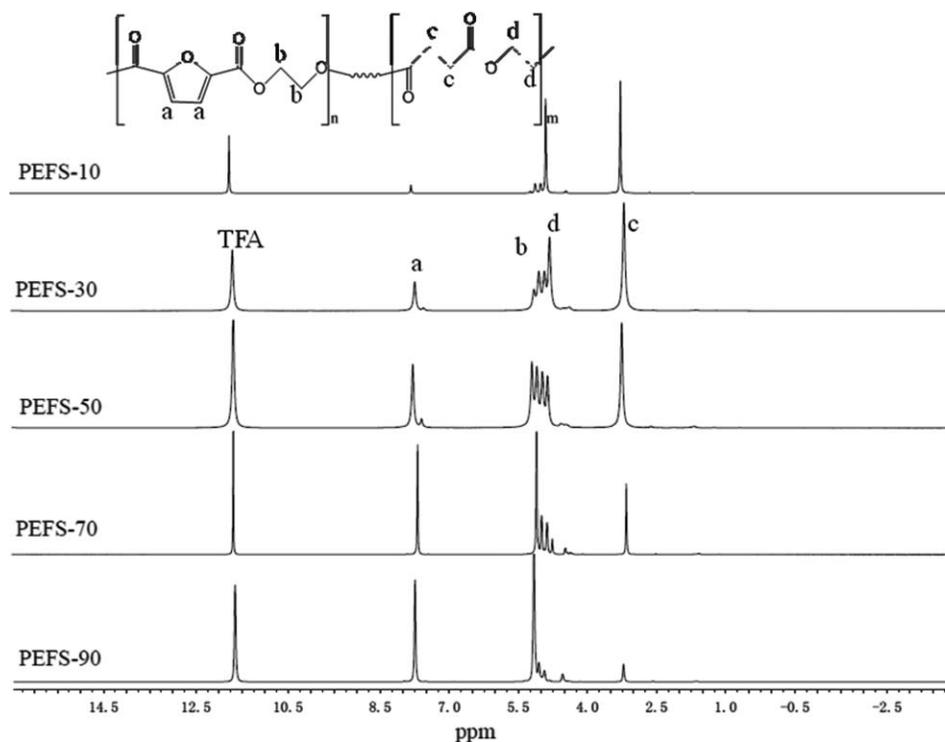


Figure 3.  $^1\text{H}$  NMR spectrum of the PEFS copolymers at 400 MHz.

It is well known that the thermal degradation behavior and stability of biodegradable polymers are of great importance for determining their potential application. Thus, to quantitatively assess the thermal stabilities of the new copolyesters, typical weight loss curves as a function of temperature were obtained under a nitrogen atmosphere. Selected results are shown in Figure 5, and the data obtained for all copolyesters are compared in Table I. As shown in Figure 5, the weight loss occurs practically in one step. All copolyesters were stable up to approximately  $300^\circ\text{C}$  and their decomposition temperature ( $T_d$ ) was about  $400^\circ\text{C}$ . These copolymers exhibited no significant differences or trends because the experiment depends on the size, shape, and crystallinity of the specimens.

The crystalline structure of the polymers has a significant impact on their mechanical properties and biodegradability. Therefore, WAXD patterns of the PEFS copolymers were

detected as shown in Figure 6. It has been reported that the WAXD patterns of PEF and PES homopolymers show prominent diffraction peaks at  $2\theta = 16.0, 20.1,$  and  $27.8^\circ$  and  $2\theta = 20.2, 22.2$  (021),  $22.6$  (110), and  $23.3^\circ$  (111), respectively.<sup>44,45</sup> PEFS-10 showed well-defined sets of crystalline diffraction peaks similar to those reported for PES. On the contrary, when the number of EF units increased, such as in PEFS-30 and PEFS-50, the copolymers appeared to be completely amorphous. As PEF and PES belong to different crystalline forms (triclinic and

Table II. Average Block Length and Degree of Randomness of the PEFS Copolymers with Various EF/ES Molar Ratios

Sample	(EF/ES)	$L_F^a$	$L_S^b$	DR <sup>c</sup>
1	11.98/88.02	1.23	2.73	1.18
2	33.38/66.62	1.64	2.31	1.04
3	52.36/47.64	2.02	1.91	1.02
4	74.35/25.65	2.46	1.50	1.07
5	91.32/8.68	2.79	1.17	1.21

<sup>a</sup>Average block length of EF, <sup>b</sup>Average block length of ES, <sup>c</sup>Degree of randomness.

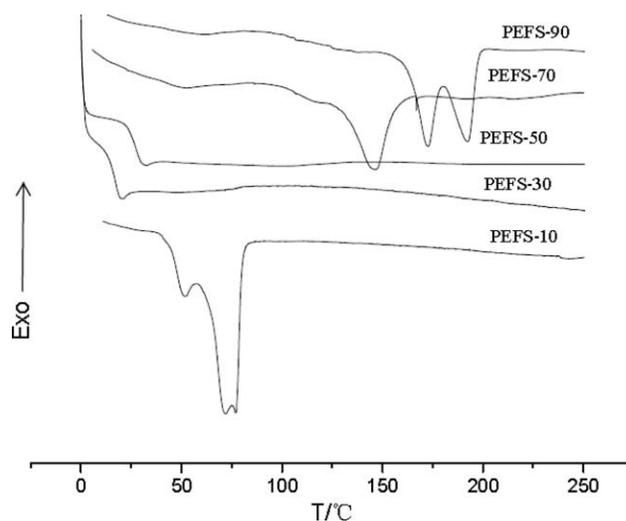
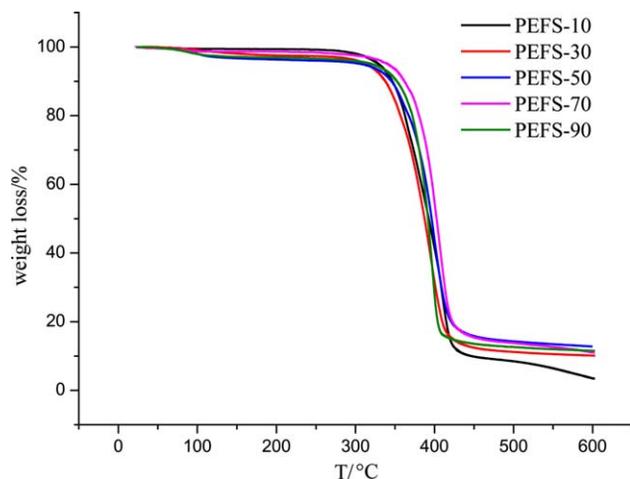


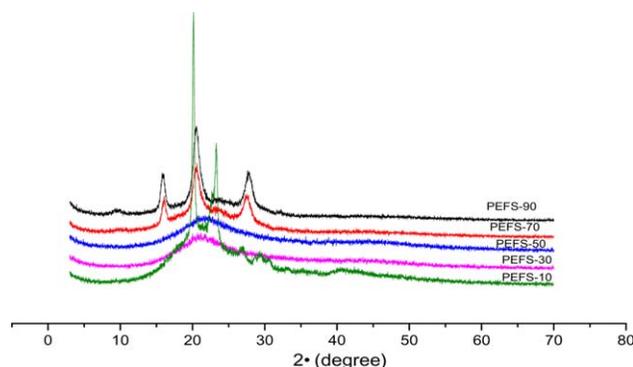
Figure 4. DSC traces of the PEFS copolymers recorded during the first heating run.



**Figure 5.** Thermal stability of the PEFS copolymers. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

monoclinic, respectively), they each disturb the structure of the other, and therefore crystallization does not occur in these copolymers. However, when the number of EF units is higher, such as PEFS-70 and PEFS-90, well-defined sets of crystalline diffraction peaks similar to those reported for PEF appeared. It should be noted that the properties of the PEFS copolymers are different from those of aromatic and aliphatic copolymers (e.g., poly(butylene succinate-*co*-terephthalate)).<sup>46</sup> These WAXD results confirm that the crystalline phase that develops in the copolyesters is related to the lattice characteristic of the ethylene 2,5-furandicarboxylate units.

Finally, the solubility of the PEFS copolymers was tested in various organic solvents at 20 wt % concentration and the data are summarized in Table III. All the copolymers were completely soluble in TFA, completely insoluble in toluene, and barely soluble in acetone. However, the PEFS copolymers synthesized using EF feed ratios up to 50% were soluble in DMSO, DMF, and CHCl<sub>3</sub>. These PEFS copolymers with a lower EF content behaved more like PES. When the EF feed ratio reached 70%, the PEFS copolymers exhibited the solubility behavior similar to that of PEF.



**Figure 6.** WAXD patterns of the PEFS copolymers determined at room temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Table III.** Solubilities of the PEFS Copolymers

	DMSO	DMF	Acetone	CHCl <sub>3</sub>	Toluene	TFA
PEFS-10	+	+	±	+	-	+
PEFS-30	+	+	±	+	-	+
PEFS-50	+	+	-	±	-	+
PEFS-70	+	±	-	-	-	+
PEFS-90	-	-	-	-	-	+

+ : Soluble; ± : partially soluble or swelled; - : insoluble.

## CONCLUSIONS

A variety of novel biodegradable copolymers were synthesized via melt polycondensation using a series of EF/ES molar ratios. Their chemical structures were verified using FTIR, intrinsic viscosity, GPC, and <sup>1</sup>H NMR analyses. GPC analysis suggested that all PEFS copolymers had number-average molecular weights of more than 25,600 and narrow molecular weight distributions. The <sup>1</sup>H NMR results indicated compositions ranging from 11.98 to 91.32 mol % of EF units and that the copolymers were random. The thermal properties of the PEFS copolymers were determined using DSC and TGA, and it was found that *T<sub>m</sub>*s of PEFS-30 and PEFS-50 were significantly lower than that of PES. In addition, all copolyesters were shown to be stable up to 300°C. Furthermore, the WAXD patterns indicated that the crystalline structure of PEFS copolymers was similar to that of PES when the EF content was 10 mol % and to that of PEF when the EF content was 70 mol %, but the PEFS copolymers appeared to be completely amorphous when EF contents were 30 and 50 mol %. Finally, the PEFS copolymers exhibited variable solubilities in different organic solvents.

By adding different amounts of SA for the modification of PEF, we obtained PEFS copolymers with physicochemical properties similar to those of PETS. Thus, PEFS can serve as a suitable alternative to PETS which is completely derived from renewable resources.

## ACKNOWLEDGMENT

The authors acknowledge the financial support from the Project of the National Natural Science Foundation (No. 21106063 and No. 30900009) and the Project of the Natural Science Foundation of Jiangsu Province (No. BK2010557).

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