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Synthesis and Properties Investigation of Thiophene-aromatic Polyesters: Potential Alternatives for the 2,5-Furandicarboxylic Acid-based Ones

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Electronic Supplementary Information

Abstract In order to explore new substitutes for 2,5-furandicarboxylic acid (FDCA) or poly(ethylene 2,5-furandicarboxylate) (PEF) and try to develop more ideal bio-based polyesters, several thiophene-aromatic polyesters (PETH, PPTH, PBTH, and PHTH) were synthesized from dimethyl thiophene-2,5-dicarboxylate (DMTD) and different diols, including ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol. The chemical structures of obtained polyesters were confirmed by nuclear magnetic resonance spectroscopy (¹H-NMR and ¹³C-NMR). Determined by GPC measurement, their average molecular weight (M_w) varied from 5.22×10^4 g/mol to 7.94×10^4 g/mol with the molar-mass dispersity of 1.50–2.00. Based on the DSC and TGA results, the synthesized polyesters PETH, PPTH, and PBTH displayed comparable or even better thermal properties when compared with their FDCA-based analogues. From PETH to PHTH, their T_g varied from 64.6 °C to –1 °C while $T_{5\%}$ ranged from 409 °C to 380 °C in nitrogen atmosphere. PETH showed elongation at break as high as 378%, tensile strength of 67 MPa, and tensile modulus of 1800 MPa. Meanwhile, the CO₂ and O₂ barrier of PETH was 12.0 and 6.6 folds higher than those of PET, respectively, and similar to those of PEF. Considering the overall properties, the synthesized thiophene-aromatic polyesters, especially PETH, showed great potential to be used as an excellent bio-based packaging material in the future.

Keywords 2,5-Thiophenedicarboxylic acid (TDCA); 2,5-Furandicarboxylic acid (FDCA); Bio-based polyesters; Barrier properties

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INTRODUCTION

With the rapid development of biotechnology and chemical industry, a large quantity of bio-based monomers, such as ethylene diol,^[1] succinic acid,^[2] adipic acid,^[3] lactic acid,^[4] isosorbide,^[5] and dodecanedioic acid (DDCA),^[6] have been produced and used as the feedstock for polymer synthesis. This strategy has attracted more and more attention due to the increasing concern on fossil resource depletion and serious environmental pollution.^[7,8] Compared with the common petroleum-based engineering plastics including polycarbonate (PC), poly(ethylene terephthalate) (PET), and poly(butylene terephthalate) (PBT), the thermal or mechanical properties of current bio-based polymers are sometimes poor. And the main reason is attributed to the lack of rigid aromatic structure in their architectures.

2,5-Furandicarboxylic acid (FDCA) is a promising bio-based

compound with chemical structure similar to that of terephthalic acid (TPA).^[9,10] It has been selected as one of the top 12 bio-based platform chemicals by US Department of Energy. Up to now, many FDCA-based polymers have been synthesized and reported. Among them, poly(ethylene 2,5-furandicarboxylate) (PEF) might be the most popular polyester derived from FDCA and has been extensively investigated.^[11] When compared with its petroleum-based analogue, PET, besides higher glass transition temperature (87 °C), better tensile modulus and strength,^[12–16] what interests us most is that PEF shows excellent barrier to O₂ and CO₂, 6–11 and 13–19 times higher than that of PET, respectively.^[17,18] However, even with these advantages, the poor crystallizability and low elongation at break (~5%) of PEF seriously limit its practical application. Therefore, different diols and diacids, such as propylene glycol,^[19–22] butylene glycol,^[23–26] 1,5-pentanediol,^[27] hexamethylene glycol,^[28,29] octylene glycol,^[30,31] poly(tetramethylene glycol),^[32] cyclohexanedicarboxylic acid,^[33] succinic acid,^[2] and adipic acid,^[34] were employed to polymerize with FDCA. Results showed that the longer aliphatic diols or diacid indeed enhanced the toughness and

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crystallizability of PEF. However, their thermal resistance, modulus, and strength were decreased dramatically. Alternatively, the cyclic monomers, *e.g.* isosorbide or isoidide,^[35,36] 2,2,4,4-tetramethyl-1,3-cyclobutanediol (CBDO),^[14] and 1,4-cyclohexanedimethylene diol,^[12,37] were also tried to tune the properties of FDCA-based polyesters. As expected, the decrement of thermal and mechanical property could be avoided to some extent with the addition of rigid cyclic compounds.^[12,14,37] Unfortunately, the gas barrier properties of PEF were seriously decreased after the addition of these comonomers.^[12,14] Besides the modification on PEF, exploration of new substitutes for FDCA or PEF, which possess similar or better properties, might be another feasible strategy for the development of high performance bio-based polyesters.

2,5-Thiophenedicarboxylic acid (TDCA) has the chemical structure similar to that of FDCA and also can be synthesized from the renewable glucaric or muconic acid.^[38,39] The only difference between FDCA and TDCA is the heteroatom in the five-membered aromatic-ring, O or S atom. Lotti *et al.* once synthesized poly(propylene 2,5-thiophenedicarboxylate) (PPTH) and poly(butylene 2,5-thiophenedicarboxylate) (PBTH) starting from TDCA, propylene glycol, and butylene glycol.^[40,41] Results showed that both PPTH and PBTH had good gas barrier properties similar to that of PEF due to the non-linear connection between thiophene ring and 1,3-propanediol or 1,4-butanediol. Unfortunately, the reported elongation at break of PPTH was not high enough^[41] and the tensile strength of PBTH was only 24.5 MPa.^[40] In Zhou's group, several TDCA-based copolyesters, including poly(ethylene 2,5-thiophenedicarboxylate-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate) (PECTFs),^[42] poly(butylene 2,5-thiophenedicarboxylate-co-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate) (PBCTFs),^[43] poly(propylene 2,5-thiophenedicarboxylate-co-propylene terephthalate) (PPTTF),^[44] poly(butylene 2,5-thiophenedicarboxylate-co-butylene terephthalate) (PBTTF),^[45] and polyesters based on long chain diols^[46] have been synthesized. In their work, TDCA served as a novel bio-based building block like FDCA, which significantly broadened the property spectrum of bio-based polyesters.

In this work, TDCA was converted into dimethyl thiophene-2,5-dicarboxylate (DMTD) *via* the reaction with methanol, and then TDCA-based homopolyesters, including PETH, PPTH, PBTH, and poly(hexylene 2,5-thiophenedicarboxylate) (PHTH) with high number averaged molecular weight (M_n) of 2.76×10^4 – 5.35×10^4 were synthesized. After that, their overall properties in terms of crystallization behaviors, mechanical performance, CO₂ and O₂ barrier properties were investigated by DSC, TGA, tensile and barrier properties testing. Summarily, the overall properties of TDCA-based polyesters were presented here and it might be a database guiding the devel-

opment of new bio-based polyesters with satisfied performance, especially the excellent gas barrier properties.

EXPERIMENTAL

Materials

Antimony trioxide (III, 99%), zinc acetate (99%), trifluoroacetic acid (99.5%), and methyl alcohol (99.5 %) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). 2,5-TDCA (99%) was purchased from Beijing Hawk Technology Co., Ltd. (Beijing, China). Ethylene glycol (EG, 99 %), 1,3-propanediol (PDO, 99%), 1,4-butanediol (BDO, 99%), and 1,6-hexanediol (HDO, 99%) were purchased from Aladdin Reagent Co., Ltd. (Shanghai, China). All chemicals were used as received without further purification.

Synthesis of Dimethyl Thiophene-2,5-dicarboxylate (DMTD)

2,5-TDCA (344.0 g) and methanol (961 g) together with 10 mL of concentrated sulfuric acid as the catalyst were added into a flask equipped with mechanical stirrer, and the mixture was refluxed at 95 °C for 24 h. When the reaction was cooled down to room temperature, the resulting dimethyl ester was collected by filtration and washed with distilled water for several times. Then, it was dried in a vacuum oven at 80 °C for 4 h to obtain the pure white crystal. The overall yield was calculated to be 86% and its chemical structure was confirmed by NMR. ¹H-NMR (δ , ppm, DMSO): 7.81 (thiophene ring, s, 2H), 3.86 (—CH₃, s, 6H). ¹³C-NMR (δ , ppm, DMSO): 134.2, 138.6 (thiophene ring, 4C), 161.7 (C=O, 2C), 53.3 (—CH₃, 2C).

Synthesis of Thiophene-aromatic Polyesters

PETH, PPTH, PBTH, and PHTH were synthesized by a two-step polycondensation reaction starting from DMTD and EG, PDO, BDO, and HDO. The molar feeding ratio of diol to DMTD was fixed at 1.6, as listed in Table 1. The predetermined DMTD, diols and zinc acetate (0.15 mol% based on DMTD) were added into a 500 mL round flask and purged with nitrogen for three times to get rid of air. After the esterification reaction was conducted at 180 °C for 3 h under the protection of nitrogen, the catalyst antimony trioxide (III) was added (0.15 mol% based on DMTD), and the temperature was increased to 200–220 °C. Then the reaction pressure was gradually decreased to ~10 Pa. The polycondensation process lasted at this condition for 3.0–4.0 h. Finally, the pressure was returned to normal atmospheric pressure with the introduction of N₂ and the target polyesters were obtained. For easy identification, the feeding ratio and reaction conditions for the synthesis of PETH, PPTH, PBTH, and PHTH are listed in Table 1.

Characterization

The composition and chemical structures of synthesized thiophene-aromatic polyesters were confirmed by NMR using a

Table 1 Feeding ratio, reaction condition, and molecular weight for PETH, PPTH, PBTH, and PHTH.

Sample	DMTD	Diol	Esterification		Polycondensation		GPC		
			Temp. (°C)	Time (h)	Temp. (°C)	Time (h)	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	$\bar{D}$
PETH	0.25	0.40	180	3.0	220	3.0	3.90	5.99	1.54
PPTH	0.25	0.40	180	3.0	220	4.0	3.33	6.65	2.00
PBTH	0.25	0.40	180	3.0	210	3.0	5.35	7.94	1.50
PHTH	0.25	0.40	180	3.0	200	4.0	2.76	5.22	1.89

Bruker AVIII400 NMR spectrometer. All the samples were dissolved in CF_3COOD and the measurement was conducted at 25 °C. Tetramethylsilane (TMS) was used as the internal standard. The molecular weights and distribution of PETH, PPTH, PBTH, and PHTH were measured at 40 °C using GPC (Agilent PL-GPC220) equipped with the column of PLgel 5 μm Mixed-D (300 mm $\times$ 7.5 mm). The chloroform and 2-chlorophenol mixture with volume ratio of 9/1 was used as solvent. The concentration was 1 mg/mL. Chloroform was used as mobile phase with a flow rate of 1 mL/min. Standard polystyrene (3070 g/mol to 2.58×10^5 g/mol) was used to calibrate the equipment for measurement.

DSC measurement was conducted on a Mettler-Toledo DSC 1 differential scanning calorimeter. The sealed sample was heated from 25 °C to 280 °C with a heating rate of 10 °C/min and maintained at this temperature for 5 min. Then it was cooled to 25 °C at a rate of 10 °C/min and heated again to 280 °C with the same heating rate. All the measurement was conducted under the protection of nitrogen. Thermal stability measurement was conducted on a TGA instrument (Mettler-Toledo TGA/DSC thermogravimetric analysis). The sample (6–10 mg) was placed in a ceramic furnace and TGA curve was recorded from 50 °C to 800 °C with the heating rate of 20 °C/min under N_2 /air atmosphere with a flow rate of 50 mL/min. X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE. Cu-K α radiation (40 kV, 40 mA) was used, and the sample was scanned from 5° to 50° with the rate of 0.2 (°)/s. Ultraviolet-visible (UV-Vis) spectra were recorded on a Lambda 950 UV/Vis/NIR spectrophotometer. Dynamic mechanical analysis (DMA) was conducted on a METTLER-TOLEDO dynamic mechanical analyzer (DMA/Q800) at a fixed frequency of 1 Hz. Samples with the dimension of 8.0 mm $\times$ 5.0 mm $\times$ 1.0 mm were prepared by hot press-molding and scanned from –100 °C to 150 °C with a heating rate of 3 °C/min.

Tensile properties were measured using Instron 5567 with a load cell of 500N. Dumb-bell-shaped samples with the dimension of 20.0 mm $\times$ 2.0 mm $\times$ 1.0 mm (length $\times$ neck width $\times$ thickness) were prepared by press-molding (melt at 200 °C for 10 min, then pressed at 20 MPa for 5 min before cooling in the atmosphere). The measurement was conducted at 25 °C and the stretching rate was 10 mm/min. At least five specimens were tested for each sample to insure accuracy.

The gas barrier properties of PETH, PPTH, and PBTH were

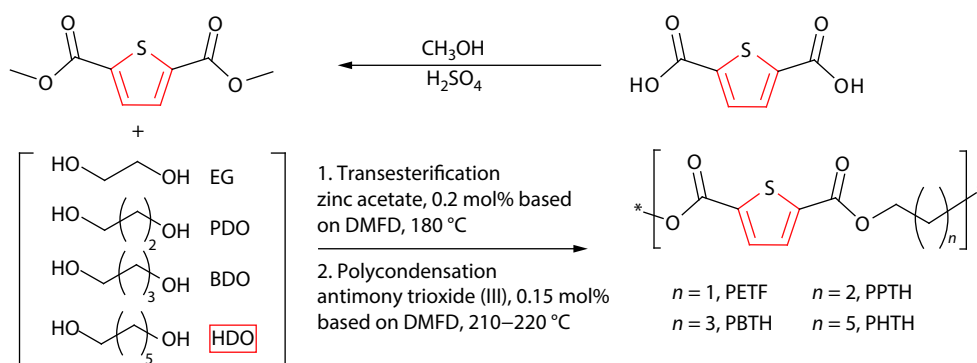
investigated by Labthink VAC-V2 gas permeability tester. The measurement was conducted at 30 °C and the relative humidity (RH) was set to be 50%. O_2 and CO_2 with the purity of 99.99% were used. The amorphous PETH, PPTH, and PBTH round films with the diameter of 97 mm were prepared by the melt-press/quench procedures. The testing area was 38.5 cm^2 and the test was conducted in the range of 0.05 cm^3/m^2 to 5.0×10^4 cm^3/m^2 for 24 h at 0.1 MPa. In order to ensure the accuracy, all the specimens were tested for three times and the averaged results were reported.

RESULTS AND DISCUSSION

Synthesis and Structure Confirmation of Synthesized Polyesters

As shown in [scheme 1](#), the thiophene-aromatic polyesters PETH, PPTH, PBTH, and PHTH were synthesized *via* a two-step procedure consisting of transesterification and polycondensation. The feeding ratio, reaction conditions, and molecular weight are listed in [Table 1](#). In order to obtain the high molecular weight polyesters and restrain the coloration in the polycondensation process, TDCA was firstly converted into dimethyl thiophene-2,5-dicarboxylate (DMTD), and then the transesterification between DMTD and different diols (ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol) was conducted at 180 °C for 3 h before the temperature was increased to 200–220 °C and the pressure was gradually decreased to 10 Pa. Using this procedure, the obtained PETH, PPTH, and PBTH showed weight-average molecular weight (M_w) varied from 5.99×10^4 g/mol to 7.94×10^4 g/mol with the molar-mass dispersity of 1.50–2.00 based on the GPC measurement (Fig. S1 in the electronic supplementary information, ESI). As for PHTH, its M_w was 5.22×10^4 g/mol with the molar-mass dispersity of 1.89. The relatively low molecular weight of PHTH was attributed to the higher boiling point of HDO, which was a little more difficult to be distilled out under the same polycondensation condition, compared with ethylene glycol, 1,3-propanediol, and 1,4-butanediol.

The ^1H -NMR spectra and characteristic signal assignments of PETH, PPTH, PBTH, and PHTH are shown in [Fig. 1](#). The chemical shift of CH on thiophene ring (signal s) was shown at 7.57–7.65 ppm and all the CH_2 (a) connected with ester bonds in different diols showed their characteristic signals in the range of 4.20–4.56 ppm. For PPTH, the signal standing for the CH_2 (b) in 1,3-propanediol, which was not connected with



Scheme 1 Synthesis of thiophene-aromatic polyesters from DMTD and diols.

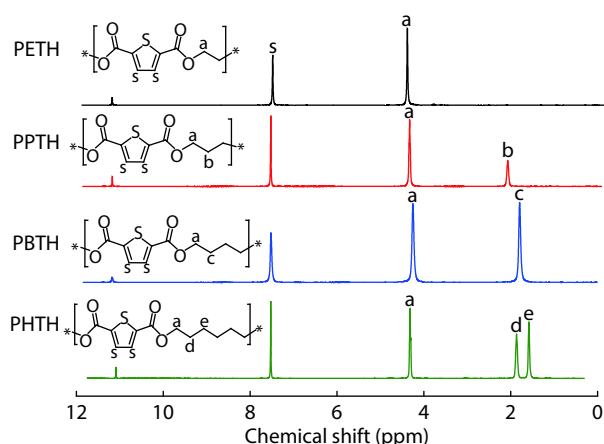


Fig. 1 ^1H -NMR spectra and signal assignments of synthesized polyesters.

the ester bond, appeared at 2.17 ppm. The signal at 1.63 ppm (c) was assigned to the CH_2 not connected with the ester bond in 1,4-butanediol. As for PHTH, besides the signals for CH in thiophene ring (s) were shown at 7.61 ppm and the CH_2 (a) connected with the ester bonds appeared at 4.30 ppm, the signals observed at 1.81 and 1.33 ppm were standing for CH_2 (d) and CH_2 (e). All the signals in Fig. 1 have been assigned accordingly, which indicated the achievement of target products.

The chemical structures of synthesized polyesters were further confirmed by ^{13}C -NMR (Fig. 2). For the aromatic carbons in TDCA unit, they showed characteristic signals at 133.8–134.6 ppm (signal z) and 138.4–138.7 ppm (signal x). The signal showing at 163.8–164.6 ppm was assigned to carbonyl carbon (signal y) and the CH_2 (a) in different diols connected with ester bonds showed the characteristic signals in the range of 63.6–67.6 ppm. As for other CH_2 units in PETH, PPTH, PBTH, and PHTH, their ^{13}C -NMR signals were also assigned. Based on these NMR results, the chemical structures of synthesized polyesters were confirmed.

Thermal Properties

The thermal properties of synthesized thiophene-aromatic

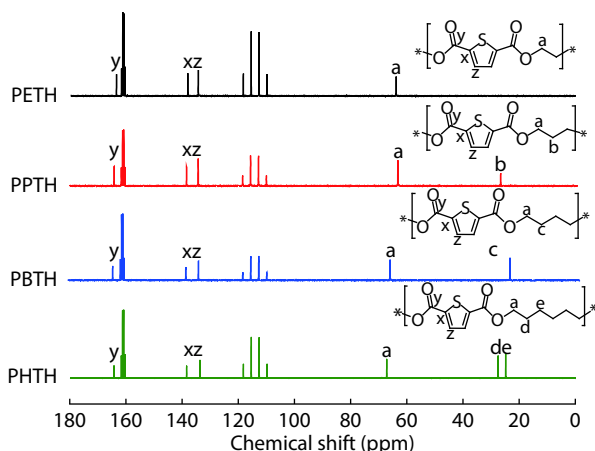


Fig. 2 ^{13}C -NMR spectra and signal assignments for the synthesized polyesters.

polyesters were measured by DSC and the first heating, cooling and second heating scans in the temperature range of $-50\text{ }^{\circ}\text{C}$ to $280\text{ }^{\circ}\text{C}$ with a scan rate of $10\text{ }^{\circ}\text{C}$ are shown in Fig. 3. The related parameters, including T_g , melting temperature (T_m) and melting enthalpy (ΔH_m), crystallization temperature (T_c) and enthalpy (ΔH_c), cold crystallization temperature (T_{cc}) and cold crystallization enthalpy (ΔH_{cc}), are listed in Table 2. In Fig. 3(a), as expected, T_m of the synthesized polyesters was decreased along with the increasing length of diols, from $192.5\text{ }^{\circ}\text{C}$ for PETH to $100.4\text{ }^{\circ}\text{C}$ for PHTH. This result was reasonable and similar to the polyesters based on FDCA or TPA. In addition, PETH demonstrated a poorer crystallizability compared with PPTH, PBTH, and PHTH as indicated by the absence of cold crystallization peaks in its heating scan curve. Fig. 3(b) shows the cooling scan curves from $280\text{ }^{\circ}\text{C}$ to $-50\text{ }^{\circ}\text{C}$ for all the samples and no crystallization peaks could be seen. In Fig. 3(c), from PETH to PHTH, T_g reasonably showed a decreasing tendency from $64.6\text{ }^{\circ}\text{C}$ for PETH to $-1.0\text{ }^{\circ}\text{C}$ for PHTH. And what should be pointed out here is that, compared with Fig. 3(a), the melting peak for PHTH showing at $100.4\text{ }^{\circ}\text{C}$ disappeared, while PPTH and PBTH showed T_m at 187.8 and $154.5\text{ }^{\circ}\text{C}$, respectively. To some extent, the ΔH_m value of semi-crystalline polyesters could be taken as an indicator to qualitatively compare their crystallizability. As listed in Table 2, the relatively high ΔH_m for PPTH (52.5 J/g) and PBTH (41.3 J/g) indicated their good crystallization properties. As previously reported, the FDCA-based analogues, PPF, showed a ΔH_m of only 0.9 J/g and ΔH_m for PBF, known as the FDCA-based polyester with good crystallization property, was 32 J/g at the same heating rate.^[14] Therefore, it can be concluded that the TDCA-based polyesters possessed better crystallization properties compared with the FDCA-based ones when the same diols were employed.

Wide angle X-ray diffraction was used to further investigate the crystallization of synthesized polyesters. In Fig. 3(d), all the samples, PETH, PPTH, PBTH, and PHTH showed obvious reflection peak. However, their main diffraction peak were different. For PETH and PBTH, only one clear reflection peak appeared at $2\theta = 20.4^{\circ}$ and 23.3° , respectively. For PHTH, except the strong reflection peak shown at $2\theta = 7.0^{\circ}$, more other peaks were observed at 20.4° , 22.7° , 25.3° , and 28.7° . PPTH showed the multiple main diffraction peaks at $2\theta = 16.7^{\circ}$, 23.2° , and 25.9° . These XRD results indicated the presence of thiophene-aromatic polyester crystalline and they were in accordance with above DSC analyses in Table 2 and Fig. 3.

Thermal Stability

The thermal stability of thiophene-aromatic polyesters was investigated by TGA under nitrogen or air (Fig. S2 in ESI). The main parameters for thermal stability evaluation, including the temperature at which 5% weight loss occurred ($T_{5\%}$), the temperature at which 50% weight loss occurred ($T_{d,1/2}$), the temperature at which the decomposition rate was the maximum ($T_{d,max}$), and the residual char at $600\text{ }^{\circ}\text{C}$ (R_{600}) are listed in Table 3. All the different thiophene-aromatic polyesters showed $T_{5\%}$ in the temperature range of $380\text{--}409\text{ }^{\circ}\text{C}$ in nitrogen atmosphere and $376\text{--}404\text{ }^{\circ}\text{C}$ in air atmosphere. From PETH to PHTH, the values for $T_{5\%}$ were slightly decreased with the increment of carbon numbers in aliphatic diol units. As for $T_{d,max}$ it also decreased from $446\text{ }^{\circ}\text{C}$ for PETH to $408\text{ }^{\circ}\text{C}$ for PHTH in

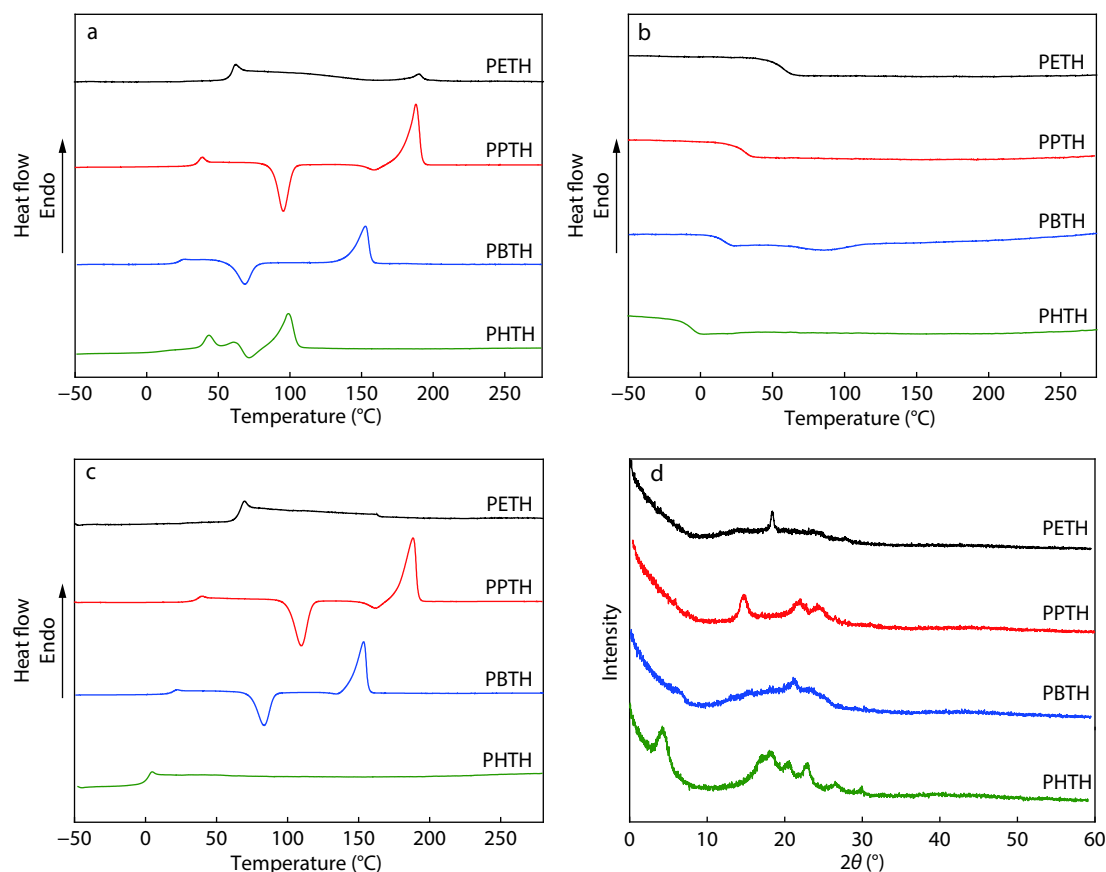


Fig. 3 DSC curves at the scan rate of 10 °C/min for synthesized polyesters: (a) the first heating scan from -50 °C to 280 °C; (b) cooling curves from 280 °C to -50 °C; (c) the second heating scans from -50 °C to 280 °C. (d) XRD patterns of synthesized polyesters.

Table 2 Thermal properties of thiophene-aromatic polyesters.

	The first heating scan				Cooling scan		The second heating scan				
	T_{cc} (°C)	ΔH_{cc} (J/g)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	T_{cc} (°C)	ΔH_{cc} (J/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)
PETH	nd	nd	192.5	1.4	nd	nd	nd	nd	64.6	nd	nd
PPTH	96.2	38.9	189.5	49.6	nd	nd	109.3	41.4	35.5	187.8	52.5
PBTH	79.8	25.2	149.8	36.8	nd	nd	85.9	29.3	22.1	154.5	41.3
PHTH	72.5	8.3	100.4	25.8	nd	nd	nd	nd	-1.0	nd	nd

Table 3 Key parameters for the thermal stability evaluation of thiophene-aromatic polyesters.

Sample	N ₂				Air			
	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)	$T_{d,1/2}$ (°C)	R_{600} (wt%)	$T_{d,5\%}$ (°C)	$T_{d,max}$ (°C)	$T_{d,1/2}$ (°C)	R_{600} (wt%)
PETH	409	446	442	7.8	404	439	438	1.8
PPTH	383	412	411	2.9	378	410	407	1.3
PBTH	381	409	408	8.2	377	407	406	1.5
PHTH	380	408	407	5.8	376	406	405	1.5

nitrogen and from 439 °C to 406 °C in air atmosphere. According to literatures' results,^[47] their petroleum based analogues, PET, PPT, and PBT, possessed $T_{5\%}$ in the temperature range of 370 – 403 °C and $T_{d,max}$ was between 400 and 442 °C. The FDCA-based polyesters, such as PEF, PPF, and PBF, showed $T_{5\%}$ in the range of 365 – 367 °C and $T_{d,max}$ varied in 398 – 405 °C.^[23] This result indicated that the thiophene-aromatic polyesters had excellent thermal resistance regardless of the testing atmosphere, which were similar to or better than their TPA- or FDCA-based analogues.

Dynamic Mechanical Properties

Fig. 4 shows the dynamic mechanical properties of thiophene-aromatic polyesters determined by DMA. In Fig. 4(a), all the polyesters, PETH, PPTH, PBTH, and PHTH, showed two obvious decrement stages. The first one appeared in the temperature range of -90 °C to 60 °C, while the second stage occurred between -20 and 150 °C. At the same temperature, their storage modulus followed the order of $PETH > PPTH > PBTH > PHTH$. Fig. 4(b) shows the variation of $\tan\delta$ as a function of temperature and two relaxation peaks, marked as β and α in

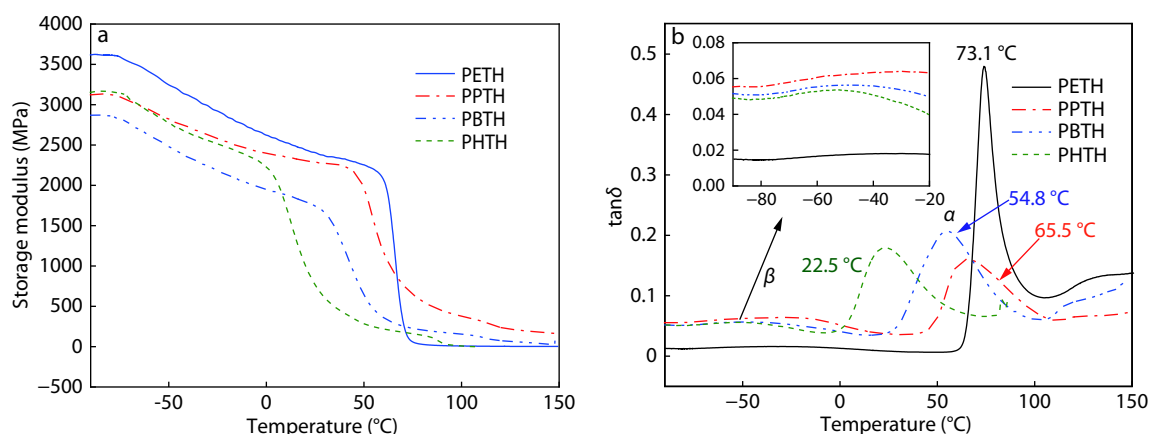


Fig. 4 DMA curves: (a) storage modulus and (b) $\tan\delta$ as a function of temperature for thiophene-aromatic polyesters.

the order of increasing temperature, were observed. Undoubtedly, the α peak should be attributed to the glass transition when the temperature was increased high enough. From PHTH to PETH, T_g was increased from 22.5 °C to 73.1 °C. These results were in line with the T_g values determined by DSC, although there were some deviations for the same specimens tested by DSC or DMA.

Compared with their FDCA-based analogues, these TDCA-based polyesters demonstrated a little lower T_g .^[12–16] In Lotti's work, the similar results were also reported, such as T_g of PPTH was 38 °C while 52 °C for PPF. The reason could be the stronger molecular interactions in furan based polyesters caused by higher electronegativity of oxygen atoms.^[41] As for the β relaxation peaks inserted in Fig. 4(b), it was attributed to the second relaxation of aliphatic chains in different diol units. Compared with the polyesters containing cycloaliphatic ring,^[37] which showed obvious β relaxation caused by the configuration transition of ring units, the β peak for polyesters in this work was much weak, and no clear distinction was detected.

Mechanical Properties

The static mechanical properties of synthesized thiophene-aromatic polyesters were studied by tensile testing machine at room temperature and the stress-strain curves are shown in Fig. 5(a) and the data shown in Table S1 (ESI). The related values for tensile strength and modulus are shown in Figs. 5(b) and 5(c). As noticed, with the increasing number of carbon in diols, the tensile strength and modulus of the polyesters decreased obviously, and their melting temperature kept the same trend. For PETH, PPTH, and PBTH, their tensile modulus was 1800, 1250, and 1190 MPa, and the tensile strength was 67, 48, and 45 MPa, respectively, which were similar to those of the petroleum-based aromatic polyesters, such as PET, PPT, and PBT.^[47] However, compared with their furan-based analogues, PEF, PPF, and PBF, the tensile strength and modulus of TDCA-based polyesters reported here were much lower. Nevertheless, what should be pointed out is that the elongation at break of PETH, PPTH, and PBTH was between 378%–667% (Fig. 5d), much higher than those of the furan-based polyesters of 5%–290%.^[14] Especially, the elongation at break of PETH was about 75 folds higher than that of PEF (~5%), which might be attributed to the differences between FDCA and TDCA. The dipole moment of

furan is about 0.7D, higher than thiophene ring of 0.51D, caused by the higher electronegativity of O compared to S. In addition, the nonlinear structure of TDCA and FDCA resulted in an angle of 148° and 129°, respectively, between the two carboxylic acid carbons. These all would lead to the higher intermolecular interaction in PEF, thus lowering its elongation at break.^[21,42] When the carbon number in diols increased up to 6, the tensile strength and modulus of PHTH were only 18 and 240 MPa, respectively, and the elongation at break decreased to 124%. The reason could be its much lower T_g of only –1 °C and poor crystallizability (Table 2). Based on these results, it could conclude that PETH, PPTH, and PBTH had satisfied tensile strength, modulus and toughness, indicating their great potential to be used as the bio-based packaging material.

Barrier Properties

In order to evaluate the barrier properties of thiophene-aromatic polyester, the amorphous polyester films were prepared by melt-press/quench procedure and investigated by Labthink VAC-V2 gas permeability tester. As the glass transition temperature of PHTH was below room temperature, only the gas barrier properties of PETH, PPTH, and PBTH were evaluated. For easy expression, the barrier improvement factor (BIF_p) widely used for gas permeability comparison,^[17,48] which represents the permeability coefficient of CO₂ or O₂ in PET divided by the CO₂ or O₂ permeability in other polymers, was employed to conduct the quantitative comparison. The testing temperature, CO₂ and O₂ permeability coefficient values, and BIF_p are listed in Tables 4 and 5. As noticed, the CO₂ BIF_p of PETH, PPTH, and PBTH was 12.0, 7.5, and 5.6, respectively, and the O₂ BIF_p was 6.6, 5.5, and 3.3, respectively. Obviously, the permeability coefficient of thiophene-aromatic polyesters was increased with the length of aliphatic diols' chain. When compared with FDCA-based polyesters, it is easy to find out that the CO₂ barrier properties of thiophene-aromatic polyesters were a little lower, but they were good enough. From Tables 4 and 5, it is also seen that the CO₂ and O₂ BIF_p values of PETH, PPTH, and PBTH were all higher than those of PEI and PEN, which indicated that, besides the polyesters synthesized from FDCA, the thiophene-aromatic polyesters might be another kind of bio-based polyester possessing excellent gas barrier properties.

Fig. 6 shows the gas barrier properties, glass transition temperature, and elongation at break of PETH, PPTH, and PBTH

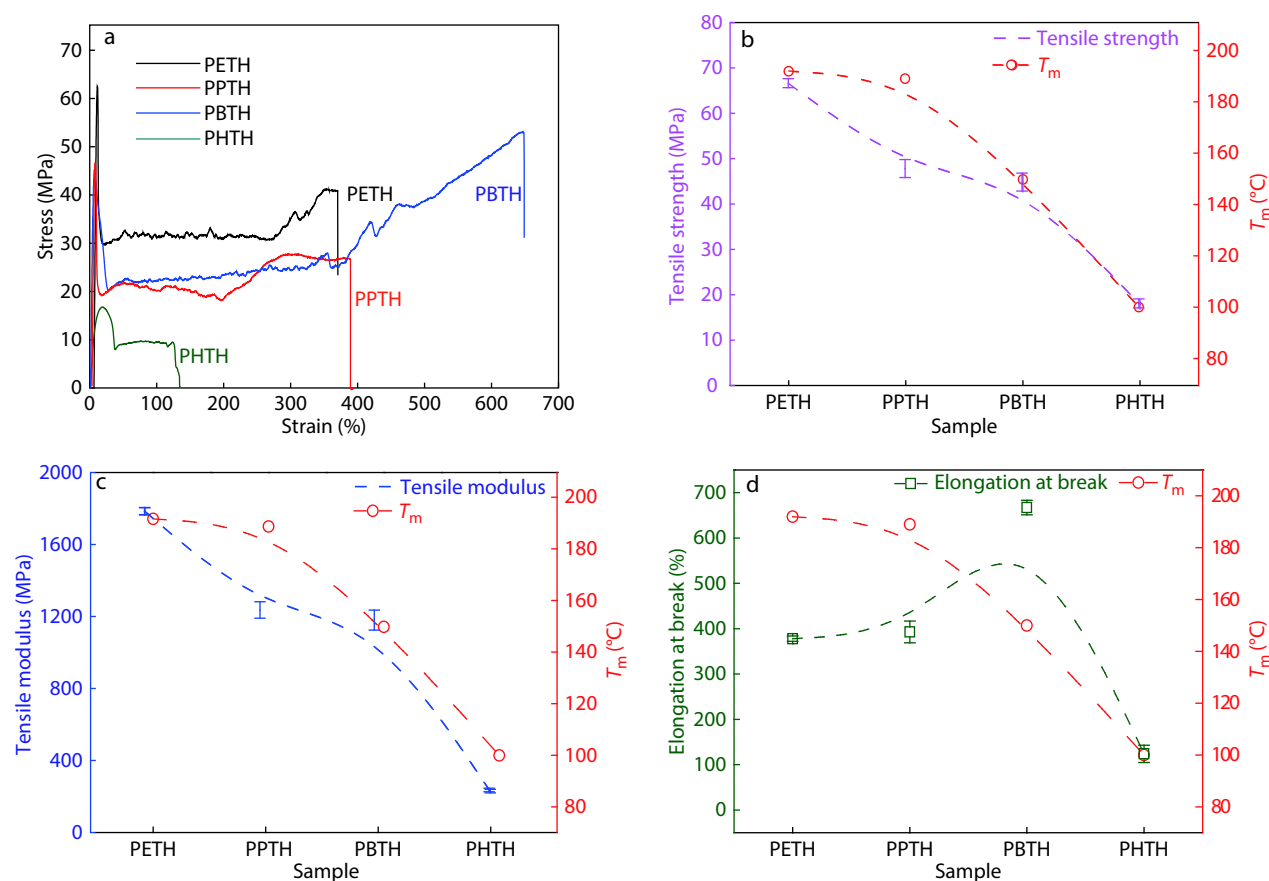


Fig. 5 Tensile properties of thiophene-aromatic polyesters PETH, PPTH, PBTH, and PHTH: (a) stress-strain curves, (b) tensile strength, (c) tensile modulus, and (d) elongation at break.

Table 4 CO_2 permeability coefficient of PETH, PPTH, PBTH and the comparison with PEF, PET, PEN as well as PEI.

Sample ^a	Temperature ($^{\circ}\text{C}$)	CO_2 permeability coefficient (barrer ^b)	BIF_p	Reference
PET	30	0.090	1	This work
PETH	30	0.0075	12	This work
PPTH	30	0.012	7.5	This work
PBTH	30	0.016	5.6	This work
PET	30	0.13	1	[14]
PEF	30	0.010	13	[14]
PPF	30	0.016	8.1	[14]
PBF	30	0.018	7.2	[14]
PET	30	0.57	1	[48]
PEI	30	0.045	13	[48]

^a The test performed at low pressure (≤ 0.1001 MPa); ^b 1 barrer = $7.5 \times 10^{-14} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{Pa}$.

Table 5 O_2 permeability coefficient of PETH, PPTH, PBTH and the comparison with PEF, PPF, and PBF as well as PET, PEN, and PEI.

Sample ^a	Temperature ($^{\circ}\text{C}$)	O_2 permeability coefficient (barrer ^b)	BIF_p	Reference
PET	30	0.060	1	This work
PETH	30	0.009	6.6	This work
PPTH	30	0.011	5.5	This work
PBTH	30	0.016	3.8	This work
PET	30	0.060	1	[14]
PEF	30	0.011	5.5	[14]
PPF	30	0.09	6.7	[14]
PBF	30	0.018	3.3	[14]
PET	30	0.054	1	[47]
PEI	30	0.015	3.6	[47]
PEN	30	0.019	2.9	[47]

^a The test performed at low pressure (≤ 0.1001 MPa); ^b 1 barrer = $7.5 \times 10^{-14} \text{ cm}^3 \cdot \text{cm} / \text{cm}^2 \cdot \text{s} \cdot \text{Pa}$.

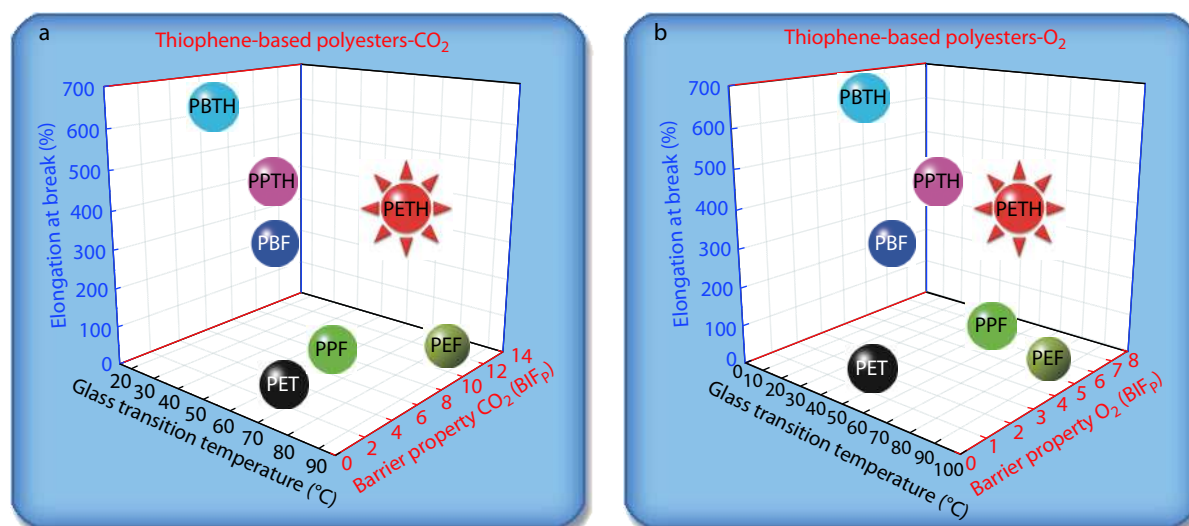


Fig. 6 Barrier properties, glass transition temperature, and elongation at break of thiophene-aromatic polyesters PETH, PPTH, and PBTH compared with FDCA-based polyesters PEF, PPF, PBF^[14,23] and petroleum based PET.^[47–50]

compared with those of the FDCA-based polyesters PEF, PPF, PBF,^[14,23] and petroleum based PET.^[47–50] Obviously, the elongation at break of PET, PPF, and PEF were much lower than those of other polyesters. Although PBF, PPTH, and PBTH performed very well on elongation at break ($\geq 300\%$), they showed the much lower glass transition temperatures (≤ 50 °C). As far as the gas barrier property was concerned, only PETH and PEF showed CO₂ and O₂ BIF_p higher than 5. Considering their overall performance, PETH might be the most excellent one in these polyesters, which was marked as a star in Fig. 6.

CONCLUSIONS

High molecular weight thiophene-aromatic polyesters PETH, PPTH, PBTH, and PHTH were synthesized by a two-step procedure consisting of transesterification and polycondensation, starting from the bio-based dimethyl thiophene-2,5-dicarboxylate and ethylene glycol, 1,3-propanediol, 1,4-butanediol, and 1,6-hexanediol. Results showed that both PETH and PPTH as well as PHTH had good crystallizability, satisfied tensile strength and modulus. Especially, the TDCA-based polyesters showed much higher elongation at break than that of FDCA-based polyesters PEF, PPF, PBF and petro-based PET. In addition, all the TDCA-based polyesters demonstrated excellent gas barrier properties as indicated by their much higher CO₂ and O₂ BIF_p in contrast to PEI and PEN. Considering the overall performance in terms of glass transition temperature, mechanical properties, and barrier to gas, PETH might be the most promising bio-based polyester, which had great potential to be used as the high barrier packaging materials.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <https://doi.org/10.1007/s10118-020-2438-2>.

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