

Research article

# High performance sulfur-containing copolyesters from bio-sourced aromatic monomers

Lesly Dasilva Wandji Djouonkep<sup>1</sup>, Zhengzai Cheng<sup>1,2\*</sup>, William Mawuko Kodjo Siegu<sup>1</sup>, Xiong Jing<sup>1</sup>, Jun Chen<sup>1</sup>, Elvis Kwame Adom<sup>1</sup>, Abubakar Muaz<sup>1</sup>, Mario Gauthier<sup>3</sup>

<sup>1</sup>Research Institute of Fine Organic Chemicals & Organic Materials at School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, 430081 Wuhan, China

<sup>2</sup>Coal Conversion and New Carbon Materials Hubei Key Laboratory, Wuhan University of Science and Technology, 430081 Wuhan, China;

<sup>3</sup>Department of Chemistry University of Waterloo 200 University Avenue West Waterloo, Ontario Canada, N2L 3G1

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**Abstract.** In this investigation, a series of novel random bio-based thiophene–aromatic copolyesters, including thiophene and phenyl units, were successfully prepared from dimethyl 2,5-thiophenedicarboxylate, dimethyl 2,5-dimethoxyterephthalate, and the aliphatic diols ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and 1,8-octanediol, via two-step melt polymerization as a facile and green semi-continuous process. Techniques used to monitor the polymerization process included Fourier transform infrared (FTIR) and proton nuclear magnetic resonance spectroscopy (<sup>1</sup>H NMR), gel permeation chromatography (GPC), differential scanning calorimetry, thermogravimetric analysis, and dynamic mechanical analysis. The copolymers had tunable  $T_g$  values ranging from 47–120 °C, while their 5% decomposition temperature ( $T_{d, 5\%}$ ) under N<sub>2</sub> varied from 405–370 °C. GPC analysis showed that the polyesters had weight-average molecular weights ( $M_w$ ) of 41 400–48 500 g/mol and polydispersity indices of 1.47–2.24. A study of structure-property relations showed that the properties of these copolymers can be tailored by varying their composition. All the copolyesters exhibited high tensile strength (45–80 MPa) and toughness values (elongation at break of 200–540%). After 28 weeks of incubation in humid soil, weight losses of up to 7.2% were observed. Considering their good mechanical properties, thermal stability and biodegradability, these renewable sulfur-containing copolyesters have great potential to replace petroleum-based commercial poly(ethylene terephthalate) in the food packaging industry, which is helpful to implement carbon neutrality and sustainable development in the polymer industry.

**Keywords:** biodegradable polymers, aromatic monomers, aliphatic diols, mechanical properties, melt transesterification

## 1. Introduction

In recent years, much effort in polymer research focused on the development of monomers from renewable bio-sourced raw materials. Environment-friendly platform chemicals derived from multiple biomass sources, at a low cost, with diverse structures and functional groups, have been used in the synthesis of new polyesters [1]. The substitution of fossil resources with molecules extracted from biomass represents one of the most important goals of Green

chemistry. This replacement is associated with two main objectives: the usage of renewable sources instead of fossil ones, and the development of a low-carbon bio-economy, geared toward reducing waste and minimizing resource consumption [2]. For instance, it has been estimated that the replacement of 20% of the carbon content in the world's current poly(ethylene terephthalate) (PET) production (~37.5 billion tons) with bio-based resources could reduce CO<sub>2</sub> emissions by 17 Mt [3]. The increased interest in

\*Corresponding author, e-mail: [hbchengzz@163.com](mailto:hbchengzz@163.com)

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bio-based renewable materials is motivated primarily by the fact that they contribute to the efficient use of natural resources, which is a prerequisite for the development of a more sustainable and resilient economy [4]. Sustainable materials that are biodegradable, such as poly(ethylene 2,5-furandicarboxylate) [5, 6] poly(1,4-butylene 2,5-furandicarboxylate) [7, 8], poly(lactic acid) [9, 10], and poly(butylene 2,5-thiophenedicarboxylate) [11, 12] thus have become ‘hot’ research topics.

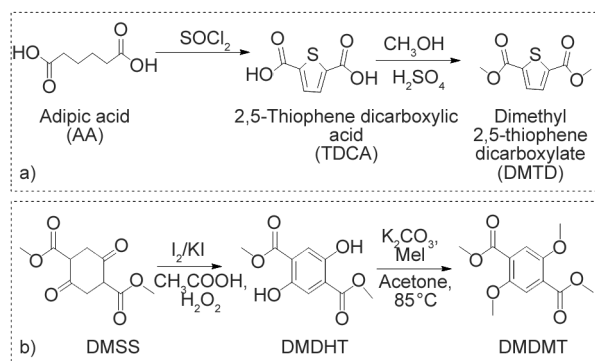
While common petroleum-based thermoplastic materials such as polycarbonate, PET, and poly(butylene terephthalate) exhibit excellent thermal, mechanical and optical properties, their degradation behavior in the environment is generally very poor. Conversely, currently available bio-based polymers generally display poorer mechanical properties partly attributed to the lack of rigid aromatic units in their structure but have interesting degradability characteristics [13, 14]. The poor mechanical properties of many biodegradable bio-based polyesters limit their commercial applications.

It was pointed out in a recent literature review that polyesters derived from 2,5-furandicarboxylic acid (FDCA) display properties similar to or better than their terephthalic acid (TPA) analogues, and that these properties can be tuned further through copolymerization [15]. 2,5-Thiophenedicarboxylic acid (TDCA), like FDCA, is a promising bio-based monomer with a chemical structure similar to TPA, and its copolymers should likewise display interesting properties [16, 17]. Studies on main-chain thiophene–aromatic polymers, comprising thiophene and phenyl repeating units within their polymer backbone, have provided an improved understanding of structure–property relationships in these materials [18, 19]. Some of these thiophene–aromatic polymers display liquid-crystalline melt behavior, but also limited solubility [20]. Wang and coworkers [21–24] also reported polyesters derived from TDCA and mesogenic moieties such as terephthalate, naphthalate or 1,4-cyclohexanedimethylene units, and found that the polyesters derived from TDCA had lower melting temperatures than their terephthalic acid-based analogues, but these materials nevertheless displayed good thermal and mechanical properties. Furthermore, TDCA-based polyesters such as poly(trimethylene 2,5-thiophenedicarboxylate-*co*-trimethylene terephthalate), poly(propylene naphthalate-*co*-propylene 2,5-thiophenedicarboxylate), poly(ethylene 2,5-thiophenedicarboxylate)

and poly(butylene-*co*-1,4-cyclohexanedimethylene 2,5-thiophenedicarboxylate) were likewise reported to have good thermal stability and mechanical properties, and to display some degree of biodegradability in a natural environment. Unfortunately, most of these polyesters exhibited low processing temperatures (usually below 200 °C), low molecular weights and moduli, high fragility and crystallization were not observed in most cases due to destruction of chain regularity by the rigid co-monomers.

To combine good material properties with biodegradability in the current investigation, we synthesized thiophene–aromatic copolyesters from TDCA and dimethyl 2,5-dimethoxyterephthalate (a symmetrical disubstituted phenyl aromatic monomer) in equimolar ratios as rigid backbone components. These were combined with aliphatic diol monomers as spacers to control backbone flexibility, affecting properties such as the glass transition temperature and the tensile properties, and possibly favoring the formation of high molecular weight polymers. A copolymerization strategy was selected to facilitate tuning of the physical and mechanical properties of these materials, which can be difficult to control in bio-based homopolymers [25]. This approach yielded polyesters with high processing temperatures, high molecular weights, and mechanical properties comparable to commercial PET. These polyesters also displayed good biodegradability, allowing them to decompose in a natural environment after their life cycle is completed, due to the presence of C–S bonds sensitive to relatively abundant strains of sulfur-loving bacteria and other microorganisms in the soil.

2,5-Thiophenedicarboxylic acid (TDCA) is a stable thiophene derivative that can be synthesized from sugars, a renewable resource, even though that monomer is currently derived from adipic acid and thionyl chloride [24] (Figure 1a). TDCA and terephthalic acid are similar in that they both contain conjugated ring structures. In the current investigation, TDCA was converted to dimethyl 2,5-thiophenedicarboxylate (DMTD, a more convenient monomer) by esterification with methanol and sulfuric acid. A derivative of bio-sourced succinic acid, dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (Figure 1b), can be converted to dimethyl 2,5-dihydroxyterephthalate (DMDHT) and methylated to yield the monomer dimethyl 2,5-dimethoxyterephthalate (DMDMT) [26]. The structures of DMTD and DMDMT were characterized by FTIR and <sup>1</sup>H NMR spectroscopy,



**Figure 1.** (a) Synthesis of dimethyl 2,5-thiophenedicarboxylate (DMTD) from adipic acid; (b) synthesis of dimethyl 2,5-dimethoxyterephthalate (DMDMT) from succinic acid.

and the monomers were reacted with aliphatic diols (Figure 1b) to obtain thiophene–aromatic copolyesters P1–P5.

We now report the synthesis and the characterization of these novel thiophene–aromatic copolyesters via a solvent-free method, from DMTD and DMDMT potentially derived from the biomass, in combination with aliphatic diols. The effects of varying the length of the diol spacer on the properties of the copolyesters were investigated to establish structure–property relations in these novel thiophene–aromatic copolyesters.

## 2. Experimental procedures

### 2.1. Materials

Dimethyl 2,5-thiophenedicarboxylate was obtained by esterification of 2,5-thiophenedicarboxylic acid (99%, Lianyungang Yiqilai Chemical Co. Ltd., Jiangsu, China) with methanol and  $\text{H}_2\text{SO}_4$ , and DMDMT was synthesized as described below. Dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate, ethylene glycol, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol, 1,8-octanediol and antimony trioxide (all of analytical purity > 99%) were purchased from the Aladdin Reagent Co. Ltd., Shanghai, China, methanol (99.9%),  $\text{H}_2\text{SO}_4$  (98%) and hydrogen peroxide solution (30%  $\text{H}_2\text{O}_2$  w/w) were from the Sinopharm Chemical Reagent Co. Ltd., Zhejiang, China, KI and  $\text{I}_2$  were from Tianjin Guangfu Technology Development Co. Ltd. (> 9%, Beijing, China), and chloroform ( $\geq 99\%$ ) from Shangdong Hengchuang New Materials Co., Ltd. (Zhangqiu, China). All the chemicals were used as received without further purification.

### 2.2. Characterization techniques and equipment

Fourier transform infrared (FTIR) spectra were obtained on a Bruker Vertex 70 spectrometer from 4000–400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ , by using KBr pellets and averaging five spectra.

Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectroscopy was performed on an AVANCE DMX600 instrument to monitor the composition and chemical structure of the copolyesters. All the samples were dissolved in  $\text{CDCl}_3$ , with tetramethylsilane (TMS) as internal standard at room temperature ( $25^\circ\text{C}$ ).

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements were performed on a Netzsch STA 449 F3 Jupiter instrument calibrated with indium. The DSC and TGA experiments were performed under  $\text{N}_2$  atmosphere from 0 to  $300^\circ\text{C}$  and 0 to  $600^\circ\text{C}$ , respectively, at a heating rate of  $10^\circ\text{C}/\text{min}$ . The melting temperature ( $T_m$ ) was determined from the second heating scan. Dynamic mechanical analysis (DMA) was carried out on a DMA Q800 Dynamic Mechanical Analyzer, at a frequency of 1 Hz and a ramping rate of  $3^\circ\text{C}/\text{min}$ . For sample preparation, 10.0 g of the polyester were compressed in a flat sheet vulcanizer at  $230^\circ\text{C}$  for 5 min and cut into strips with 24 mm length, 5.6 mm width, and 1.18 mm thickness.

Tensile testing was achieved on a UTM6503 Electronic Universal Testing Machine (Shenzhen Sansi Material Testing Co., Shenzhen, China) at  $23^\circ\text{C}$ , at an extension rate of 50 mm/min. The samples were prepared according to Chinese Standard GB528–2008 for type II dumbbells.

Polystyrene-equivalent molecular weights ( $M_n$ ,  $M_w$ ) and polydispersity indices ( $M_w/M_n$ ) were determined by gel permeation chromatography (GPC) analysis on a Viscotek GPC Max instrument using THF ( $25^\circ\text{C}$ ) or DMF ( $40^\circ\text{C}$ ) as eluents, at a flow rate of 1.0 ml/min. The system was calibrated with polystyrene standards.

The biodegradability of the polyesters was studied by the soil burial technique. The testing was conducted in an incubator with air and soil relative humidity levels maintained at 60 and 80%, respectively. The temperature was maintained at  $25\text{--}30^\circ\text{C}$ . The copolyester films, with a thickness of about 200  $\mu\text{m}$  and side lengths of  $1 \times 1 \text{ cm}^2$ , were buried at 0.10 m in the soil. They were retrieved at predetermined

times over a 28 week incubation period, when they were cleaned and dried at 50 °C for 5 h in a vacuum oven. The extent of biodegradation was calculated using Equation (1):

$$\text{Biodegradation [\%]} = \frac{W_1 - W_2}{W_2} \cdot 100 \quad (1)$$

where  $W_1$  and  $W_2$  are the film weights before and after soil biodegradation, respectively.

### 2.3. Synthesis of dimethyl

#### 2,5-dimethoxyterephthalate

Using dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate as starting material, DMDMT was successfully prepared by a two-step synthesis. In the first step, the intermediate DMDHT was synthesized from the dione, followed by methylation of the phenol groups to produce dimethyl 2,5-dimethoxy terephthalate.

Dimethyl 1,4-cyclohexanedione-2,5-dicarboxylate (13.7 g, 60.0 mmol) and glacial acetic acid (<4 ml) were combined in a 250 ml three-neck flask fitted with a reflux condenser and the mixture was heated to 80 °C for 30 min under  $N_2$ . Then 2.49 g (15 mmol) KI and 3.81 g (15 mmol)  $I_2$  were gradually added sequentially, followed by 10 ml (0.10 mol) of  $H_2O_2$  solution dropwise, and the mixture was heated to reflux for 1 h.  $^1H$  NMR analysis revealed that 98% conversion was attained after that time. Upon cooling the flask in an ice bath, large amounts of brown crystals formed. The crude product was dissolved in a minimum amount of hot water and precipitated in methanol to give white needle-like crystals, that were filtered and vacuum-dried at 60 °C for 3 h to give 11.5 g (51 mmol) of DMDHT in 85.1% yield.

DMDHT (9.05 g, 40 mmol) and  $K_2CO_3$  (25.15 g, 182 mmol) were dissolved in 320 ml of acetone in a three-neck flask fitted with a reflux condenser. The mixture was heated to reflux for 30 min before 13.7 g (96 mmol) of  $CH_3I$  was added drop-wise, and refluxing was continued for 8 h. The mixture then was allowed to cool to ambient temperature and filtered. The solvent was removed on a rotary evaporator, and

the solid product was washed with 10%  $K_2CO_3$  solution, followed by distilled water three times. The purified product was finally dried under vacuum at 60 °C for 3 h to give 8.13 g (32 mmol) of white DMDMT in 79.8% yield and >98% purity. The controlled temperature setup used for the synthesis is shown in Figure 2.

### 2.4. Synthesis of random copolyesters P1–P5

For sample P1, dimethyl 2,5-thiophenedicarboxylate, dimethyl 2,5-dimethoxyterephthalate and ethylene glycol in a molar ratio of 0.5:0.5:1.1, with 0.25 mol% of antimony trioxide  $Sb_2O_3$  catalyst (based on DMTD), were combined and the mixture was gradually heated to 140–160 °C under  $N_2$  (esterification step). After 3–5 h the reaction mixture was transparent and methanol droplets formed in the attached condenser, confirming that the esterification reaction proceeded. Cycles of evacuation and  $N_2$  purging were repeated 5 times in the first step. The temperature was then increased slowly from 160 to 230 °C over 4 h (polymerization step), and vacuum was applied slowly until the polyester became too viscous for stirring. The final product was a hard, sticky and whitish fiber-forming polymer. For polyesters P2–P5, 1,3-propanediol, 1,4-butanediol, 1,6-hexanediol and 1,8-octanediol with varying diol molar ratios (1.3–1.5) and a set (0.5:0.5) diester ratio were used. The resulting polyesters were dissolved in chloroform, precipitated in methanol, and recovered by centrifugation. The product was rinsed by dispersion in 200 ml of water–ethanol (1:1 v/v), isolated by filtration, and dried for 4 h at 60 °C in a vacuum oven. The esterification and polymerization temperatures yield, and appearance for each sample are provided in Table 1, while the synthetic procedure is summarized in Figure 3.

## 3. Results and discussion

The molar ratio of diesters was held constant at 0.5:0.5 in the reactions, but the diol:diester ratio was varied from 1.1–1.5 to ensure complete transesterification of the methyl ester groups of the monomers, and that the polymer chains were terminated with hydroxyl groups. Since DMTD can decompose at high temperatures, it was necessary to adjust the reaction conditions for different compositions to minimize thermal degradation. The random copolyesters were synthesized by melt transesterification polymerization using the monomer feed ratios, esterification and

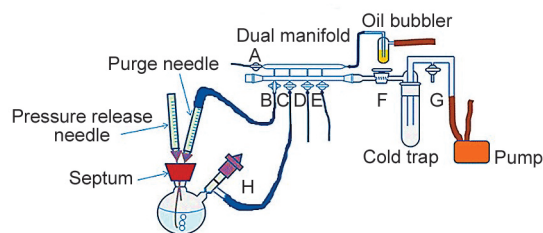
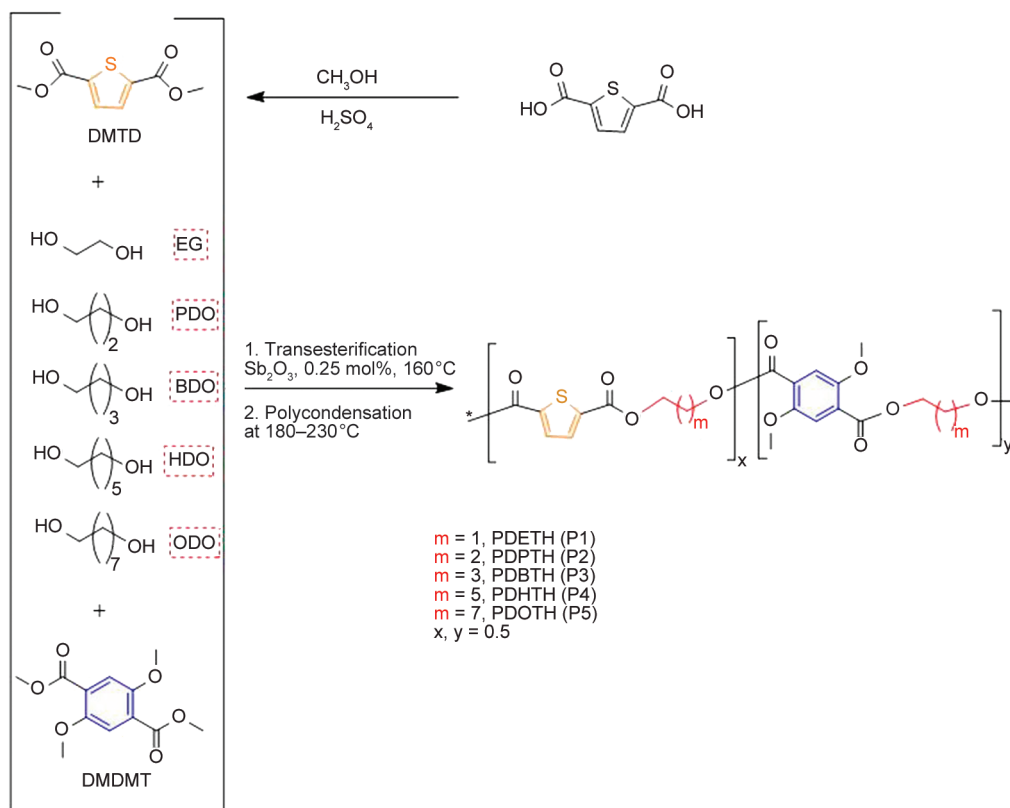


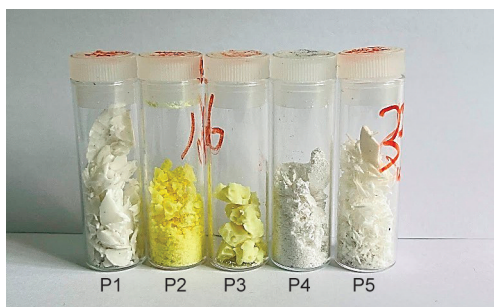
Figure 2. Synthesis setup.

**Table 1.** Synthesis and characteristics of copolyesters.

Sample	P1	P2	P3	P4	P5
Diester:Diol	1.1	1.3	1.5	1.4	1.3
Yield [%]	89	87	83	82	90
Esterification temperature [°C]	160	160	170	180	180
Polymerization temperature [°C]	200	220	230	210	200
$M_n$ [ $10^4$ g/mol]	2.50	2.33	2.15	2.75	2.63
$M_w$ [ $10^4$ g/mol]	4.85	4.23	4.62	4.14	4.31
Polydispersity, $\bar{D}$	1.95	1.73	2.24	1.75	1.47
Appearance	white	yellow	light yellow	light yellow	white

**Figure 3.** Synthesis route for copolyesters P1–P5; in spite of the representation used, the two types of repeating units are expected to be randomly distributed along the chains.

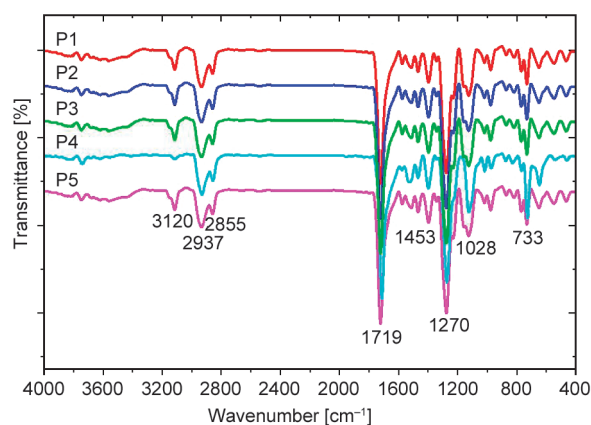
polymerization temperatures specified in Table 1. The coloration of the copolyesters, shown in Figure 4, varied from white to yellow. The incorporated monomer fractions at half conversion (determined by  $^1\text{H}$  NMR spectroscopy), and the reactivity ratios

**Figure 4.** Appearance of copolyesters P1–P5.

for the statistical copolymerization of DMTD and DMDMT indicated the formation of truly random copolymers [27].

### 3.1. Fourier transform infrared (FTIR) and nuclear magnetic resonance (NMR) analyses

The copolyesters P1–P5, prepared as KBr pellets for FTIR analysis, displayed different characteristic absorption bands (Figure 5). The =CH stretching peak, representative for the thiophene ring, appeared at  $3120\text{ cm}^{-1}$ . The asymmetric and symmetric  $-\text{CH}_2-$  stretching peaks were observed at  $2927$  and  $2855\text{ cm}^{-1}$ , respectively. All the spectra had characteristic ester absorptions, including a strong and



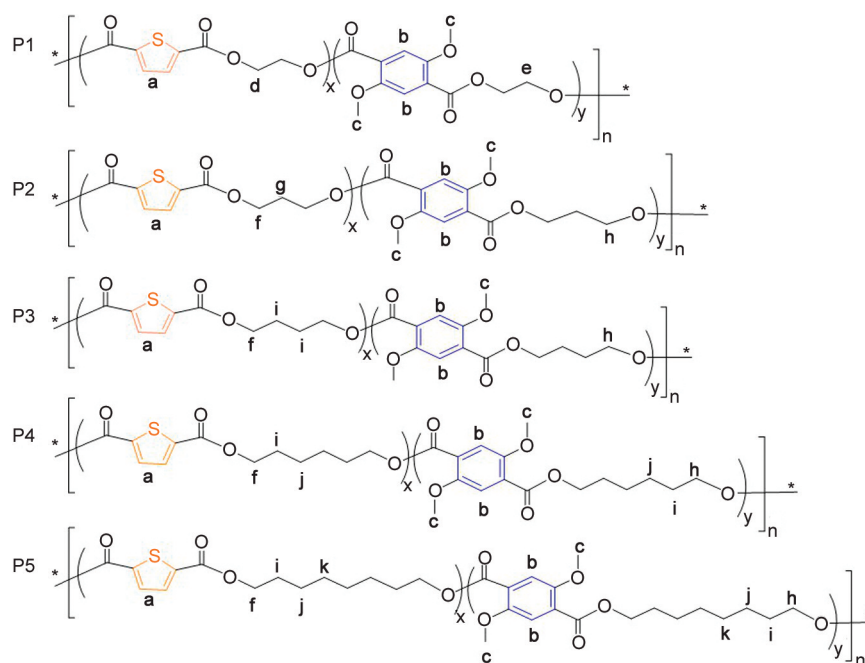
**Figure 5.** FTIR spectra of copolyesters P1–P5.

sharp C=O stretching peak at  $1720\text{ cm}^{-1}$ , and two strong C–O stretching absorptions in the regions of  $1270\text{ cm}^{-1}$  ( $\text{sp}^2$  stretch) and  $1050\text{ cm}^{-1}$  ( $\text{sp}^3$  stretch). The peak at  $1453\text{ cm}^{-1}$  corresponds to an aromatic C=C stretch, and the peaks at  $1071$  and  $724\text{ cm}^{-1}$  is for 1,4-C–H bending, characteristic for DMDMT. The assigned peaks therefore confirm the presence of thiophene and phenyl units in the copolyesters chains.

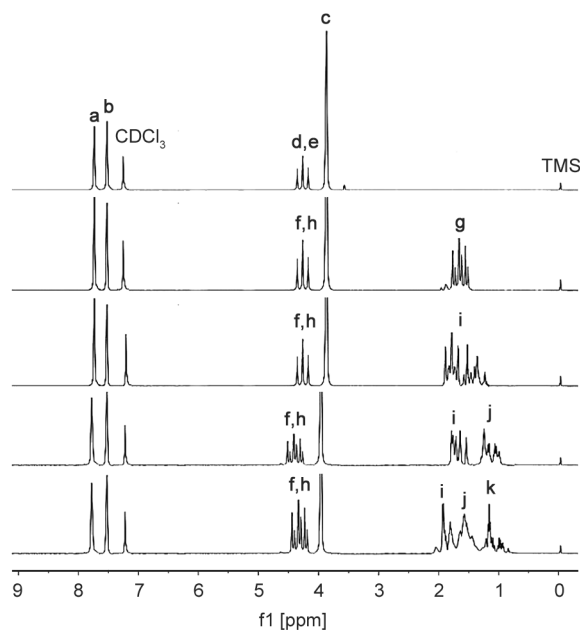
The chemical structure of the copolyesters is shown in Figure 6, while the  $^1\text{H}$  NMR spectra and characteristic signal assignments for the copolyesters are provided in Figure 7. The chemical shift for the –CH= absorption on the thiophene ring (signal **a**) is at  $7.77\text{--}7.80\text{ ppm}$ , while for DMDMT it is at  $7.55\text{--}7.62\text{ ppm}$ , and the –CH<sub>2</sub>– (**d**, **e**) connected to the

ester bonds in P1 is at  $4.66\text{ ppm}$ . All the –CH<sub>2</sub>– (**f**, **h**) units connected to the ester bonds in the different diols produced characteristic signals in the  $4.30\text{--}4.33\text{ ppm}$  range. For P2, the signal for the –CH<sub>2</sub>– (**g**) not connected to the ester bond appeared at  $2.01\text{ ppm}$ , while for P3, (**i**) was at  $1.79\text{ ppm}$ ; for P4, (**j**) was at  $1.45\text{ ppm}$ , and for P5, (**k**) was at  $1.23\text{ ppm}$ . The peak at  $3.88\text{ ppm}$  corresponds to the –OCH<sub>3</sub> units (**c**). The chloroform (CHCl<sub>3</sub>) peak appeared at  $7.30\text{ ppm}$ , and the signal at  $0\text{ ppm}$  was for the tetramethylsilane (TMS) reference.

Analysis by  $^{13}\text{C}$  NMR spectroscopy revealed carbon resonances corresponding to different functional groups in the copolyesters.  $^{13}\text{C}$  NMR [ppm] (CDCl<sub>3</sub>), **P1**: 190, 162, 164 (C=O ester), 149, 143, 135, 134 (thiophene), 153, 164, 114, (phenyl), 55 (O–CH<sub>3</sub>), 63, 64 (OCH<sub>2</sub>–); **P2**: 190.1, 162, 164.2 (C=O ester), 149.5, 134, 135, 143.1 (thiophene), 153, 127.6, 114.9, (phenyl), 55.5 (O–CH<sub>3</sub>), 70.8, 61.1 (OCH<sub>2</sub>–), 28.4, 27.6 (aliphatic); **P3**: 190.3, 162, 164.2 (C=O ester), 149.7, 143.1, 135, 134.8 (thiophene), 153, 164, 114, (phenyl), 55 (O–CH<sub>3</sub>), 63, 64 (OCH<sub>2</sub>–), 25.9, 25.2, 25.1 (aliphatic); **P4**: 190.1, 162, 164.2 (C=O ester), 149.5, 134, 135, 143.1 (thiophene), 153, 127.6, 114.9, (phenyl), 55.5 (O–CH<sub>3</sub>), 73, 64.8 (OCH<sub>2</sub>–), 31.7, 29.5, 29, 25.5, (aliphatic); **P5**: 190.6, 162.5, 164.2 (C=O ester), 149.7, 134.5, 135.7, 143 (thiophene), 153.3, 127.6, 114.9, (phenyl), 55.5 (O–CH<sub>3</sub>), 73, 64.8 (OCH<sub>2</sub>–), 31.7, 29.7, 29.6, 29.3, 25.8 (aliphatic) All the signals assigned again confirm the synthesis of the



**Figure 6.** Chemical structure of the synthesized copolyesters P1–P5.

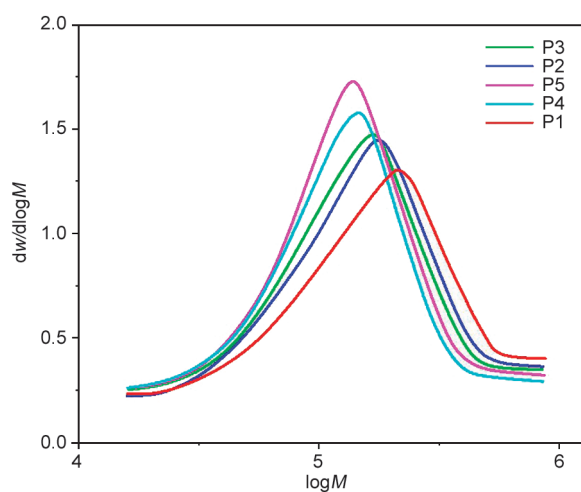


**Figure 7.**  $^1\text{H}$  NMR analysis of copolyesters P1–P5.

target products. The observation of multiple signals for the C=O, and particularly the OCH<sub>2</sub>– carbons, is consistent with the formation of random copolymer structures, as the chemical shifts of these carbon atoms would be sensitive to longer range inductive effects due to the presence of different types of ester linkages, derived from the TDCA and DMTD monomers, along the chain.

### 3.2. GPC analysis

To investigate structure-property relationships among the copolyesters, the molecular weight of the samples was measured by gel permeation chromatography (Figure 8), to ensure that the chains were sufficiently long for the properties to be molecular



**Figure 8.** Gel permeation chromatography analysis of copolyesters P1–P5.

weight-independent. The GPC analysis revealed that the weight-average molecular weight ( $M_w$ ) of the samples ranged from 41 400 to 48 500 g/mol (Table 1), and the polydispersity indices ( $\mathcal{D}$ ) were between 1.47 and 2.24. The polyesters were thus obtained with molecular weights satisfactory for most applications. The  $M_w$  of P1 was highest (48 500 g/mol), possibly due to its amorphous character (no melting point observed) and the higher reactivity of ethylene glycol as compared with the longer chain diols. The relatively small variations in molecular weight observed among the copolyesters are likely the result of different reactivities of the diols towards the diesters, as all the diols used in the reactions had a chemical purity >99%.

In all cases, the molecular weight of the copolyesters was significantly higher than for furan-based copolyesters reported by Maniar *et al.* [28], with  $M_w$  of only 35 000 g/mol, or for vanillin-based polyesters investigated by Zhao *et al.* [29], with  $M_w$  varying from 17 000 to 40 000 g/mol, indicating that thiophene monomers are more easily amenable to polyesters with high molecular weights.

### 3.3. Thermal analysis

The DSC curves obtained for the copolyesters are compared in Figure 9. The glass transition temperature of the samples varied between 47 and 120 °C, depending on the chain stiffness determined by the diol spacer length. Crystallization and melting peaks were observed for copolyesters P2, P3, and possibly for P4, but not for P1 nor P5. As compared with analogues derived from FDCA by Kasmi *et al.* [30], Knoop *et al.* [31], and Chebbi *et al.* [32], the polyesters synthesized in the current investigation have higher  $T_g$  values. For example,  $T_g$  values of 69.5, 38 and 20.6 °C were reported for poly(vanillin-*co*-ethylene furanoate), poly(ethylene 2,5-furandicarboxylate-*co*-ethylene terephthalate) and poly(decamethylene-*co*-isobornide 2,5-furandicarboxylate), respectively, much lower than  $T_g = 120$  °C measured for P1 in our work. The difference could lie in the larger bond angles for the more electronegative O atom as compared to S, differences in electron mobility, and lower average electronic coupling for furan-based as compared to thiophene-based polyesters. The thiophene  $\pi$ - $\pi$  interactions are strikingly similar to furan, but higher non-local (hole)-phonon coupling is observed for thiophene than for furan, due to non-planarity of the thiophene ring [33]. Additionally, our results can be

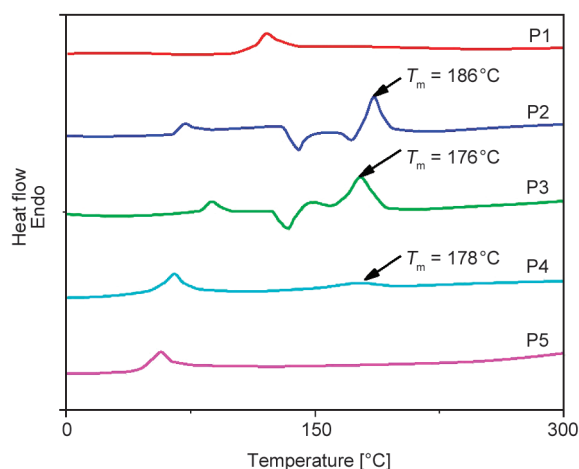


Figure 9. DSC curves for copolyesters P1–P5.

compared with vanillic acid-based polyesters, due to their structural similarity to TPA and their properties similar to PET. Two polyesters of interest, poly(ethylene vanillate) [34] and poly(propylene vanillate) [35], had  $T_g$  values of 83 and 68 °C, respectively, as compared with 120 and 72 °C for samples P1 and P2 synthesized in our work.

In Figure 10a, it is clear from the dTGA curve provided for P1 as an example that the polyesters followed a single-step thermal decomposition process, and in TGA (Figure 10b) all the copolyesters experienced a 5% weight loss ( $T_{d,5\%}$ ) within a temperature range of 370–406 °C under  $N_2$  atmosphere. Key parameters for thermal stability evaluation include the temperatures at which 5% ( $T_{d,5\%}$ ) and 50% ( $T_{d,50\%}$ ) weight losses occur, the temperature at which the decomposition rate is maximum ( $T_{d,max}$ ), and the residual char at 600 °C ( $R_{600}$ ), as provided in Table 2. The high decomposition temperatures observed are interesting because they provide a very broad processing window for these materials.

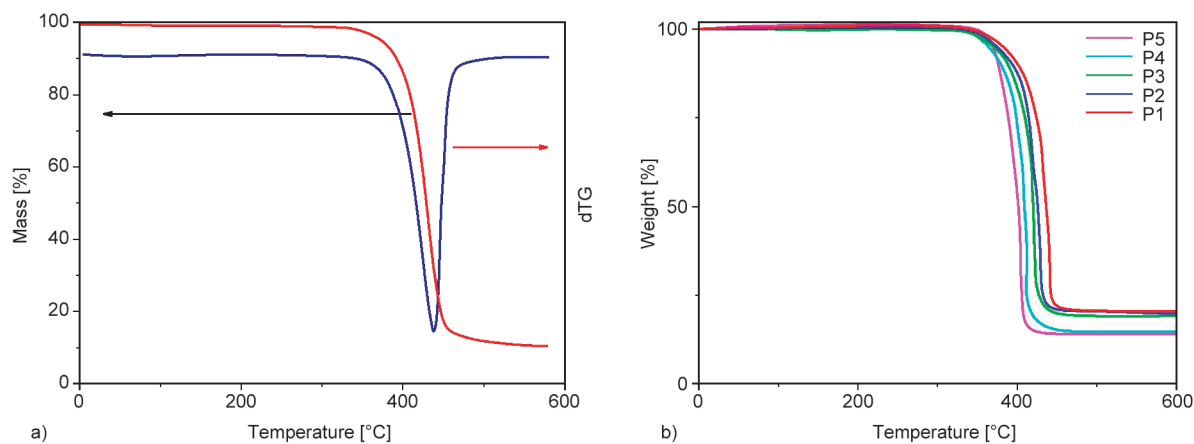


Figure 10. (a) Mass loss (TGA) and dTGA for P1; (b) TGA curves for copolyesters P1–P5 at 10 °C/min in  $N_2$ .

Table 2. Thermal properties of the copolyesters.

Sample	$T_{d,5\%}$ [°C]	$T_{d,max}$ [°C]	$T_{d,50\%}$ [°C]	$T_m$ [°C]	$T_g$ [°C]	$R_{600}$ [wt%]
P1	406	425	421	nd	120	7.9
P2	390	418	418	186	72	3.8
P3	389	414	413	176	88	8.5
P4	380	406	408	178	56	5.9
P5	370	393	391	nd	47	4.7

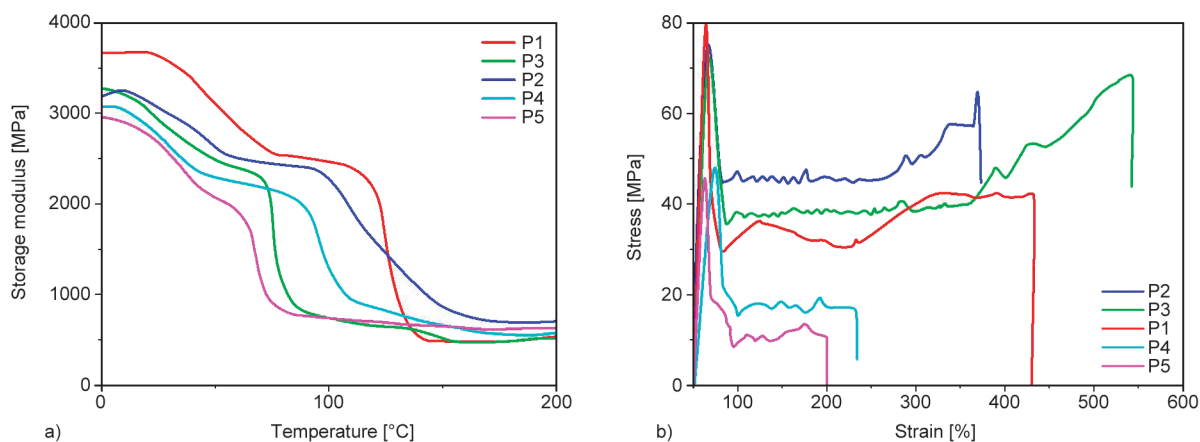
nd = could not be determined.

A particular trend noticed for the copolyesters is that the 5% decomposition temperature decreased slightly as number of carbon units in the aliphatic diols increased from the 1,2- to the 1,8-diol. As for the maximum decomposition temperature ( $T_{d,max}$ ), it also decreased from 425 °C for P1 to 393 °C for P5 under  $N_2$  atmosphere. The thermal stability of the copolyesters therefore decreased as the number of methylene units in the diols increased, and the residual char at 600 °C ( $R_{600}$ ) also tended to decrease somewhat (Table 2). These results are comparable to the findings of Zamboulis *et al.* [34], when comparing the thermal stability of the petroleum-based analogues poly(ethylene terephthalate), poly(propylene terephthalate) and poly(butylene terephthalate), possessing  $T_{d,5\%}$  values in a range of 370–403 °C.

### 3.4. Mechanical properties

To determine the influence of the alkyl diol spacers on the mechanical properties of the copolyesters, dynamic mechanical and tensile testing were performed. The dynamic mechanical properties of the synthesized copolyesters are compared in Figure 11a. All the samples display two obvious transitions in the 0–200 °C range. At most temperatures, the storage modulus follows the order P1 > P2 > P3 > P4 > P5,





**Figure 11.** (a) Storage modulus and (b) tensile testing curves for copolyesters P1–P5.

attributed to the influence of the alkyl diol spacer length, and as temperature increases further, there exist a plateau region for the copolyesters beyond which further increase in temperature causes a large decrease in the storage modulus. These variations correlate with the  $T_g$  of the materials for amorphous samples P1 and P5, but are scrambled for samples P2–P4 due to the combined influence of crystallinity.

Wang *et al.* [22] measured a tensile strength of 56 MPa and an elongation at break of 510% for PET. In Figure 11b, the tensile strength of copolyesters P1–P3 was 72–80, 16–24 MPa higher than for PET, with elongations at break of 390–540%. These results are also much better than for poly(ethylene-*co*-2,2,4,4-tetramethyl-1,3-cyclobutanediol 2,5-furandicarboxylate) (PETF) synthesized by Wang *et al.* [21], exhibiting a tensile strength of only 69 MPa and an elongation at break of 270%. The superior performance of the current samples is attributed to differences in crystallinity for polymers containing thiophene and aromatic rings, and to the length of the alkyl spacers, all of which contributed to the remarkable properties of the bio-based copolyesters.

These characteristics also caused a decrease in tensile strength, modulus, and/or melting point for samples P4 and P5, confirming the existence of a peak in performance for the  $C_3$ – $C_4$  diol alkyl spacers. The elongation at break of all the copolyesters synthesized was still in the range of 200–540%, much higher than for furan-based polyesters (5–290%) [36, 37], possibly due to differences in molecular weight and to the bond angles for the heteroatoms in the furan and thiophene rings of 148 and 129°, respectively, but also to the higher degree of aromaticity of the thiophene ring as compared with the furan ring [38, 39]. When the alkyl spacer length in the diol increased to

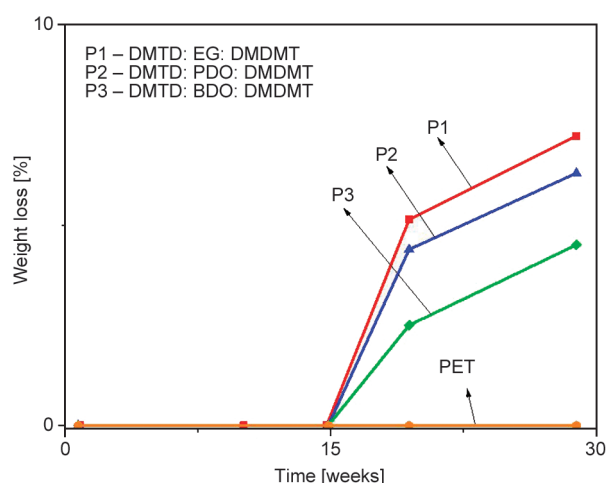
**Table 3.** Mechanical properties copolyesters P1–P5 and selected reference samples.

Sample	Tensile modulus [MPa]	Tensile strength [MPa]	Elongation at break [%]
PET [22]	1170±40	56±3	508±90
PETF [22]	1430±20	69±2	270±10
PDETH (P1)	2700±10	80 ±2	440±30
PDPTH (P2)	2200±10	73±2	390±30
PDBTH (P3)	2350±10	72±2	540±30
PDHTH (P4)	2060±10	48±2	240±30
PDOTH (P5)	1890±10	45±2	200±30

$C_6$  and  $C_8$ , the tensile strength of P4 and P5 dropped to 48 and 45 MPa, and the elongation at break decreased to 240 and 200%, respectively. This could be related to their lower  $T_g$  of only 56 and 47°C, in addition to their poor crystallizability (Table 2). The tensile strength values observed at the yield and break points for P1, P2 and P3 are nevertheless comparable to high-density polyethylene (HDPE) [40] and polypropylene [41], whereas P4 and P5 are close to low-density polyethylene (LDPE) [42].

### 3.5. Soil degradability of polyesters P1–P5

A critical factor in the development of greener and eco-friendly polymeric materials lies in the ability of the materials to biodegrade in the environment after their life span is exceeded. In this investigation, a commercial PET sample and selected copolymers were subjected to soil degradation assays. The extent of biodegradation was quantified by recording the weight loss of the samples at predetermined time intervals. Biodegradation became significant after 15 weeks, but the degradation rate slowed down at longer times (Figure 12). The weight of the copolyesters decreased by 4.5–7.2% over the



**Figure 12.** Biodegradation for copolyesters P1–P5.

28 week period of the investigation. In comparison, no apparent change was observed for commercial PET, confirming the poor degradability of that material.

An induction time at the beginning of the biodegradation processes has been observed for bio-based materials such as poly(lactic acid) and furan-based polyesters reported by Lyyra *et al.* [43] and Chebbi *et al.* [32], respectively, both in aqueous and controlled compost media. The explanation of this phenomenon lies in the nature of the hydrolytic chain scission process (combination of random and chain-end scissions) occurring in the first step under the influence of enzymatic action. Initially, hydrolytic degradation occurring at the ester bonds within the macromolecular chains brings about random cleavage, resulting in the production of shorter chain segments and oligomers (micromolecular chains). As the phenomenon persists, the magnitude of the molecular weight reduces to threshold values allowing their easy solubilization and diffusion in the biodegradation medium [44]. Additionally, the C–S bonds derived from dimethyl 2,5-thiophenedicarboxylate (DMTD) units is an added advantage for degradation, since sulfur serves as substrate for microorganisms (sulfur-loving bacteria), thereby promoting hydrolytic degradation. The weight losses were still lower than for furan-based polyesters reported by Lyyra *et al.* [43] (maximum weight loss of 12.5%, as compared with 7.2% in the current investigation), mainly due to the higher electronegativity of O as compared with S, and also due to the insertion of small amounts of isosorbide in the backbone. Since isosorbide is a sugar-derived diol of biological origin,

it is easily digestible by microorganisms in the soil, thereby contributing to increased degradability [15]. Another feature observed in the plots is that the weight loss tends to increase for decreasing alkyl diol spacer lengths in the polyester backbone. From the biodegradation test results, it is understood that the rate of biodegradation decreases as the number of methylene units in the diol spacer increases, therefore copolyester P1 was more strongly degraded than P2 and P3. The main distinguishing feature of P1 is its amorphous character, which likely contributed to its higher degradation rate due to enhanced accessibility of the ester bonds to the depolymerizing microorganisms [45]. In addition, it is well known that amorphous regions of semi-crystalline polymers are more prone to degradation than the well-ordered and more densely packed crystalline ones. Differences in crystallinity and chemical reactivity may therefore explain the observed trends. Indeed, similar findings were reported for certain starch-based bioplastics and isosorbide-furan based polyesters, which began to decompose after a certain time due to crystallinity [46–48].

Irrespective of the results obtained, a better way to degrade these polymers would likely be enzymatic catalysis since their degradation efficiency may be similar to poly(ethylene furanoate), and the resulting monomers could be recovered and reused for the synthesis of polyesters rather than ‘lost’ in the ground. This method has proven to be more efficient (selective) when specific enzymes are used, as described in recent investigations of Weinberger and coworkers [49, 50].

#### 4. Conclusions

Fully bio-based random thiophene–aromatic polyesters were synthesized from dimethyl 2,5-thiophenedicarboxylate (DMTD), dimethyl 2,5-dimethoxyterephthalate (DMDMT) and aliphatic diols via an environmentally sustainable catalytic method. In all cases, the weight-average molecular weight was over 40 000 g/mol and the polydispersity indices varied between 1.47 and 2.24. DSC analysis revealed that copolymers P2, P3, and possibly P4 were semi-crystalline, while no clear melting nor crystallization peaks were observed for P1 and P5. The degree of flexibility (or rigidity) present in the polymer chains is obviously related to the length of the alkyl spacer in the diol units. Tensile testing showed that all the

polyesters exhibited good toughness (elongation at break of 200–540%). Remarkable degradability reaching 7.2, 6.3 and 4.5% after 28 weeks were observed for P1, P2 and P3, respectively, much higher than for commercial PET, despite their high  $T_g$ .

In summary, the copolymers synthesized in this work possess many outstanding features of interest for practical applications including sustainability, good thermal stability, tunable mechanical properties, and biodegradability, such that they should be suitable to replace petroleum-based commercial PET in the food packaging industry, which is helpful for the polymer industry to implement carbon neutrality and contribute to sustainable development.

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