Synthesis of a Bio-based and Biodegradable Poly(ethylene-co-isosorbide [2,2'-bithiophene]-5,5'-dicarboxylate) with Enhanced Thermal and Degradability Properties

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Abstract—In this investigation, a synthetic biopolymer prepared from bithiophene monomer, isosorbide and ethylene glycol, was synthesized through melt polycondensation. The result showed the polyesters to possess promising thermal and mechanical properties. The bithiophene monomer, [2,2'-bithiophene]-5,5'-dicarboxylic acid, was synthesized from a palladium-catalyzed, phosphine ligand-free direct coupling protocol, using polyethylene glycol palladium (Pd/PEG) as catalyst. The procedure was found effective at polymerizing the bithiophene monomer with isosorbide and glycol. The bithiophene polyester displayed several intriguing properties among good thermal resistance, crystallinity and high tensile modulus. Additionally, the bithiophene monomer coupled to isosorbide enhanced the polyester with a comparatively high glass transition temperature. Films cast out these polyesters display excellent oxygen and water barrier properties, and were interestingly superior to those of poly(ethylene terephthalate). Moreover, the novel polyester also has good soil degradability properties.

Keywords— *direct coupling synthesis; melt polycondensation; bithiophene; degradability studies; thermal stability; gas barrier properties*

I. INTRODUCTION

In view to match up the emerging needs of plastic production, while at the same time enhancing sustainability, has been a big point of focus for both academic and industrial research. Producing a replacement generation of sustainable materials capable of competing with existing petroleum-based plastics, and for these new materials to match both the performance and cost-effectiveness of commonly used Petro-plastics has become a true challenge.^[1] Nowadays, biomass as natural resource of natural products is popularly used as starting materials for the synthesis of bio-based polymers. Bio-thiophene polymers derived from natural products are one among the foremost promising materials. In fact, thiophene derivatived polyesters are considered to be very competitive as biodegradable commercialized polymers, attracting increasing attention to unravel “white pollution” concerns caused by conventional non-biodegradable polymers.^[2-3] Additionally, they found good application as specialty polymers in applications

that mainly involve the biomedical field. Substituted thiophenes are among the foremost important aromatic heterocyclic derivatives. Many molecules incorporating the thiophene nucleus have shown important degradability activities.^[4-6] Thiophene derivatives have an outsized domain of application like in material science, coordination chemistry and as intermediate in organic synthesis.

Thiophene poses a five-membered aromatic ring structure within the heterocyclic chemistry. It contains one sulfur atom as a heteroatom and 4 carbon atoms. It is extremely reactive because of the presence of π -electron cloud structure similar to benzene. The substituted thiophene derivatives are also known for in medicinal and thermal applications.^[7] As far as on-going research involving the synthesis of polymeric materials and therefore the synthesis of varied substituted heteroaromatic compounds, and the stabilization of polymers, growing interest on the synthesis of thiophene derivatives have been reported. Herein, we reported the syntheses of varied copolyesters derived from thiophenes, namely, bis(2-hydroxyethyl) [2,2'-bithiophene]-5,5'-dicarboxylate(EET), 5-(2-hydroxyethyl)5'-(6-hydroxyhexahydrofuro[3,2-b]furan-3-yl) [2,2'-bithiophene]-5,5'-dicarboxylate(IET), bis(6-hydroxyhexahydrofuro[3,2-b]furan-3-yl) [2,2'-bithiophene]-5,5'-dicarboxylate (IIT), and [2,2'-bithiophene]-5,5'-dicarboxylic acid acid (3). However, the “dimeric” homologue of two ,5-TDCA, [2,2'-bithiophene]-5,5'-dicarboxylic acid acid (3) (BTDCa, Figure 1), has also received similar attention, and its preparation was disclosed in 1966. Recently, BTDCa was used as a monomer to organize coordination polymers with various transition metal cations. This copolyester is more suitable for high-temperature, high-performance applications. Over the years, BTDCa derivatives has regularly appeared in patent applications regarding polyesters. It might be therefore intriguing to think about BTDCa as an alternate building block for various polymers so as to reinforce their material properties.^[8-9] Polyesters containing BTDCa and isosorbide have not been characterized or disclosed before to the best of our knowledge. Among popular

ecofriendly monomers commonly used, isosorbide (ISO) may be a promising renewable diol produced at industrial scale by dehydration of sorbitol, via the hydrogenation of D-glucose derived from cornstarch.^[10-11] This monomer has interesting rigidity and chirality properties, nontoxicity, bioavailability, and good thermal stability. Insertion of this diol as part of polymer main chain proved to very helpful for stabilization and enhancement of their thermal properties, as well as a spectacular increase in the glass transition temperature (T_g) as experiment demonstrated. All these numerous advantages was possible by the insertion of isosorbide units into polymers backbone. However, the increasing composition of isosorbide to an extent can destroy the chain's regularity and thus leading to a very poor crystallinity and in many cases to totally amorphous materials, which drastically hinders their applications at the industrial level. An example was reported by Gomes et al., who synthesized a fully renewable and wholly amorphous homopolyester (PIsF) derived from isosorbide and FDCA. To remedy this problem, addition of isosorbide in the polymer backbone was done in small molar ratios with optimum isosorbide insertion at 10 to 15% of the whole polymer chains.^[12-14] This can be explained based on the lower reactivity of secondary hydroxyl groups of isosorbides, so using it in excess will hinder the chain structure. The presence of these hydrocarbon chains into thiophene-based polyester structures enhances the crystallization, and participate to boost ability the hydrophobicity and thermal properties of the prepared materials. Herein it adjusted their melting temperatures to ones suitable for thermoplastic processing. In this light, one among numerous studies published on thiophene-based polyesters has dealt with the synthesis, as well as the structural, thermal, and degradability characterization, of an aliphatic polyester, poly (ethylene-co-isosorbide[2,2'-bithiophene]-5,5'-dicarboxylate) PEIsTs.^[15-17] The polyester display a significant degree of crystallinity, prepared from a renewable aliphatic diol, ethylene glycol (EG). This building block obtained derived from biomass originates from castor oil, via esterification and hydrogenation processes, as well as applying a green synthetic route was disclosed in a recent patent.^[18]

To the best of our knowledge, the study of the relationship between the structure and properties for the long-chain aliphatic PBIIsTs polyester with incorporated isosorbide has been examined for the first time in the present work. In this context, we aimed to synthesize through a melt polycondensation procedure a new renewable resources-based bithiophene copolyesters series containing BTDCa, EG and a varied rigid and flexible segments molar ratio of ISO respectively. The ISO as comonomer, had great effects on the properties of the resulting material, including the thermal and mechanical properties and their excellent biodegradation in soil.^[19]

II. EXPERIMENTAL SECTION

A. Materials

5-(methoxycarbonyl) thiophen-2-ylum (purum 99%) was obtained from Sinopharm Chemical Reagent Co., Ltd, using 2,5-Thiophene dicarboxylic acid (TDCA) (Aldrich, 97%), from Zhengzhou Xipaike Technology Co., Ltd, methyl 5-bromothiophene-2-carboxylate and potentially bio-renewable formaldehyde or acetaldehyde. Ethylene Glycol (EG, purum 98%), polyethylene glycol palladium (Pd/PEG) (purum 97%)/ Antimony trioxide (Sb_2O_3) as catalyst, and Isosorbide (ISO, purum 99%) reagents were purchased from China sigma Co. All other materials and solvents used were of analytical grade. Methanol, ethanol, dibromoethane, acetonitrile, potassium carbonate, N,N-dimethylformamide, Trichloromethane are analytical pure, 30% H_2O_2 solution, Wuhan Squire Test Agent Liability Co., Ltd.

B. Characterization and Equipment

FTIR test: BRUKER VERTEX 70 Infrared spectrometer, wavenumber range $4000\sim 400\text{ cm}^{-1}$, resolution 0.4 cm^{-1} , number of scans 80 s^{-1} , KBr tableting. 1H NMR test: Bruker Advance DMX600 Nuclear magnetic resonance instrument, TMS for Internal standard, $CDCl_3$ for solvent, resonance frequency 600 Hz.

DSC test: The differential scanning calorimeter was operated on a Mettler Toledo DSC 821e at temperature variations of $25^\circ C$ to $300^\circ C$ with heating and cooling rates of 15 K/min under N_2 gas flow ($60\text{ cm}^3/\text{min}$). Then the temperature was raised from room temperature to $300^\circ C$ by $10^\circ C/\text{min}$ to get the heating curve.

TG test: For thermogravimetric analyses, a Mettler Toledo TGA851e was used, with 10 mg of the polymer dipped into a $70\text{ }\mu\text{L}$ Al_2O_3 crucible. This was later covered with a pierced lid and operated by varying temperature from $25^\circ C$ to $500^\circ C$ by $10^\circ C/\text{min}$ to achieve TG curve.

Solution Casting: dissolving the polyester (800 mg) to prepare a solution-cast film in TFA-chloroform mixture (2:1 v/ v, 30 mL). The solution was filtered to remove any insoluble material and poured onto a Teflon Petri dish (diameter 100 mm). The solvent was allowed to evaporate under reduced pressure to give a film, which was finally dried under vacuum for several days ($20^\circ C$). The formed PEIsTs films were almost clear with yellow hue.

Melt Pressing and Gas permeability: prior to the melting process, PEIsTs was initially dried at $120^\circ C$ for 24 h, cooled, and stored in a desiccator to minimize the potential risk of degradation caused by moisture or possible solvent residues. The pressed films (Fontijne Presses LabEcon series press) were fabricated with a

thickness of about 0.1 mm (tensile specimens) or 0.3 mm (gas barrier specimen) using thin metal strips as spacers. The polymer sample was placed as filers in-between sheets of Teflon-coated glass fiber mat of two steel plates. The plates were heated inside the press for 3 min under 10 KN force at 245–255 °C. After the melting stage, the pressing force was increased to 250 KN for 1 min. The pressed plates were then removed from the press and immediately cooled in cold water. To preserve their shapes, the 0.3 mm thick gas barrier specimen was instead cooled inside the press using the integrated water-cooling system.

Dynamic Mechanical Analysis (DMA): The thermomechanical properties of the films were operated by a dynamic mechanical analyzer (TA Instruments DMA Q800,) equipped with tension (film) clamps and operating at a multi-frequency mode. The same procedure for the tensile tests was utilized for the specimen preparation. DMA at variable temperature was conducted as follows: test specimens were heated, at a rate of 5 °C/min, to 250 °C using 13 mm gap distance, 20 µm amplitude, 0.01 N preload force, and 125% force track.

C. Synthesis of [2,2'-bithiophene]-5,5'-dicarboxylic acid [BTDCA (3)]

5-(methoxycarbonyl)thiophen-2-ylum (1) (6 mL, 14 equiv.), methyl 5-bromothiophene-2-carboxylate (2) (836.8 mg, 1 equiv.), potassium acetate (785.3 mg, 2 equiv.), pivalic acid (126.4 mg, 30mol %), and polyethylene glycol palladium(Pd/PEG) (9.0 mg, 1mol %) were added to a dry 50 mL round-bottom flask with a magnetic stirring bar. A balloon was equipped with a reflux condenser attached to the flask. Series of N₂ purging was done five times in a roll. The starting reaction temperature of the mixture was 120 °C under stirring. After 24 h, the reaction system was cooled to room temperature. This reaction mixture was dissolve with chloroform and later filtered through a silica gel plug. The silica layer in column layer was washed with chloroform till the product was completely collected. Vacuum extraction of chloroform was applied and the excess of reacting material 1 was recovered by vacuum distillation and recycled in subsequent reactions. The dry product was washed by stirring it in 14 mL of hot 1:1 (v/v) mixture of chloroform and ethanol for about 15 min. Vacuum filtration was later re-applied to recovery the cold solution, and further washing with small amounts of cold ethanol yielded product 3, in light yellow-white crystalline powder. (876.3 mg, 88~90%). ¹H NMR (400 MHz, CDCl₃, ppm): δ 7.26 (d, 2H (thiophene), J = 3.8 Hz), 6.90 (d, 2H (thiophene), J = 3.8 Hz), 3.93 (s, 6H (methyl ester)). ¹³C NMR (100 MHz, CDCl₃, ppm): δ 158.8 (ester carbonyl), 148.2 (thiophene

ring), 145.3 (thiophene ring), 120.7 (thiophene ring), 110.4 (thiophene ring), 54.1 (ester methyl group).

Figure 1 The synthesis route of BTDCA monomer.

D. 2.4. Synthesis of poly(ethylene-co-isosorbide [2,2'-bithiophene]-5,5'-dicarboxylate) (PEISTS)

[2,2'-bithiophene]-5,5'-dicarboxylic acid (3), ethylene glycol (6 equiv.), isosorbide (10~40%) composition and tetrabutyl titanate (1mol %) were added to a dry 50 mL round bottom flask with a magnetic stirring bar. The flask was connected to a distillation bridge coupled to both N₂ and vacuum lines. Air inside the system was replaced N₂ purging. These was repeatedly done five times. The flask was pre-heated at 180°C to start the transesterification process with an aluminum-heating block. Within 30 min, the heterogeneous mixture had turned into a pale-yellow solution. After 4 h, the transesterification was considered complete from the water droplets observed from the condensed bulb. At this stage, the monomer was no longer detected (TLC), and methanol ceased to distill over. Vacuum then applied gradually to remove the excess ethylene glycol under a pressure of (3–4 mbar). The temperature was increased to 300°C for 9 h until the “Weissenberg effect” was observed and the reaction flask was later cool under vacuum. The polyester was removed from the flask by dissolution in trifluoroacetic acid (TFA) chloroform mixture (1:1) and further precipitated in methanol. The obtained product was dried after vacuum filtration and washing with methanol, yielding an off-white, fibrous material (94~96% yield). To prepare NMR samples, small amounts of PEI₅T₅ was dissolved in TFA-d. The data (Figure 3a) conform to the expected structure. ¹H NMR (400 MHz, TFA-d, ppm): δ 7.48 (d, 2H (thiophene), J = 3.9 Hz), 7.01 (d, 2H (thiophene), J = 3.9 Hz), 4.87 (s, 4H (ethylene unit).

III. RESULTS AND DISCUSSION

As shown in Figure 2, a series of BTDCA-based polyesters were synthesized by a two-step process (the preferred technology route). Initially, the dimethyl ester of BTDCA, [2,2'-bithiophene]-5,5'-dicarboxylic acid (3), was been synthesized via transition-metal-mediated homo-coupling of methyl 5-bromothiophene-2-carboxylate (2), but this method produced large amounts of iodine and/ or metal waste despite the good product yield (68–90%). To reduce waste, new ways were developed using a direct coupling approach, where a half fold of the bromide (2) can be replaced with the non-

brominated methyl 2-thiophenecarboxylate (1). Thus, the starting point of our new approach was the direct coupling where a similar, but asymmetric, bithiophene diester was synthesized.³

Looking at the first investigation we noticed that pivalic acid (PivOH) produces faster and more effective coupling (entries 1 and 2) in dry DMAc solvent with polyethylene glycol palladium (Pd/PEG) catalyst. On tested basis, potassium acetate displayed the highest reaction yield at optimal reaction temperatures (entries 2–7). Also, an increase in the amount of starting material 1 from 2 to 3 equiv., and then from 3 to 4 equiv., increased the yield of compound 3 (entries 3, 8, and 9, respectively), but any further increase of the amount to 5 equiv., had a slight or no improvement effect (entry 10). Doing this reaction in the presence of excess liquid 1 (1.5 mL total, 14 equiv., entry 11) without additional organic solvent, interesting results were observed: even though the bromide was not fully consumed and the reaction yield was much lower, the reaction nevertheless proceeded with minimal side-products.

Figure 2 Synthetic route of PEIsTs Polyester.

By simply increasing the reaction time from 4 to 24 h under vacuum finally gave a significant amount of the product 3 at 88–90% yield, fully consuming the bromide (entry 12). Herein, PivOH showed to be more vital for this reaction and its conditions, as the reaction did not finish within 24 h in the absence of PivOH (entry 13).

A. Copolyester synthesis

In this study, a novel series of bio-renewable copolyesters derived from BTDCA, ISO, and EG was successfully synthesized via an esterification/polyesterification/polycondensation process, shown in Figure 2. First, the transesterification bishydroxy products were prepared from BTDCA and EG using

polyethylene glycol palladium (Pd/PEG) as catalyst, and then, subjected the corresponding bishydroxyalkylene-2,5'-bithiophene carboxylate monomer (BTDCa) to polyesterification in the presence of EG with molar ratio of 1:2.

Isosorbide has a bulky structure and EG a high boiling point, which block their removal from the reactor during the melt polycondensation stage even under high vacuum pressure; BTDCa was added at the esterification step instead of carrying out the melt polycondensation step. This innovative trick played an important role guaranteeing that all added amounts of EG and ISO are totally reacted. In final step, the polycondensation stage was carried out at 220–300 °C for 2h under vacuum 4.0 Pa, applied slowly over a time to initiate the melt phase polycondensation of intermediate. This was to minimize oligomer sublimation and avoid excessive foaming, which is a potential problem during the melt polycondensation. The final product yielded a translucent polymer with light-brown appearance. The weight-average molecular weight (M_w) of the purified PEIsTs copolyesters was measured by GPC and determined to be in the range of 55,200–95,500 g/mol.

TABLE 1 Optimized Reaction Conditions for the Synthesis of Compound 3

Entry	Equiv. of (1)	Base(2 equal)	Temp (°C)	Time (h)	Yield
1 ^b	2	KOAc	130	4	46
2	2	KOAc	120	2	52
3	2	KOAc	100	4	54
4	2	KOAc	80	24 ^c	26
5	2	KOAc	100	4	51
6	2	KOAc	100	24 ^c	25
7	2	KOAc	100	24 ^c	
8	3	KOAc	100	4	63
9	4	KOAc	100	4	70
10	5	KOAc	100	4	71
11 ^d	14	KOAc	100	4 ^c	38
12 ^d	14	KOAc	100	24	89
13 ^{b,d}	14	KOAc	100	24 ^c	53 ^c
14	14	KOAc	100	24	88 ^f

Table 1: (a) Reaction conditions: 1equiv of bromide 2 (0.2 g), 1mol % of polyethylene glycol palladium (Pd/PEG), dry DMAc (4mL), N₂ atmosphere. All yields are isolated yields, (b) No PivOH, (c) Bromide not fully consumed, (d) No DMAc, (e) Crude yield after silica gel filtration, (f) the average yield of 10 reactions done at a scale of 1.6 g of bromide 2.^[20]

Yosra Chebbi and al.,^[21] mentioned, that the number-average molecular weight (M_n) showed a significant decrease by increasing the ISO content in the polymer chain. This is because of the lower reactivity induced by

the secondary hydroxyl groups of isosorbides compared to primary –OH moieties of EG. Additionally, the presence of the endo secondary hydroxyl functionality in the comonomer produces a further decrease in the reactivity due to the extraordinary steric hindrance effects. Carboxyl end-group analysis (–COOH) was carried out for the resulting PEI₅T₅ copolyesters samples. The existence of the carboxyl end-groups can be explained by the decomposition reactions such as thermal degradation occurring at the melt polycondensation stage. As demonstrated, the concentration of the –COOH content decreases when the M_w value increases (Table 2). These findings are in good agreement with what was reported in other works.

The as prepared polyester, “poly(ethylene-*co*-isosorbide bithiophene) PEI₅T₅, was as well soluble in both TFA and TFA–chloroform mixtures, but no obvious solubility was observed in different tested organic solvents such as dichloromethane, chloroform, methanol, N-methylpyrrolidone, or 1,1,2,2-tetrachloroethane. However, TFA is highly acidic and corrosive, and could potentially participate in the degradation of the polyesters, but interestingly under the same conditions, no degradation of the polyester chains was reported at room temperature.

TABLE 2 PEI₅T₅ polyester Characteristics

samples	PEI ₅ T ₅ ratios	PEI ₅ T ₅ ¹ HNMR	M _n (gmol ⁻¹)	M _w (gmol ⁻¹)	COOH (eq/10 ⁶ g)
PEI ₁₀ T ₉₀	90/10	87/12.5	21,500	85,300	25.54
PEI ₁₅ T ₈₅	85/15	85.5/14.5	25,300	95,500	32.60
PEI ₂₀ T ₈₀	80/20	81/19	23,400	80,700	31.7
PEI ₃₀ T ₇₀	70/30	73/27	15,000	55,200	47.56
PEI ₄₀ T ₆₀	60/40	62/38	18,100	65,500	53.48

B. FTIR and ¹H NMR characterization

A high molecular weight BTDCa-EG copolymer were synthesized as shown in Figure 2 via a two-step melt polymerization method. Using NMR and FTIR analyses, the expected synthesized polyester structure was determined. In the ¹H NMR spectrum (Figure 3b), we have doublets corresponding to the bithiophene moiety still present, but a broad peak from the ethylene unit is observed instead of the methyl ester peak from the bithiophene monomer. Looking at the FTIR spectrum, we observed carbonyl groups related to absorptions at 1718 cm⁻¹ and 2,5-substituted thiophene rings at 1255, 1570, and 3120 cm⁻¹. The absorption peak at 2986 cm⁻¹ corresponds to the *sp*³ carbon C–H bonds of the ethylene unit. Further, a closer look of the ¹H NMR spectrum did not reveal any distinct end-group signals. This probably tells us that the number average

molar mass lies beyond the 10000g/mol range, and all polyester chains are presumed to be hydroxyalkyl capped at end-chains. Two extra signals corresponding to ether and ester type –CH₂– groups are observed, indicating the presence of ethylene units. Since EG has two hydroxyl groups (reaction sites), it can easily incorporate itself into the polyester structure during the polycondensation. In commercial PET, EG is often present in different grades, where the more flexible EG moieties can possibly increase the thermal behavior of the polyester among other effects. Polyesterification between 2,5-TDCA and EG also leads to the synthesis materials with similar properties to PET. Referring to the analysis of the ¹H NMR spectrum integrals, the ethylene content in PEI₅T₅ is estimated to be lower than 1 mass %. This is almost similar to the EG content reported for PET in previous report^[22-25].

Figure 3a ¹H NMR spectrum (4–8 ppm) of PE₅T₅ polyester

FIGURE 3b The whole ^1H NMR spectra of PEIsTs according to the incorporated ISO%.

C. DSC and TGA analysis

DSC analyses shows the thermal properties of the PEIsTs copolyesters in Figure 4a. The related thermal transition data collected in this analysis, includes the melting temperature (T_m), glass transition temperature (T_g), and the heat temperature scan, all gathered in Table 3. The high thermal behavior of copolymers especially thermoplastics is significant for their processing and potential applications. Therefore, the effect of the composition-structure and the thermal properties were characterized by DSC and TGA measurements. Due to its rigid structure and less flexible nature, ISO hinders the crystallization to an extent, but also greatly improves the T_g of the polymer. PEIsTs copolyesters are semi-crystalline materials having a relatively high glass transition temperature of 127°C , attributed to the polyester with a relative low molar content of ISO not more than 10%, enabling it to meet the heat resistance requirements with a T_g value of 100°C value suitable for most daily used products, such as nursing bottles and plastic cups. For comparing sake, PET^[22] have lower typical T_g value of 87°C where as PEIsTs shows greatly enhanced glass transition temperature when compared to PET (Figure 4b). In other words, bithiophene monomers with straight chain links to ISO are suitable for thermally robust polymers. Even with its higher T_g , PEIsTs has a slightly lower melting point ($T_m=237.5^\circ\text{C}$) than PET. Figure 5a, shows the TGA traces of PET and PEIsTs between 150 and 650°C under N_2 , where both polyesters decomposed in a single-step (Figure 5b). Weight loss values at 5% and 10% ($T_{d,5}$, $T_{d,10}$) were observed at 413.5°C , and the weight loss rate reached a maximum ($T_{d,max}$) at 443.8°C . For PET, $T_{d,5}$ and $T_{d,max}$ were both high at 400 and 458°C , respectively. After the TGA runs, About 20% of the initial sample weight was left as

residue for PEIsTs after the TGA runs, while only 15% was left of the PET sample. These values agree with the higher content of aromatic units in PEIsTs. Review from thermal weight loss in PEIsTs is quite comparable to thiophene-based PET, which is reasonable when considering the similarities in thiophene ester linkages. Results from previous reviews shows, T_g to significantly increase broadening the applications of the materials via copolymerization with rigid monomers as a common solution. Inserting ISO has been a major “hot topic” in modifying PBT, PES or PEF structures. However, it is of difficulty to simultaneously improve the T_g and the molecular weight without compromising the sustainability. In Figure 5b, the T_g of polyesters PEIsTs are compared with those of previously reported polyesters.

D. Gas barrier properties

The barrier properties strongly depend on characteristics such as solubility, diffusion, permeability, and others, the nature of the fluid, temperature, and other factors displayed by the polymer. Here, the polymer barrier-film application in packaging, construction, and agriculture are discussed. Thus, in order to evaluate their potential application in the packaging industry, the CO_2 and O_2 barrier properties of PEIsTs, except brittle PEI₆₀T₄₀, were characterized by complementary pressure decay sorption and permeation techniques. The investigation proves that bithiophene-based PEIsTs would have lower gas permeability compared to commercial PET. Gas-barrier properties of PEIsTs were studied measuring the O_2 and H_2O vapor permeability of melt-pressed films, and comparing the results to a PET specimen in Table 5. The barrier improvement factor (BIFp) was defined as the permeability coefficient of PET.

FIGURE 4 (a) DSC trace of PEIsTs measured under N_2 , (b) TGA traces of PEIsTs and PET measured under N_2 .

FIGURE 5: TGA curves of the pure copolyesters (PEIsTs): (a) remaining mass and (b) first derivative of mass loss.

TABLE 5 Oxygen and water vapor permeability

Polyester	Oxygen permeability ^a (barrier)	BIFp	Water vapor permeability ^b ($\mu\text{mm}^{-2} \text{ day}^{-1}$)	BIFp
PEIsTs	0.063	2.6	358.463	2.0
PET ^[22]	0.099	1.0	616.711	1.0

(a) Oxygen permeability at 25 °C at normal atmospheric pressure, 0% RH, (b) Water vapor permeability at 25 °C, normal atmospheric pressure, 100% RH.

E. Dynamic Mechanical Analysis

Figure 6 shows the test conducted on the melt-pressed PEIsTs film in further support of the findings from the thermal experiments: $\tan \delta$ reaches its peak value at 127 °C, designating a transition of phase from glassy state to rubbery state, whereas the loss modulus (E'') curve display a glass transition temperature of 117 °C. Furthermore, the storage modulus (E') shows an increase after a rise in temperature to 160°C, which is consistent with cold crystallization.

FIGURE 6 Storage modulus (E'), loss modulus (E''), and $\tan \delta$ of PEIsTs as functions of temperature.

F. Degradation Properties

In regards for polymer application in commercial field such as packaging industry, properties like biodegradability has become a necessity. The degradation properties of PET (synthesized through commercial EG) and its copolymers with or without lipases have been investigated via various research revealing that PET is hardly degradable under ambient temperature. Here we revealed that the copolyesters PEIsTs under the effect of soil hydrolysis underwent biodegradation. The decrease in the sample weights over an incubation period of 28 days in a phosphate buffer solution at a suitable pH (7.4) shown in Figure 7. With the assistance of porcine pancreatic lipases, monitor scans for PEIsTs were obtained except for sample $\text{PEI}_{40}\text{T}_{60}$, which became very fragile and brittle making it impossible to form intact films. As shown in Figure 7, compared to commercial PET, all the PEIsTs samples showed an appreciable degradation, which correlate the great-enhanced biodegradation under the effect of copolymerization. The weight loss of PEIsTs increased from 4.8 to 10.2% with increase in feeding molar content of ISO from 10 to 40%. Observing sample $\text{PEI}_{10}\text{T}_{90}$ and $\text{PEI}_{15}\text{T}_{85}$ showed a degradation rate with a weight loss of 13.2% and 12.7% after 28 days in phosphate buffer solution upon the addition of lipases. Compared to the initial samples, studies revealed that the degradation behavior of PEIsTs was mainly caused by the degradation of the ethylene and isosorbide units, breaking down via soil hydrolysis and degradation. This is consistent with the phenomenon of increased content of E_T unit causing an improved degradation rate in all samples. Unfortunately, the I_T unit was unable to degrade under the testing conditions. In addition, the dark holes on the films are indicative indicated of the biodegradation occurring in the entire sample. Noteworthy, it is one of the few ever-reported

degradation sensitive to ISO-containing copolymers with such high T_g values, which is of interest in developing new green packaging materials.

FIGURE 7 Degradation properties of PEIsTs in phosphate buffer solution with porcine pancreatic lipases.

IV. CONCLUSION

The synthesis of biomass-based bithiophene monomer (3) was studied and optimized. A series of bio-based polyester-carbonate containing BTDCa, EG and ISO were successfully synthesized by a two-step melt polymerization. This facile environmentally friendly method not only enables semi-continuous production, thus making it possible to supply materials on an outsized scale, but also produces green materials for the environment. Unlike in previous methods, a high yield is achieved using a direct coupling method for BTDCa synthesis. Besides, utilization of a non-brominated coupling partner is a great initiative toward a green synthesis of potentially useful bithiophene monomer (3). The oligomer obtained by the transesterification of ISO and BTDCa makes it possible to easily incorporate a high content of ISO into the polymer chains without destroying its structure. Thus, in the second step, we prepared copolyesters containing isosorbide moieties via transesterification polymerization with BTDCa and EG copolymers, yielding polyester with high molecular weights (M_w of 95,500–55,200 g mol^{-1}) and improved T_g . The monomer BTDCa with the highest M_w was obtained when KOAc was used as a catalyst and PEIsTs had polyethylene glycol palladium (Pd/PEG) as catalyst. Looking at the thermal properties, the observed values were satisfactory, with high T_g of 127 °C and decomposition temperatures in the range of 400°C. The observed property of PEIsTs would make ethylene-*co*-isosorbide-bithiophene-based materials promising for packaging and substrate applications, due to their high

temperature resistant barrier properties. We can possibly note that BTDCa, or other copolymers derivative of (3), coupled to ISO, could be of great effect for enhancing and modifying the mechanical, thermal, or barrier characteristics of materials in a green manner. TGA results confirmed that the PEIsTs samples are thermally stable ensuring safe processing below temperatures of 300°C. Moreover, the synthesized copolymers are biodegradable under enzyme action and the degradation rate could be varied by simply tuning their composition ratio. In summary, the copolymers synthesized during this work possess many outstanding features for practical interest and applications, including sustainability, high heat-resistant performance, good thermal stability, adjustable mechanical properties, and biodegradability.

CONFLICT OF INTEREST

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

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