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— **A synthetic biopolymer was prepared from bithiophene ($C_8H_6S_2$) monomer, isosorbide ($C_6H_{10}O_4$) and ethylene glycol ($C_2H_6O_2$) was synthesized via melt polycondensation process. The results show that the polyester has good thermal and mechanical properties. The bithiophene monomer (2,2'-dithiophene)-5,5'-dicarboxylic acid was prepared by direct coupling of combined phosphine-free palladium ligand with polyethylene glycol palladium (Pd/PEG) as catalyst. This method can effectively polymerize bithiophene monomer with isosorbide and ethylene glycol. The series of polyesters display good heat resistance, crystallinity and high-tensile modulus. In addition, the bithiophene monomer coupled with isosorbide units increased the glass transition temperature of the polyesters. These polyester films exhibit excellent oxygen/water barrier properties, which are interestingly superior to those of polyethylene terephthalates, and has a significant degradation in soil degradation under the influence of microorganisms.**

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

I.   INTRODUCTION

The view to match up with 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 or 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 such as natural products are 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 derived 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 have 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 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 medicinal and thermal applications.[7] As far on-going research involving the synthesis of polymeric materials and therefore the synthesis of varied substituted heteroaromatic compounds, the stabilization of polymers, growing interest on the synthesis of thiophene derivatives have been reported. Herein, we report the synthesis of various copolyesters derived from thiophene, 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'-dicarboxylicacid acid (3). However, the "dimeric" homologue of 2,5-thiophenedicarboxylic acid (TDCA), [2,2'-bithiophene]-5,5'-dicarboxylicacid acid (3) (BTDCA, Figure 1), has also received similar attention. Recently, BTDCA was used as a monomer to organize coordination polymers with various transition 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 therefore be 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 eco-friendly monomers commonly used, isosorbide (ISO) is 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, non-toxicity, 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 were possible by the insertion of isosorbide units into the polymer 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 amorphous materials, which drastically hinders their applications at the industrial level. Gomes et al.[12], for example synthesized a fully renewable and amorphous homopolyester (PIsF) derived from isosorbide and FDCA. To transit from amorphous to semi-crystalline, addition of fine isosorbide units in the polymer backbone (10-15%) enhanced the polymer chains.[13-14] This can be explained based on the lower reactivity of secondary hydroxyl groups presence in ISO which hinders the chain structure when put in excess in the reaction milieu. The presence of these hydrocarbon chains into the bithiophene polyester structures enhances the crystallization, the hydrophobicity and thermal properties of the prepared materials. In addition, it adjusted their melting temperatures to ones suitable for thermoplastic processing. In this light, we dealt with the synthesis, as well as the structural, thermal, and degradability and 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 and ethylene glycol (EG). This building block obtained from biomass extracted from castor oil, via esterification and hydrogenation processes, as well as a green synthetic route was for this was disclosed in a recent patent.[18]

To the best of our knowledge, the study of the structure and properties of long-chain aliphatic PBIsTs polyester with incorporated isosorbide units has been examined for the first time in the present work. In this work, we synthesized via a melt polycondensation procedure a new renewable bithiophene copolyesters series containing BTDCA, EG and rigid fragments of ISO (10-15%) respectively. The ISO as comonomer, has 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-ylium (purum 99%) was obtained from Sinopharm Chemical Reagent Co., Ltd, 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 4000~400 cm^{-1}, resolution 0.4 cm^{-1}, number of scans 80 s^{-1}, KBr tableting.

^{1}H NMR test: Bruker Advance DMX600 Nuclear magnetic resonance instrument, tetramethylsilane (TMS) for Internal standard, and chloroform (CDCl$_3$) for solvent, resonance frequency 600 Hz.

DSC: The differential scanning calorimeter was operated on a Mettler-Toledo DSC 821e with a temperature range of 25 -300°C, and a heating and cooling rate of 15 K/min at N_2 gas flow (60 cm^3 /min). Then the heating curves were obtained by increasing the temperature from room temperature to 300ºC by 10°C/min.

TGA test: For thermogravimetric analysis, a Mettler Toledo TGA851e was used, with 10 mg of the polymer dipped into a 70 µl Al_2O_3 crucible. This was later covered with a pierced lid and operated by varying temperature from 25 - 500 ºC by 10 ºC /min to achieve TG curve.

Solution casting: Polyester (800 mg) was dissolved in a TFA-chloroform mixture (2:1 V/V, 30mL) to prepare a solution-casting film. The solution was filtered to remove any insoluble substances, and later poured into 100 mm diameter Teflon petri dishes. The solvent evaporates under pressure to form a film, which is finally dried in vacuum for several days (20°C). The resulting PEIsTs film is almost clear and yellow in coloration.

Melt extrusion and permeability: Prior to the melting process, PEIsTs are first dried for 24 hours at 120°C, cooled to ambient tempearture, and stored in a dryer to minimize potential degradation risks from moisture or possible solvent residues. Pressed films of approximately 0.1 mm thickness (tensile sample) or 0.3 mm thickness (gas barrier sample) were prepared using thin metal strips as spacers (Fontijne press LabEcon series). The polymer sample is placed as a filler between two steel plates of teflon coated fiberglass mat, heated in a press for 3 minute at a force of 10kN at 245−255°C. After the melting stage, the pressure is increased to 250 KN for 1 minute. The pressed flake is then removed from the press, and cooled immediately in cold water. To maintain their shape, 0.3 mm thick gas barrier samples are cooled inside the press using an integrated water cooling system.

Dynamic Mechanical Analysis (DMA): The dynamic mechanical analyzer (TA Instruments DMA Q800,) operates on the thermo-mechanical properties of thin films. The analyzer is equipped with a tension (thin film) clip and operates in multi-frequency mode. The specimens were prepared using the same tensile test procedure. The variable temperature DMA method was as follows: the specimen was heated to 250°C at a rate of 5°C/min, the gap distance was 13 mm, the amplitude was 20 μm, the preload was 0.01N, and the force diameter was 125%.

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

5-(methoxycarbonyl)thiophen-2-ylium (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 N_2 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 until 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%). ^{1}H 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)). ^{13}C 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).
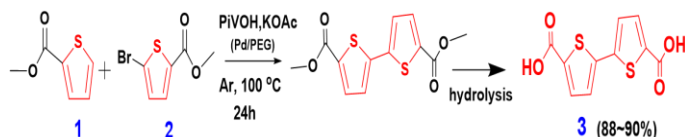

Figure 1 The synthesis route of BTDCA monomer.

D. 2.4. Synthesis of poly(ethylene-co-isosorbide [2,2'-bithiophene]-5,5'-dicarboxylate) (PEI$_S$T$_S$)

[2,2'-dithiophene]-5,5' -dicarboxylic acid (3), ethylene glycol (6 equiv.), isosorbide (10-40%) and tetrabutyl titanate (1mol%) were added to a 50ml dry round-bottom flask and stirred with a magnetic stirring bar. The flask was connected to the distillation bridge, which is connected to N_2 and vacuum pump. The air in the system is purged with N_2 several times.

The flask is pre-heated at 180°C and the transesterification process begins with an aluminum-heating block. Within 30 minutes, the heterogeneous mixture turns into a yellowish solution. After 4 h, the water droplets observed from the condensation sphere inferred transesterification have occurred. At this stage, no monomer (TLC) is detected and methanol ceases to be distilled. The excess ethylene glycol was then progressively vacuumed off at (4 mbar) pressure. The temperature was then raised to 300°C for 9 h until the "Weissenberg effect" was observed, and the reaction flask was cooled under vacuum. The polyester is dissolved in a mixture of trifluoroacetic acid (TFA) chloroform (1:1) and further precipitated in methanol. After vacuum filtration and methanol washing, the product was dried to obtain gray fiber material (yield 94~96%). A small amount of PEI$_S$T$_S$ was dissolved in TFA-d to prepare NMR samples. The data (Figure 3a) conform to the expected structure. ^{1}H 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 synthetic route). Initially, the dimethyl ester of BTDCA, [2,2'-bithiophene]-5,5'-dicarboxylicacid 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.
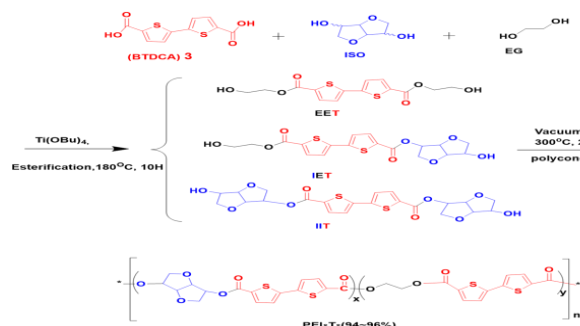
Figure 2 Synthetic route of PEI$_S$T$_S$ Polyester.

By simply increasing the reaction time from 4 - 24 h under vacuum, finally gave a significant amount of the product 3 at 88~90% yield thereby 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 synthesized via an esterification-polyesterification-polycondensation process, shown in Figure 2. First, the transesterification bishydroxy product was prepared from BTDCA and EG using polyethylene glycol palladium (Pd/PEG) as catalyst, and then, subjecting the bishydroxyalkylene-2,5′-bithiophenecarboxylate 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 had an important role guaranteeing that all added amounts of EG and ISO were totally reacted. Finally, the polycondensation stage was carried out at 220−300 °C for 2h under vacuum (4.0 Pa), 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 PEI$_S$T$_S$ copolyesters was measured by GPC and determined 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 (ºC)	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	4c	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), N$_2$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, possibly due to 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 PEI$_S$T$_S$ 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).

The prepared polyester poly(ethylene-*co*-isosorbide bithiophene (PEI$_S$T$_S$) was soluble in both TFA and TFA−chloroform mixtures, but no obvious solubility was observed in different tested organic solvents such as dichloromethane, chloroform, methanol, or N-methylpyrrolidone. 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 PEIsTs polyester Characteristics

samples	PEIsTs ratios	PEIsTs ¹HNMR	M_n (gmol⁻¹)	M_w (gmol⁻¹)	COOH (eq/10⁶ 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-ISO-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 ^{1}HNMR 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 ^{1}H 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 −CH$_2$− 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 ^{1}H NMR spectrum integrals, the ethylene content in PEI$_S$T$_S$ is estimated to be lower than 1%. This is almost similar to the EG content reported for PET in previous report[22-25].
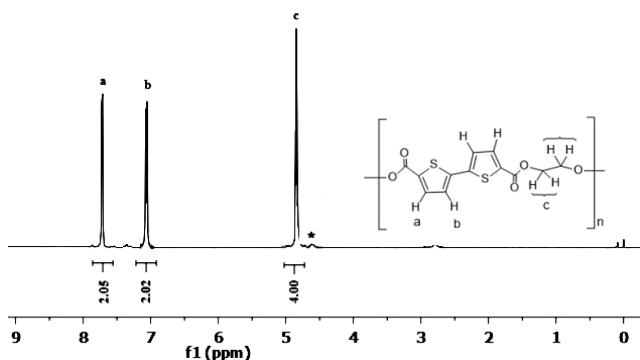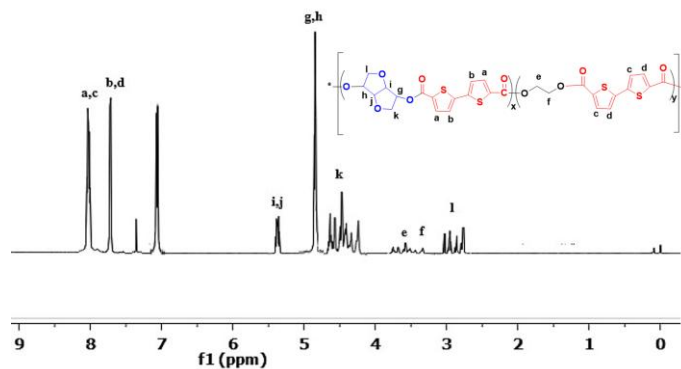

Figure 3a ^{1}H NMR spectrum (4−8 ppm) of PEsTs polyester

FIGURE 3b ^{1}H 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 scans, 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 analyzed via 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. PEI$_S$T$_S$ copolyesters are semi crystalline materials having a relatively high T_g of 127°C, attributed to the polyester with a relative low molar content of ISO not more than 10%. This composition enabling it to meet the heat resistance requirements with a T_g value superior to 100°C suitable for most daily use products, such as nursing bottles and plastic cups. For comparing sake, PET[22] have lower T_g value of 87°C where as PEI$_S$T$_S$ 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. Nevertheless, even with its higher T_g, PEI$_S$T$_S$ has a slightly lower melting point (T_m=237.5 °C) than PET. Figure 5a, traces of PET and PEI$_S$T$_S$ at 150 °C under N$_2$, where both 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, observed at 413.5 °C, and the weight loss rate reached a maximum ($T_{d,Max}$) at 443.8 °C $T_{d,5}$ and $T_{d,Max}$ were both max at 400 and 458 °C respectively. After the TGA runs, about 20% of the initial sample weight was left as residue for PEI$_S$T$_S$ while only 15% was left of the PET sample. These values agree with the higher content of aromatic units in PEI$_S$T$_S$. Review from thermal weight loss in PEI$_S$T$_S$ is quite comparable to thiophene-based PET, which is reasonable when considering the similarities in thiophene ester linkages. Herein, T_g increases significantly, thereby broadening the applications of the materials via copolymerization with rigid monomers like ISO. However, Inserting ISO has been a major "hot topic" in modifying PBT, PES or PEF structures. 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 PEI$_S$T$_S$ 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.
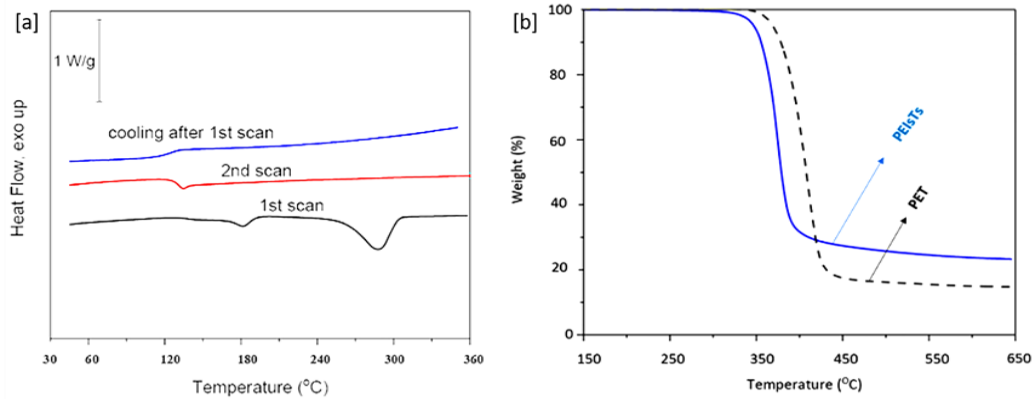
FIGURE 4 (a) DSC trace of PEIsTs measured under N_2, (b) TGA traces of PEIsTs and PET measured under N_2.
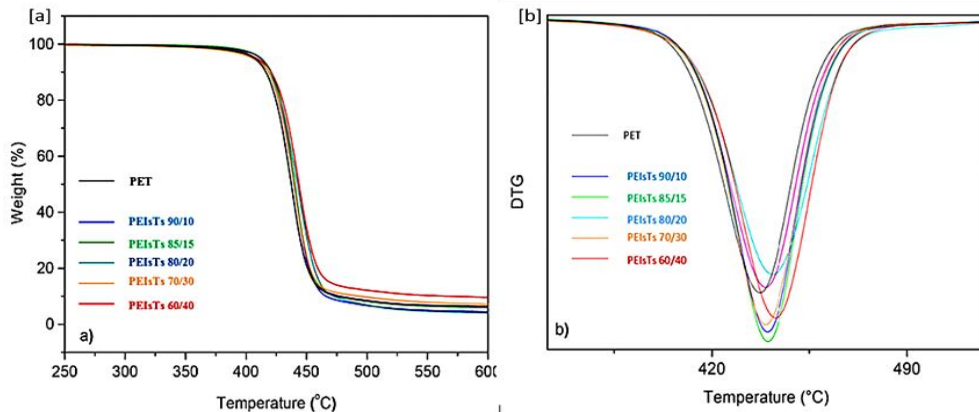

FIGURE 5: TGA curves of the pure copolyesters (PEIsTs): (a) remaining mass and (b) first derivative of mass loss.

TABLE 5 Oxygen and water vapor permeability

Polyester	Oxygen permeability[a] (barrier)	BIFp	Water vapor permeability[b] (μmm^{-2} 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.

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.

E. Dynamic Mechanical Analysis

Fig.6 shows the results of the melt-pressed PEIsTs film test to further support the thermal experiment: Tan δ peaked at 127°C, specifying a transition stage from glassy to rubber, while the loss modulus (E) curve showed a glassy transition temperature of 117°C. The storage modulus (E′) increases at 160°C, which is consistent with cold crystallization.
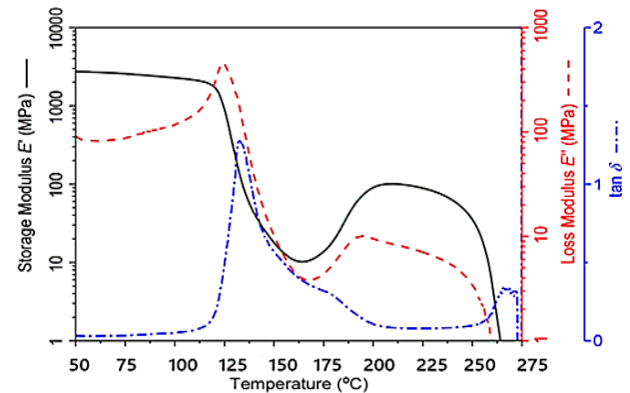

FIGURE 6 Storage modulus (E′), loss modulus (E″), and tan δ of PEIsTs as functions of temperature.

F. Degradation Properties

For the application of polymers in commercial fields such as packaging industry, biodegradability and other properties have become necessary. Through various studies, the degradation performance of PET (synthesized by industrial EG) and its copolymer with or without lipase was studied, and it was found that PET was difficult to degrade at room temperature. Here we found that copolyester PEIsTs were

biodegraded under the action of soil hydrolysis.[26] As shown in Figure 7, the sample weight decreased after being cultured in phosphate buffer solution at a suitable pH(7.4) for 28 days. Monitoring scans of the PEIsTs were carried out with the help of porcine pancreatic lipase, but the sample $PEI_{40}T_{60}$ became too fragile to form a complete film. As seen in Fig.7, compared with commercial PET, all PEIsTs samples showed significant degradation, which was related to significantly enhanced biodegradation under copolymerization. As the ISO addition increased from 10 to 40%, the weightlessness rate of PEIsTs increased from 4.8 to 10.2%. The degradation rates of Samples $PEI_{10}T_{90}$ and $PEI_{15}T_{85}$ were 13.2% and 12.7%, respectively, after 28 days of lipase addition in phosphate buffer. Compared with the initial samples, the study showed that the degradation behavior of PEIsTs was mainly due to the degradation of ethylene and isosorbitol units, which were decomposed by soil hydrolysis and degradation. This is consistent with the phenomenon that the degradation rate increases with the increase of E_T unit content in all samples. Unfortunately, the I_T unit cannot degrade in test conditions. In addition, black holes in the film indicate that biodegradation has occurred throughout the sample. It is worth noting that it is one of the few materials reported to be sensitive to degradation of copolymers containing ISO with high T_g values, which is of great significance for the development of new green packaging materials.[27]
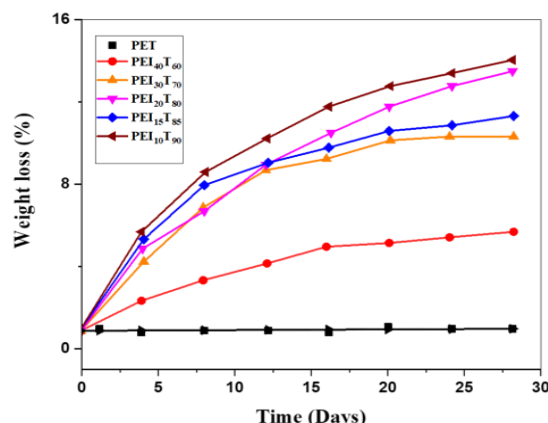

FIGURE 7 Degradation properties of PEIsTs in phosphate buffer solution with porcine pancreatic lipases.

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 achieve using 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 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 95,500–55,200gmol^{-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, and 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 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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