Synthesis of novel biobased polyimides derived from isomannide with good optical transparency, solubility and thermal stability†

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Novel biobased polyimides (PIs) with good optical transparency and comprehensive properties were synthesized from isomannide-derived diamine and dianhydride monomers. Three kinds of diamines including 2,5-diamino-2,5-dideoxy-1,4:3,6-dianhydroiditol (**M1**), 1,4:3,6-dianhydro-2,5-di-*O*-(4-aminophenyl)-D-mannitol (**M2**), and 1,4:3,6-dianhydro-2,5-di-*O*-(2-trifluoromethyl-4-aminophenyl)-D-mannitol (**M3**), as well as 1,4:3,6-dianhydro-2,5-di-*O*-(3,4-dicarboxyphenyl)-D-mannitol dianhydride (**M4**), were prepared based on isomannide. These diamines **M1**–**M3** were reacted with **M4** and a commercial dianhydride, 4,4′-oxydiphthalic anhydride (**ODPA**), via a two-step polymerization method, respectively, to yield a series of biobased PI films, **PI-1** to **PI-6**. The resultant PIs had a high content of biomass up to 48 wt%, and they can be readily soluble in various non-proton polar solvents at room temperature. Most of the biobased PIs showed good optical transparency (transmittances at 450 nm over than 80%), along with a cut-off wavelength of 343–364 nm. Furthermore, due to the existence of rigid alicyclic isomannide among the polymeric backbone, biobased PIs maintained fairly high thermal stability with a glass transition temperature of 227–264 °C, and temperature at 5% weight loss over 400 °C in nitrogen. Meanwhile, these PIs exhibited outstanding mechanical properties with tensile strengths greater than 90 MPa and elongation at break higher than 6.0%. It was also found that the biobased PI series with alicyclic **M1** possessed higher thermal stability than PIs with semi-aromatic diamines **M2** and **M3**. Thereof, the introduction of biomass building blocks into PIs can offer a great opportunity to develop new sustainable materials with high performance for microelectronic and optoelectronic applications.

Introduction

Polyimides (PIs), as one of the most important classes of high-temperature polymers, have been widely applied in engineering fields for several decades, due to their excellent combined properties such as outstanding thermal stability, high mechanical strength, and good dielectric property.[1] It is also known that conventional aromatic PIs generally exhibit deep color and low optical transparency, as well as poor solution processability, caused by intra- or intermolecular charge transfer complex (CTC) formation in their conjugated molecular structures. However, in recent years, with the rapid

development of advanced optoelectronic engineering, PIs (glass transition temperature, T_g > 200 °C) with good optical transparency, are of more and more importance, and they have been considered as one of the most promising flexible substrates for prospective electronic and optical devices.[2,3] The common transparent polymers, such as polyethylene naphthalate (PEN) and polyethylene terephthalate (PET) cannot support the high-temperature processing of those devices, e.g., barrier coating, electrode deposition, and patterning, due to their low T_g values (80–150 °C). Thus, more and more interests have been drawn to erase the color of PIs. Considerable progresses have been achieved to synthesize new optically transparent PIs by introducing alicyclic units,[4–6] fluorinated,[7–9] chlorinated[10] or sulfurated[11,12] groups, and bulky or twisted rigid moieties[13,14] into PIs, so as to inhibit or reduce the CTC formation.

Currently, the common and effective approach to the synthesis of optically transparent PIs is to use alicyclic diamine and/or dianhydride monomers. There are two synthetic strategies to obtain alicyclic diamines or dianhydrides: one is that alicyclic moieties are formed during the preparation of monomers;[15] the other is that the existing alicyclic units are directly

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introduced into monomers through chemical modification.[16] For the former one, several typical alicyclic dianhydrides, such as 1,2,3,4-cyclobutane tetracarboxylic dianhydride,[15] 2,3,5,6-bicyclooctane tetracarboxylic dianhydride[17] and 1,2,4,5-cyclohexane tetracarboxylic dianhydride[18] have been widely prepared to generate various transparent PIs. Some of the monomers are commercially available. However, it is difficult to modify the structures of these alicyclic monomers, thus to tune the performance of the resultant PIs. Moreover, it is mostly limited to the synthesis of dianhydrides. For the second strategy, whereas, alicyclic dianhydrides or diamines can be facilely prepared, based on alicyclic moieties containing reactive groups; furthermore, it can combine different functional units such as trifluoromethyl group (CF₃), to form more desirable monomers. Nevertheless, only a few alicyclic moieties including cyclohexane,[19,20] adamantane[21] and recently reported heterocyclic piperazine,[22] were utilized to obtain new monomers. Adamantane, a rigid aliphatic compound composed of three cyclohexane rings, have been introduced into various alicyclic diamines. Although adamantine-based PIs exhibited colorless and transparent with high thermal stability, they often possessed low solubility.[21] Recently, a heterocyclic moiety, piperazine, was reported to form a new kind of alicyclic dianhydride, and fully aliphatic PIs with good solubility and transparency can be prepared. Unfortunately, thermal properties of such PIs are not well enough and some of their T_gs are even lower than 200 °C.[22] Thereof, the synthesis of optically transparent PIs with excellent combined properties is still a great challenge. The key issue is how to design and develop new suitable monomers, so as to realize the balance among optical transparency, thermal stability, solubility, and other properties of the resultant PIs. Currently reported alicyclic diamines or dianhydrides are still limited; meanwhile, the monomers of PIs are almost confined to petroleum chemicals.

In recent decade, the research on the biobased polymers from abundant biomass building blocks is being in bloom stage, which is driven by the shortage of oil resources and their escalating prices, as well as the deterioration of global environment.[23,24] One type of biomass building blocks that has been gained increasing attention is the isohexide compound derived from natural cereal through reduction of sugars and subsequent dehydration reaction. Due to its rigid heterocyclic structure and chirality, as well as the commercial product of its isomers, isosorbide and isomannide, considerable progresses have been achieved in synthesis of various isohexide-based polymers, *e.g.*, polyesters, polyamides, polycarbonates and polyurethanes.[25–27] It was also found that the incorporation of rigid isohexides or their diamino derivatives can effectively improve the thermal stability of biobased polymers.[28,29] Recently, biobased PIs composed of petroleum dianhydrides and isohexide diamines were synthesized, and they had good optical transparency in a patent.[30] However, the solubility of these PIs was not investigated, which was a key factor to determine their application. In addition, isohexides could be easily transformed into different kinds of diamines and dianhydrides by using their hydroxyl groups. It means that optically transparent biobased PIs with good combined properties

such as solubility and thermal properties would be prepared by tuning the structures of isohexide-derived monomers. Up to now, although a great deal of studies have been reported on the synthesis of biobased polymers, the research on biobased PIs is still scarce.[31,32]

In this article, we demonstrated the synthesis of novel biobased PIs derived from isomannide biomass with good optical transparency and combined performance. For detailed study on the structure–property relationship of biobased PIs, three kinds of isomannide-based diamines, **M1–M3** as shown in Scheme 1, were designed and prepared, including aliphatic, semi-aromatic, and semi-aromatic diamine containing CF₃ group. Meanwhile, an isomannide-based dianhydride monomer **M4** was also synthesized, to further increase the biomass content of the resultant PIs. These biobased diamines were reacted with a biobased dianhydride **M4** and a commercial dianhydride **ODPA**, respectively, *via* a two-step method, to yield a series of new tough PI films. The solubility, thermal property, optical transparency and mechanical properties of these biobased PIs were investigated.

Experimental

Materials

1,4:3,6-Dianhydro-D-mannitol (isomannide, 96%) was purchased from Accela Company. Phthalimide potassium salt (99%), triphenylphosphine (PPh₃, 99%), 1-fluoro-4-nitrobenzene (98%), 4-chloro-1-nitro-3-(trifluoromethyl) benzene (99%), **ODPA** (97%), *p*-toluenesulfonyl chloride (TsCl, 99%), palladium on activated charcoal (Pd/C catalyst, 5%), hydrazine hydrate (80%), 4-nitrophthalonitrile (98%), and 1-methyl-2-pyrrolidinone (NMP) were purchased from Aladdin Company. All solvents including *N,N′*-dimethylacetamide (DMAc), *N,N′*-dimethylformamide (DMF), tetrahydrofuran (THF), and dichloromethane (CH₂Cl₂) are analytical grade from Guangzhou Chemical Reagent Factory. All the materials were used directly except DMF and NMP, which were dried over CaH₂ and distilled prior to use.

Characterization

The attenuated total reflection Fourier-transform infrared spectra (ATR FT-IR) were measured on a Bruker Vector 22 spectrometer in the range of 400–4000 cm⁻¹. ¹H/¹³C NMR spectra were recorded on a Bruker Avance 400 spectrometer with DMSO-d_6, CDCl₃, or D₂O as the solvents. Inherent viscosities were measured with an Ubbelohde viscometer placed in water at 35 °C. Molecular weights were tested by gel permeation chromatography (GPC) on a Waters equipped with a set of Waters Styragel HT-2, HT-4 and HT-6 columns, and a 2414 refractive index detector. The columns were maintained at 50 °C in an oven. DMF containing 0.01 M lithium bromide was used as an eluent with 1.0 mL min⁻¹. Calibration was performed with narrow-molecular-weight polystyrene as standards. The thermal decomposition behaviors were recorded by thermogravimetric analysis (TGA) using a Pyris TG 2000 equipment with about 5 mg of film samples at a heating rate of 10 °C min⁻¹ in N₂ atmosphere. Measurements of T_gs were performed by
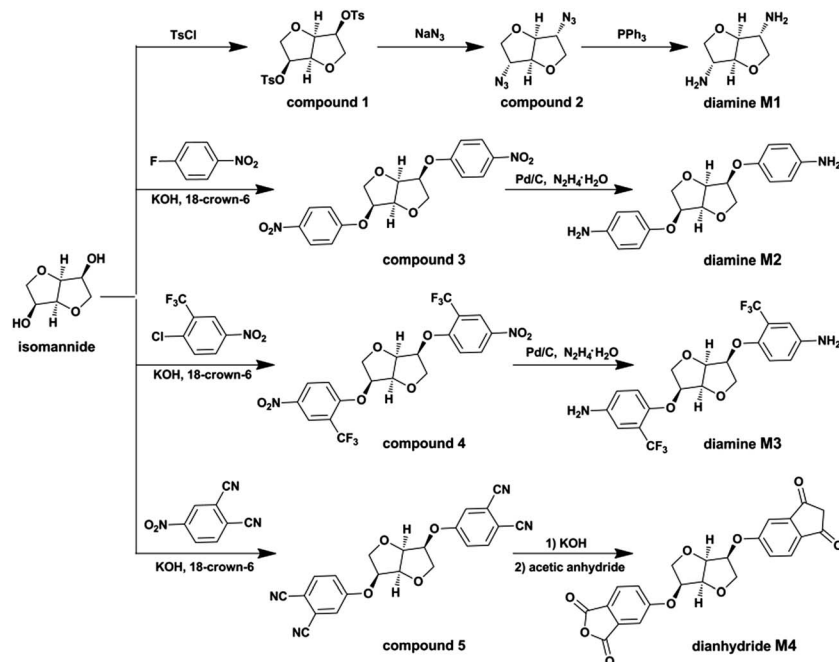
Scheme 1 The synthetic routes of diamines **M1–M3** and dianhydride **M4** derived from isomannide.

differential scanning calorimetry (DSC) using a Netzsch DSC-204 instrument with a heating rate of 20 °C min^{-1} under N$_2$. The coefficients of thermal expansion (CTEs) were conducted by thermo mechanical analysis (TMA) using TA Q400 equipment with a heating rate of 10 °C min^{-1}, ranging from 50 to 200 °C. Ultraviolet-visible (UV-vis) spectra of the films (about 20 μm) were evaluated by a Thermo Evolution 201 spectrometer in transmittance mode, with spectrometer width of 300–800 nm at room temperature. Tensile properties were measured with Universal Testing Measurement (UTM) of Xinsansi Company. Materials were tested with 4 mm × 25 mm at a strain rate of 10 mm min^{-1} at room temperature and the maximum strength was 50 N. Wide-angle X-ray diffraction (WXRD) patterns were obtained with a RIGAKU D-MAX 2200 VPC, using graphite-monochromated Cu K$_\alpha$ radiation ($\lambda = 1.5418$ Å) and a 0.5 mm collimator at room temperature.

Synthesis of biobased monomers

1,4:3,6-Dianhydro-2,5-di-O-p-tosyl-D-mannitol (compound 1).[33] To a solution of isomannide (24.01 g, 0.16 mol) in pyridine (30 mL) and CH$_2$Cl$_2$ (100 mL) at 0 °C was added a solution of TsCl (62.62 g, 0.33 mol) in the mixture solvents of pyridine (10 mL) and CH$_2$Cl$_2$ (150 mL) dropwise. The mixture was stirred under N$_2$. After 10 h, the reaction product was poured into 0.5 L of an ice–water mixture, stirred and warmed up to room temperature. The resulting precipitate was filtered and the product was recrystallized from ethanol to afford isomannide bis-tosylate as white crystals (52.7 g, 84%). ^{1}H NMR (CDCl$_3$, ppm): $\delta = 7.78$ (d, 4H, Ph), 7.32 (d, 4H, Ph), 4.83 (q, 2H, SO$_3$CH), 4.46 (dd, 2H, OCH$_2$), 3.91 (dd, 2H, OCH$_2$), 3.71 (dd, 2H, OCH$_2$), 2.46 (s, 6H, PhCH$_3$).

2,5-Diazido-2,5-dideoxy-1,4:3,6-dianhydroiditol (compound 2). 10.12 g (22.12 mmol) of compound **1** was dissolved in 110 mL of

DMF. The mixture was treated with stirring at 80 °C for 36 h after 1.57 g (22.0 mmol) of sodium azide was added. As soon as the temperature came down, water (60 mL) was added and the mixture was extracted with diethyl ether (15 mL × 7). The combined layers were dried over anhydrous MgSO$_4$, and then concentrated under vacuum. The crude diazide was purified by column chromatography (cyclohexane/EtOAc, 5 : 1) to afford the compound **2** (2.0 g, 90.4%) as a colorless liquid. ^{1}H NMR (CDCl$_3$, ppm): $\delta = 4.65$ (s, 2H, CH), 4.09 (q, 2H, N$_3$CH), 3.96 (dd, 2H, CH$_2$), 3.90 (dd, 2H, CH$_2$).

2,5-Diamino-2,5-dideoxy-1,4:3,6-dianhydroiditol (M1).[34] To the colorless liquid compound **2** (0.95 g, 77.76 mmol), was added PPh$_3$ (5.10 g, 19.44 mmol), followed by a 10 : 1 solution of water in THF (total 110 mL). The reaction was conducted in 66 °C for 6 h. After the reaction, the THF was removed under reduced pressure. The residue was dissolved in the mixture of diethyl ether (25 mL) and 0.2 M aq. HCl (25 mL). After stirred thoroughly, the water was washed with diethyl ether (25 mL × 7), then using aq NaOH to neutralize the water layer. After removing water, most of the residue were dissolved with CH$_2$Cl$_2$ (70 mL × 3), and filtered. CH$_2$Cl$_2$ solvent was collected and dried with MgSO$_4$ and then evaporated to yield the product **M1** (0.5 g, 73%). ^{1}H NMR (D$_2$O, ppm): $\delta = 4.67$ (s, 4H, NH$_2$), 3.94 (dd, 4H, CH$_2$), 3.77 (dd, 2H, CH), 3.67 (dd, 2H, CH). Elemental analysis: found: C, 50.0; H, 8.4; N, 19.4%. Calc. for C$_6$H$_{12}$N$_2$O$_2$: C, 50.1; H, 8.3; N, 19.6%.

1,4:3,6-Dianhydro-2,5-di-O-(4-nitrophenyl)-D-mannitol (compound 3).[35] In a round-bottom flask fitted to the oil and water separation device, 1.46 g (9.99 mmol) of isomannide was mixed with 1.68 g (29.94 mmol) of KOH and 0.53 g (2.01 mmol) of 18-crown-6 were dissolved in DMF 15 mL. We next added 4.23 g (30.00 mmol) of p-fluoronitrobenzene and toluene 10 mL. The

reaction mixture was maintained under magnetic stirring in 110 °C for 12 h. After cooled to room temperature, the reaction mixture was washed by K_2CO_3 saturated solution, then the residue was recrystallized by THF. The product was yellow granular crystal (2.6 g, 67%). ^{1}H NMR (CDCl$_3$, ppm): δ = 8.04 (d, 2H, Ph), 7.07 (d, 2H, Ph), 4.97 (dd, 2H, CH), 4.91 (q, 2H, CH), 4.13 (dd, 2H, CH$_2$), 4.14 (dd, 2H, CH$_2$).

1,4:3,6-Dianhydro-2,5-di-O-(4-aminophenyl)-D-mannitol (M2). In a flask, 1.94 g (5.00 mmol) of dinitro compound **3** was dissolved in 100 mL of THF with 1.12 mL of hydrazine monohydrate. Under stirring, 0.05 g of palladium catalyst was added. The reaction mixture was maintained under magnetic stirring in 66 °C for 12 h. Then the residue was recrystallized by THF. After purification, the compound **M2** was obtained in a 91% (1.5 g) yield. ^{1}H NMR (DMSO-d_6, ppm): δ = 6.72 (m, 2H, Ph), 6.56 (m, 2H, Ph), 4.68 (m, 2H, CH), 4.65 (s, 4H, NH$_2$), 4.63 (m, 2H, CH), 4.00 (dd, 2H, CH$_2$), 3.68 (dd, 2H, CH$_2$). Elemental analysis: found: C, 65.1; H, 5.9; N, 8.2%. Calc. for C$_{18}$H$_{20}$N$_2$O$_4$: C, 65.6; H, 6.1; N, 8.5%.

1,4:3,6-Dianhydro-2,5-di-O-(2-trifluoromethyl-4-nitrophenyl)-D-mannitol (compound 4). Compound **4** was prepared with the similar experimental procedure of compound **3**, except that the temperature here was 130 °C. The product was obtained through recrystallization with acetone to yield 64%. ^{1}H NMR (CDCl$_3$, ppm): δ = 8.51 (dd, 2H, Ph), 8.50 (d, 2H, Ph), 7.69 (d, 2H, Ph), 5.35 (m, 2H, CH), 5.24 (m, 2H, CH), 4.22 (dd, 2H, CH$_2$), 4.05 (dd, 2H, CH$_2$).

1,4:3,6-Dianhydro-2,5-di-O-(2-trifluoromethyl-4-aminophenyl)-D-mannitol (M3). M3 diammine was prepared via the same procedure for M2, except that the reaction solvent was ethanol and the temperature was 78 °C. After crystallized from ethanol, the final **M3** was obtained as white needles in a 90% yield. ^{1}H NMR (DMSO-d_6, ppm): δ = 7.05 (d, 2H, Ph), 6.82 (d, 2H, Ph), 6.76 (dd, 2H, Ph), 5.07 (s, 4H, NH$_2$), 4.79 (m, 2H, CH), 4.71 (m, 2H, CH), 4.01 (m, 2H, CH$_2$), 3.70 (m, 2H, CH$_2$). Elemental analysis: found: C, 51.7; H, 3.7; N, 5.6%. Calc. for C$_{20}$H$_{18}$F$_6$N$_2$O$_4$: C, 51.7; H, 3.9; N, 6.0%.

1,4:3,6-Dianhydro-2,5-di-O-(3,4-dinitrile-phenyl)-D-mannitol (compound 5). 1.46 g (9.99 mmol) isomannide, 1.68 g (29.94 mmol) KOH, 0.53 g (2.01 mmol) 18-crown-6 and 3.9 g (22.50 mmol) 4-nitrophthalonitrile was dissolved in 70 mL DMF and 12.5 mL toluene. Then the mixture was stirred and refluxed at 140 °C for 12 h. After the mixture cooled down to room temperature, it was added in 400 mL pure water drop by drop and brown solid products were precipitated at the same time. The brown precipitation was recrystallized from acetone and water to afford light yellow solid products. After filtered, it was dried on vacuum for 4 h. Yield: 2.9 g, 73%. ^{1}H NMR (CDCl$_3$, ppm): δ = 7.76 (d, 2H, Ph), 7.39 (d, 2H, Ph), 7.32 (dd, 2H, Ph), 4.99 (d, 2H, CH), 4.89 (q, 2H, CH), 4.12 (dd, 2H, CH$_2$), 4.09 (dd, 2H, CH$_2$).

1,4:3,6-Dianhydro-2,5-di-O-(3,4-dicarboxyphenyl)-D-mannitol dianhydride (M4).[36] 2.89 g (7.25 mmol) compound **5** and 5.14 g (90.0 mmol) KOH was dissolved in 80 mL pure water and refluxed for 24 h. Then the mixture was drop into 130 mL cold dilute HCl aqueous to afford white precipitation. The solid product was filtered and dried on vacuum for the next reaction. Yield: 2.3 g, 67%. ^{1}H NMR (CDCl$_3$, ppm): δ = 7.72 (d, 2H, Ph), 7.18 (dd, 2H, Ph), 7.16 (s, 2H, Ph), 5.04 (q, 2H, CH), 4.91 (d, 2H, CH), 4.00 (dd, 2H, CH$_2$), 3.81 (dd, 2H, CH$_2$). Then, 2.21 g (4.66 mmol) of the solid product was dissolved in 15 mL anhydrous THF, and 3 mL acetic anhydride was added into the solution. After reflux at 70 °C for 8 h, the yellow solution was dropped into 250 mL pure water and solid product was precipitated. The crude product was recrystallized from acetone and water to afford light yellow product. The final product **M4** was filtered and dried on vacuum. Yield: 1.5 g, 74%. ^{1}H NMR (DMSO-d_6, ppm): δ = 8.00 (d, 2H, Ph), 7.75 (d, 2H, Ph), 7.58 (dd, 2H, Ph), 5.22 (dd, 2H, CH), 5.22 (q, 2H, CH), 5.02 (q, 2H, CH), 4.01 (dd, 2H, CH$_2$), 3.88 (dd, 2H, CH$_2$). Elemental analysis: found: C, 60.8; H, 3.5%. Calc. for C$_{24}$H$_{18}$O$_8$: C, 60.3; H, 3.2%.

Preparation of biobased PI films

Three kinds of diamine monomers (**M1, M2, M3**) were reacted with two kinds of dianhydrides, **M4** and **ODPA**, to give the corresponding PIs (Scheme 2). To illustrate the general synthetic route, the synthesis of **PI-1** (**M1/ODPA**) is used as an example. 0.6796 g **ODPA** (2.19 mmol) was added to a solution of 0.3158 g **M1** (2.19 mmol) in 2.53 g NMP. Extra 3.11 g NMP was added to adjust the solid content of the reaction system to 15 wt%. The mixture was stirred at room temperature for about 12 h to form a viscous poly(amic acid) (PAA) solution.

PI-1 films were obtained by thermal imidization of PAA solutions casting onto glass plates, followed by a preheating program (60 °C/1 h, 80 °C/3 h, 120 °C/0.5 h, 150 °C/1 h) and an imidization procedure under vacuum (180 °C/1 h, 200 °C/36 h, 300 °C/1 h) to produce a fully imidized PI film. **PI-1** film was stripped through placing the glass plates into hot water.

Results and discussion

Synthesis and characterization of biobased diamine and dianhydride

Three kinds of isomannide-derived diamines, **M1**, **M2** and **M3** were designed to investigate the effect of molecular structure of monomers on their polymerizability and physical properties of PIs. Their synthetic routes are illustrated in Scheme 1.

The preparation of **M1** monomer was reported by a couple of groups, and three synthetic routes have been summarized by Thiyagarajan et al.[37] Yet, there is no best way to synthesize **M1**. We utilized the strategy involved of tosylation of isomannide,
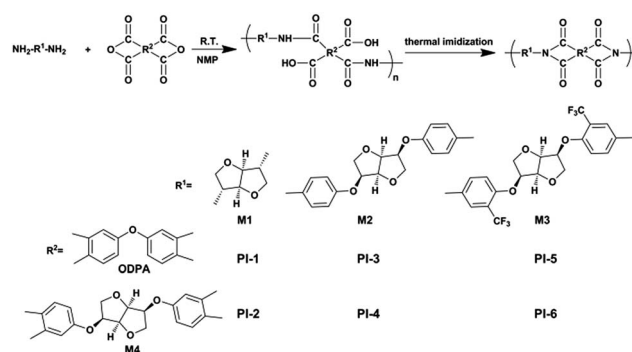
Scheme 2 The synthetic routes of all the isomannide-based PIs.

nucleophilic substitution with sodium azide, followed by reduction of diazide. Here, during reduction reaction of diazide, triphenylphosphine, not H_2 atmosphere, was used as a reducing agent *via* the mild Staudinger reaction, to obtain **M1** in 73% yield. For two semi-aromatic diamines **M2** and **M3**, they were prepared *via* the simple two-step reaction through nucleophilic substitution and subsequent reduction of the nitro group into the amino catalyzed with Pd/C. Additionally, in order to further increase the biomass content in final PI materials, a new dianhydride **M4** derived from isomannide was prepared (Scheme 1). Its synthetic route is involved with a procedure of nucleophilic substitution of isomannide with 4-nitrophthalonitrile and alkaline hydrolysis of bis(ether dinitrile) followed by dehydration of the corresponding tetra-acid.

The structure of isomannide-based diamines and dianhydride were confirmed by $^1H/^{13}C$ NMR spectroscopy, and elemental analysis (the data in Experimental part). Fig. 1 shows the ^1H NMR spectra of all the diamine and dianhydride monomers where all peaks are clearly assigned. The signals of amino groups of **M1** and **M2** monomers appear at around 4.6 ppm as a singlet, while the corresponding signal of **M3** obviously shifts to down field, at 5.0 ppm, because of the strong electro-withdrawing CF_3 group in benzene ring of **M3**. Their ^{13}C NMR spectra are provided in ESI.† All the spectra data of monomers are in accordance with their designed structures.

Preparation of biobased PIs

Three resultant diamines, **M1**–**M3**, were reacted with **M4** and **ODPA**, respectively, to yield six kinds of biobased PIs as shown in Scheme 2. The biobased PIs were prepared using a two-step procedure through the ring-opening polyaddition to form PAA intermediates, and subsequent thermal imidization. In general, when aliphatic and alicyclic diamines with high basicity were used, the insoluble salts were often formed during the polymerization of PAA, thus leading to a prolong reaction period up to several days, or even completely inhibition of the polymerization.[38] However, in our case, when alicyclic diamine **M1** was reacted with **ODPA** or **M4** at room temperature, carboxylic acid salts occurred at the very beginning of the reaction, and then the system became homogeneous within few minutes. As a result, the polymerization of **M1** only needed 12 hours to obtain its corresponding PAA with relatively high molecular weight. That should be attributed to the presence of ether bonds in the five-membered ring of **M1**, thus reducing its basicity. In addition, when **M3**, containing CF_3 group, was used to polymerize, we tried different reaction temperature and time, and found that the suitable reaction temperature was below 0 °C, and polymerization time extended up to 24 hours, to yield PAA precursors of high molecular weight.

The inherent viscosities of all PAAs were over than 0.40 dL g^{-1} measured in NMP solvent at 35 °C as listed in Table 1, indicating that the PAAs with high molecular weight were obtained, thus yielding tough PI films after thermal imidization. Meanwhile, for some of PIs (**PI-4**, **PI-5** and **PI-6**) soluble in DMF solvent at room temperature, their molecular weights were further determined by GPC measurement, and it was found that they had high molecular weights (M_n) ranging from 2.14×10^4 to 4.04×10^4 g mol^{-1}, with narrow-molecular-weight

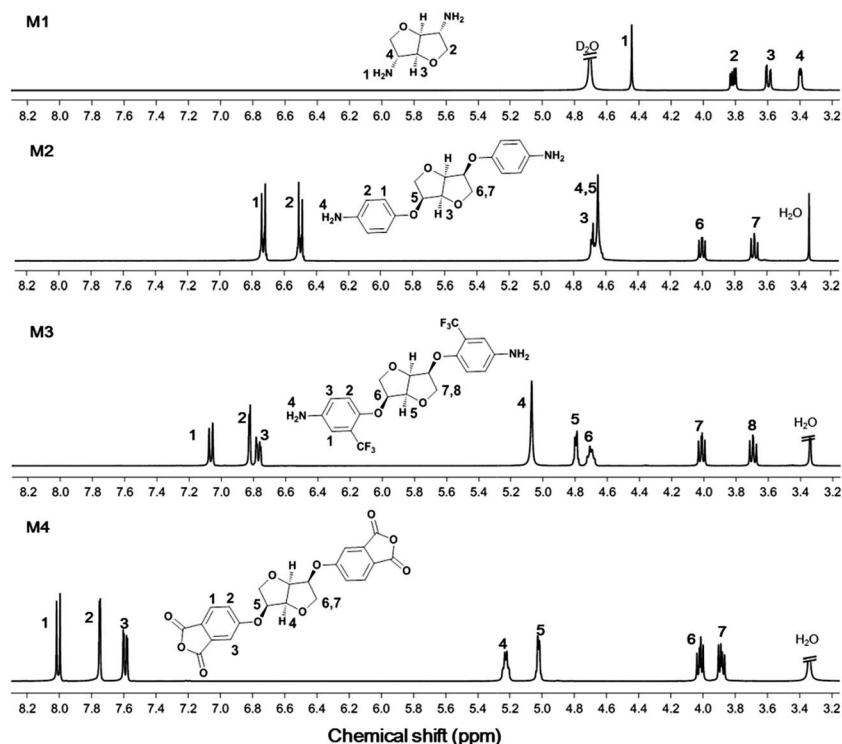Fig. 1 ^1H NMR spectra of diamines **M1**–**M3** and dianhydride **M4** derived from isomannide (DMSO-d_6 for **M2**–**M4**, and D_2O for **M1**, 400 MHz).

polystyrene as standards, as well as relatively narrow molecular weight distribution (PDI) between 1.33 and 1.53.

The chemical structures of biobased PIs were confirmed by ^{1}H NMR and ATR FT-IR spectroscopy. Fig. 2 shows ATR FT-IR spectra of the resultant PIs. All the PIs exhibit characteristic imide absorptions at 1780–1772 and 1720–1710 cm^{-1}, attributed to the asymmetrical and symmetrical stretching vibrations of carbonyl units, respectively. Meanwhile, the characteristic absorptions of the amide group at the region of 3200–3500 cm^{-1} disappeared. These results clearly indicate that all the PIs have been fully imidized.

The typical ^{1}H NMR spectrum of PI film is also shown in Fig. 3, where the proton signals of the alicyclic isomannide ring can be seen in the upfield region from 3.7 to 5.2 ppm, while the signals of the phenyl protons appear between 7.4 and 8.0 ppm. Furthermore, the ratio of such two sets of protons matched with the expected structure of PI polymer. In addition, it is mentioned that the biomass isomannide contents of PIs can be tuned by using different monomers from 17–48 wt%, and **PI-2** (**M1/M4**) possesses the highest isomannide content.

Morphology of the biobased PIs were also characterized by WXRD, and their X-ray diffraction patterns were presented in Fig. 4. All the isomannide-based PIs possess a certain degree of crystallization, as evidenced by the appearance of two sharp scattering signals in the 2θ range of 14–17°; moreover, these polymers have the same d spacing of 6.23 Å (2θ = 14.2°) and 5.27 Å (2θ = 16.8°). This might be ascribed to the rigid isomannide structure and its ordered arrangement.[33] It is noted that the scattering signals of **PI-3** is quite weak, and it should be related to its crystallization.

Solubility of biobased PIs

The solubility of the biobased PIs was measured by dissolving the PI films in various solvents with the same concentration of 10 mg mL^{-1}, and the results are listed in Table 2. Most of the PIs exhibit good solubility in non-proton polar solvents, such as DMF, NMP, DMAc, DMSO and m-cresol at room temperature or upon heating at 100 °C. Among them, DMSO is the best solvent
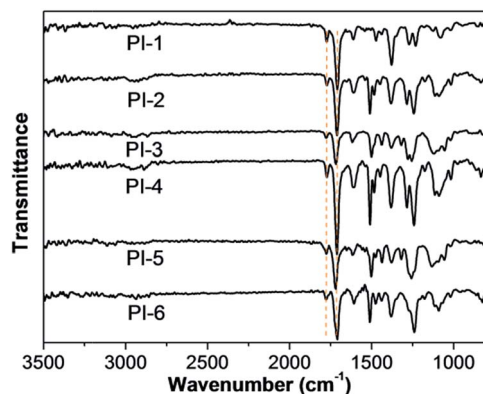

Fig. 2   ATR FT-IR spectra of all the isomannide-based PI films.

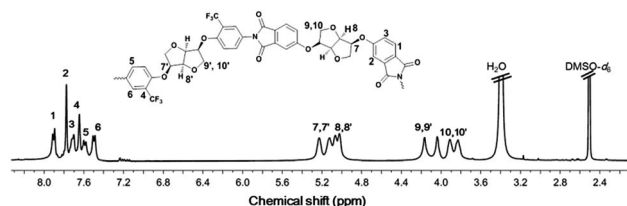Fig. 3   ^{1}H NMR spectrum of **PI-6** polymer (DMSO-d_6, 400 MHz).
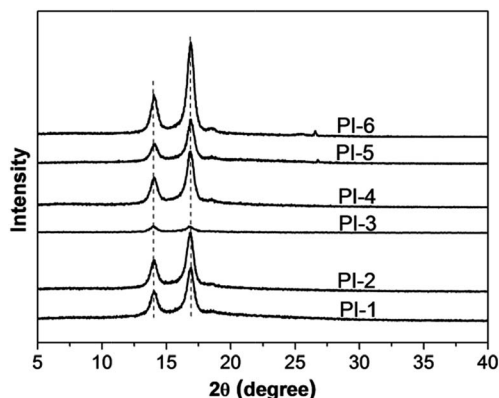

Fig. 4   X-ray diffraction profiles of all the isomannide-based PI films.

for dissolving the isomannide-based PIs. The good solubility of PIs is mainly ascribed to the presence of flexible ether bonds in polymeric backbone, which can reduce the interaction between polymer chains. Besides, the introduction of bulky CF$_3$ group into isomannide-derived diamines, leading to less efficient chain packing, can further improve the solubility of PIs. Thus, the ability of diamines to enhance the solubility of PIs follows this order: **M3** > **M2** > **M1**. As thus, **PI-5** polymer composed of **M3** and **ODPA** exhibits the best solubility in our systems, which can be soluble even in nonpolar solvents of low boiling point, such as CH$_2$Cl$_2$, 1,4-dioxane, and pyridine, at room temperature. These results indicate that isomannide-based PIs possess good solution processability, and it is highly desirable for the

Table 1   Inherent viscosities of all the isomannide-based PAAs and molecular weights of isomannide-based PI films including **PI-4**, **PI-5** and **PI-6**

| | | Molecular weights of PIs^c | | |
PIs	PAA/$\eta_{inh}{}^a$ (dL g^{-1})	M_n (10^4 g mol^{-1})	M_w (10^4 g mol^{-1})	PDI
PI-1	0.68	^{b}	^{b}	^{b}
PI-2	0.40	^{b}	^{b}	^{b}
PI-3	0.73	^{b}	^{b}	^{b}
PI-4	0.71	3.19	4.87	1.53
PI-5	0.82	4.04	5.36	1.33
PI-6	0.40	2.14	3.17	1.48

^{a} Measured at polymer concentration of 0.5 g dL^{-1} in NMP at 35 °C. ^{b} Not completely dissolved in DMF. ^{c} Measured by GPC in DMF; polystyrene was used as standard.

preparation of polymeric films or coatings in advanced micro-electronic applications.

Thermal properties of biobased PIs

For alicyclic PI materials, thermal property is one of the crucial factors to determine their practical applications. Here, we evaluate thermal properties of biobased PI films including T_gs, thermal decomposition, and CTEs by DSC, TGA and TMA, respectively, and their data are summarized in Table 3. Fig. 5 presents DSC second heating scans of PIs.

In general, the T_g values of polymers would increase along with the chain rigidity. As shown in Table 3, **PI-1** sample composed of alicyclic diamine **M1** and dianhydride **ODPA**, which possesses the most rigid polymer backbone in our system, shows the highest T_g value of 264 °C. However, the PI series with **M4** as dianhydride monomer exhibit lower T_gs (about 228 °C) than those of PIs based on **ODPA** (over than 245 °C), due to the presence of two flexible ether linkages in **M4** monomer. Also, it is found that the introduction of ether linkages into diamines plays minor influence in reducing T_gs than those into dianhydrides, which is supported by comparison **M1**-based PI series, *e.g.*, **PI-1**(**M1**/**ODPA**) with **M2**-based PIs, *e.g.*, **PI-3** (**M2**/**ODPA**). What is more, when the same or similar commercial dianhydrides were used, PIs with isomannide-derived diamine **M1** possess obviously higher T_gs than those of reported PIs with alicyclic diamines such as 1,3-
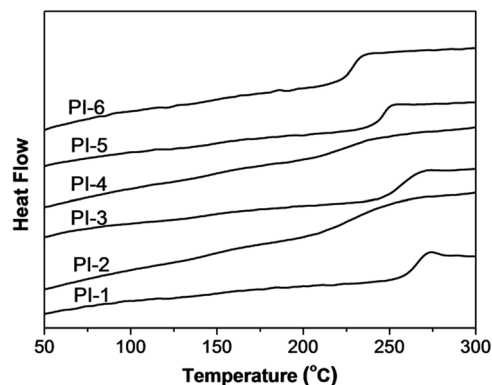

Fig. 5 DSC second heating scan curves of the isomannide-based PI films with 20 °C min^{-1}.

diaminoadamantance (DAD),[39] 1,4-diaminocyclohexane (DACH)[40] and its derivative 1,4-bis(4-aminophenoxy)cyclohexane (HDA). For examples, in the literature, the T_g values of PIs composed of DACH/biphenyltetracarboxylic dianhydride[40] and HDA/**ODPA**[19] were lower than 230 °C. Thus, the incorporation of isomannide unit into PIs is favorable to improve the thermal performance of current PI materials based on petroleum aliphatic diamine. In addition, it is mentioned that there is no observable melting peaks in the DSC heating curves of PIs even when heating up to 390 °C, and the melting temperatures of biobased PIs may be higher than their decomposition temperatures.

The thermal stability of biobased PI films was estimated with the decomposition temperatures at 5% and 10% weight loss ($T_{d,5\%}$ and $T_{d,10\%}$) by using TGA in nitrogen, and the data are summarized in Table 3. Obviously, the incorporation of biomass isomannide unit, ether linkage, and CF_3 group into PI polymeric chains would affect their thermal decomposition behaviors, thus leading to the two-step decomposition in most of the resultant PIs (Fig. 6). Nevertheless, these PIs still maintain a fairly high thermal stability, as evidenced by their $T_{d,5\%}$ values (>400 °C) and $T_{d,10\%}$ ones (>430 °C). Among them, **PI-1** polymer (**M1**/**ODPA**) possesses the best thermal stability, which is accordance with the above DSC results of PIs. The T_d data of isomannide-based PIs can be comparative with those of semi-aromatic PIs[18,21] and are also high enough for practical applications of less harsh thermal requirement, such as the substrates for flexible display devices. Besides, the weight residues of PIs, except **PI-6**, are rather low, ranged from 2 to 23% at 700 °C. **PI-6** film has high char yield of 45%, it should be due to the presence of CF_3 group and high weight content of isomannide unit in this polymer.

In addition, as listed in Table 3, the CTEs of biobased PIs range from 50.4 to 68.4 ppm °C^{-1}. The CTE value is associated with the rigidity and linearity of the polymer chain. As thus, the PI series based on **M3** containing CF_3 group exhibit higher CTEs, compared with PIs with monomer **M1** or **M2**, while **PI-4** (**M2**/**M4**) film shows the lowest CTE value. That is probably because the diamine **M2** and dianhydride **M4** have the same isomannide unit and their structure is similar, which would be beneficial for the formation of in-plane chain orientation

Table 2 Solubility of all the isomannide-based PI films^a

Solvent	PI-1	PI-2	PI-3	PI-4	PI-5	PI-6
DMF	+	+−	+	++	++	++
DMAc	++	+−	++	++	++	++
DMSO	++	++	++	+	++	++
NMP	++	+−	++	++	++	++
m-Cresol	++	++	+	+	++	++
THF	+−	−	−	−	+−	+−
CH$_2$Cl$_2$	+−	−	−	−	++	+−
1,4-Dioxane	−	−	−	−	++	−
Pyridine	+−	−	+−	−	++	++

^{a} ++, soluble at room temperature; +, soluble upon heating at 100 °C; +−, partially soluble upon heating at 100 °C or the boiling point; −, insoluble upon heating. Solubility was measured with the concentration of 10 mg mL^{-1} for 24 h.

Table 3 Thermal properties of the isomannide-based PI films

PIs	$T_g{}^a$ (°C)	$T_{5\%}{}^b$ (°C)	$T_{10\%}{}^b$ (°C)	$R_w{}^c$ (%)	CTE^d (ppm °C^{-1})
PI-1	264	440	460	23	58.7
PI-2	228	435	445	2	56.9
PI-3	255	406	439	5	61.1
PI-4	227	416	433	22	50.4
PI-5	246	428	450	13	68.4
PI-6	229	424	440	45	77.7

^{a} Measured by DSC with 20 °C min^{-1} in nitrogen. ^{b} Temperature at 5% and 10% weight loss determined by TGA with 10 °C min^{-1} in nitrogen. ^{c} Residual weight percentage at 700 °C in nitrogen. ^{d} Measured by TMA from 50 to 200 °C with 10 °C min^{-1}.
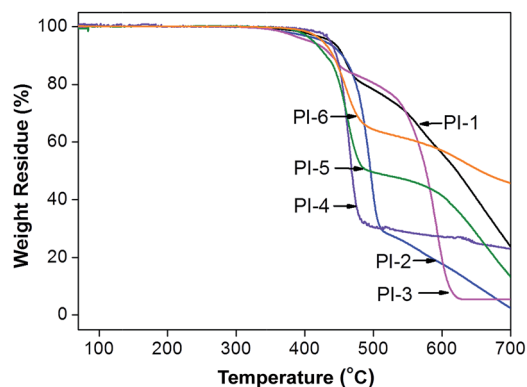
Fig. 6 TGA curves of the isomannide-based PI films with 10 °C min⁻¹ in nitrogen.

during thermal imidization, thus increasing the linear structure among **PI-4** polymer.

Transparency of biobased PIs

Optical transparency of PI films is of more and more importance with the rapid development of advanced optoelectronic technology. Conventional aromatic PI films exhibit deep color from yellow to brown, due to the strong CTC. Fig. 7 shows UV-vis absorption spectra of PI films and the data are presented in Table 4. All of these biobased PI films exhibit very light color or nearly colorless. The cut wavelengths ($\lambda_{0\%}$) of the isomannide-based PIs with **ODPA** as dianhydride, including **PI-1**, **PI-3** and **PI-5**, are shorter than 350 nm, and their transmittances at 450 nm ($T_{450 \, nm}$) exceed 80% (Table 4). These results indicate that the isomannide-derived PIs possess good optical transparency. It is also found that the introduction of CF₃ group in diamines would improve optical transparency of biobased PIs, in accordance with the researches on fluorinated PI films.[7,8] It is reasonable that the CF₃ group in the diamines can effectively inhibit the formation of CTC, due to the bulky steric hindrance, as well as its electron-withdrawing effect to weaken the electron-donating ability of diamine units. Additionally, PI series with **M4** do not exhibit better optical transparent as expected, although the content of alicyclic unit is higher than that of PI
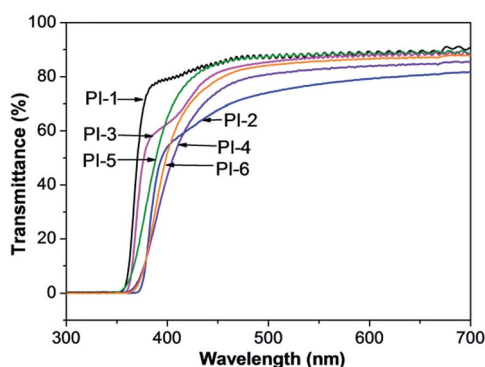

Fig. 7 UV-vis absorption spectra of the isomannide-based PI films.

Table 4 Optical and mechanical properties of the isomannide-based PI films

PIs	$T_S{}^a$ (MPa)	$E_B{}^b$ (%)	$T_M{}^c$ (GPa)	$T_{450 \, nm}{}^d$ (%)	$\lambda_{0\%}{}^e$ (nm)
PI-1	124	8.2	1.3	84	347
PI-2	98	6.5	2.1	68	364
PI-3	184	6.0	1.5	82	350
PI-4	100	6.5	1.9	75	360
PI-5	93	10.0	1.6	85	343
PI-6	112	6.3	2.3	79	357

^{a} T_S, tensile strength. ^{b} E_B, elongation at break. ^{c} T_M, tensile modulus. ^{d} $T_{450 \, nm}$, transmittance at 450 nm. ^{e} $\lambda_{0\%}$, cut-off wavelength.

series with **ODPA**. It may be related to the crystallinity of bio-based PIs.

Mechanical properties of biobased PIs

The mechanical properties of the PI films, including the tensile strength, tensile modulus, as well as elongation at break are summarized in Table 4. All the isomannide-based PIs have good tensile modulus of 1.3–2.3 GPa, and elongation at break of 6.0–10.0%. Especially, these PIs exhibit high tensile strength in the range of 93–184 MPa, while most of PI films reported in the literature were generally between 70 and 100 MPa.[1] The outstanding mechanical properties of biobased PIs mainly result from the rigid alicyclic ring of isomannide unit in the polymeric backbone. Thus, the result clearly indicates that the introduction of suitable biomass units into petroleum-based polymers can effectively improve the mechanical performance of the materials.

Conclusions

In conclusion, this work demonstrates the design of a new kind of biobased transparent PIs with good combined properties, which were prepared by directly introducing biomass alicyclic moiety into diamine or dianhydride monomers. Three kinds of isomannide-derived diamines, including aliphatic **M1**, semi-aromatic **M2**, and semi-aromatic **M3** containing CF₃ group, were successfully synthesized, and they showed high polymer-izability with a commercial dianhydride **ODPA** or an isomannide-based dianhydride **M4**, to yield a series of biobased PI films with a fairly high content of biomass up to 48 wt%. Most of these PIs possessed good optical transparency ($T_{450 \, nm} >$ 80%), and excellent solution processability (soluble in various non-proton polar solvents at room temperature). Furthermore, because of the incorporation of the rigid isomannide alicyclic ring into diamines, the biobased PIs exhibited improved thermal stability in comparison with fully petroleum-based PIs with aliphatic diamines; at the same time, they possessed outstanding mechanical properties, especially high tensile strength ranging from 93 to 184 MPa. Thereof, the utilization of biomass building blocks to construct biobased PIs is beneficial to develop environmental-friendly and sustainable materials for future engineering and optical applications. Moreover, it can offer a great opportunity to improve the properties of the

existing petroleum-based PIs, thus leading to exploit novel high-performance materials.

Acknowledgements

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