



# Synthesis and characterization of novel bio-based polyesters and poly(ester amide)s based on isosorbide and symmetrical cyclic anhydrides

Ban H. Al-Tayyem<sup>1</sup> · Bassam A. Sweileh<sup>1</sup>

Received: 10 July 2022 / Accepted: 3 November 2022 / Published online: 12 December 2022  
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## Abstract

Three bio-based isosorbide bis(acid ester)s were synthesized by condensation of isosorbide with three symmetrical cyclic anhydrides (namely, succinic, diglycolic and phthalic anhydrides). The isosorbide-based diacids were obtained in high yields (79–97%) and converted to their diacid dichloride derivatives, which were then utilized to design series of bio-based polyester and poly(ester amide)s with wide range of thermal properties. The polyesters were synthesized in *o*-dichlorobenzene, utilizing either *cis/trans*-1,4-cyclohexanediol or 1,6-hexanediol, the polyesters were obtained in high yields (78–91%), showed good thermal stabilities, excellent solubility in organic solvents and glass transition temperatures in the range of -13.7 to 102.8 °C. Additionally, a series of novel aliphatic poly(ester amide)s was synthesized interfacially by polyamidation of the isosorbide bis(diglycolic acid) or isosorbide bis(succinic acid) derivatives with either *trans*-1,4-diaminocyclohexane or 1,6-hexanediamine. The aliphatic poly(ester amide)s obtained showed good thermal stabilities, good solubility in organic solvents and glass transition temperatures up to 129 °C.

**Keywords** Isosorbide · Polyesters · Poly(ester amide)s · Symmetrical cyclic anhydrides

## Introduction

Stimulated by concerns related to petroleum depletion and environmental sustainability, good share of scientific attention has been oriented toward the development of materials by inclusion of bio-derived monomers extracted from feedstock's [1, 2]. Biomass feedstock's provides a considerably rich variety of renewable monomers that can replace their existing counterparts from fossil sources.

The majority of agro-industrial biomass composed of lignin, hemicelluloses and cellulose carbohydrates, all together called lignocelluloses biomass [3]. However, hemicelluloses and cellulose carbohydrates are among the most important classes of agro-industrial biomass residues; they can be depolymerized to offer pentose and hexose sugars, which can be catalytically converted to renewable sugar-based monomers [1, 3].

1,4:3,6-Dianhydrohexitols (also known as isohexides) are heterocyclic carbohydrate-derived diols that exist as the stereoisomers isosorbide, isomannide and isoidide, which are derived from D-glucose, D-mannose and L-iditol, respectively [4]. Isohexides consist of two *cis*-fused tetrahydrofuran rings with V-shaped molecular structures and two secondary hydroxyl groups positioned at carbons 2 and 5 with *exo*- or *endo*- orientations; isosorbide isomer has both *exo*- and *endo*- hydroxyl groups in its molecular structure situated at carbons 2 and 5, respectively. On the other hand, the isomannide isomer has two *endo*- whereas isoidide isomer has two *exo*- hydroxyls. In view of this difference in the hydroxyl groups orientation, 1,4:3,6-dianhydrohexitols exhibit different physical properties (*e.g.*, melting point). Additionally, the reactivity of the hydroxyl groups depends on both their orientation and their involvement in an intramolecular hydrogen bonding, although the involvement of the *endo*-hydroxyl groups in intramolecular hydrogen bonding leads to higher nucleophilicity, the relatively reduced steric hindrance of the *exo*- hydroxyl group makes it more chemically reactive [5]. Industrially, the large-scale availability of glucose gave the isosorbide isomer an exceeding value over the isoidide isomer, while synthetically, the higher reactivity of

✉ Bassam A. Sweileh  
sweilehb@ju.edu.jo

<sup>1</sup> Chemistry Department, School of Science, The University of Jordan, Amman 11942, Jordan

isorbide made it more applicable as monomer in material synthesis than isomannide isomer [5, 6].

Isorbide has been employed to produce a large variety of polyesters (PEs) [7–20] and poly(ester amide)s (PEAs) [21–24]. The presence of isorbide unit in the polymer backbones was found to impart many desirable features such as stiffness, improved thermal stabilities and enhanced glass transition temperatures ( $T_g$ ) [4]. However, the low reactivity of isorbide led to difficulties in obtaining high-molecular weight polymer [25, 26].

Several series were reported on direct polyesterification of isorbide with a variety of cycloaliphatic [7, 8] and aliphatic dicarboxylic acid derivatives containing methylene units of different chain lengths [9, 10]. The aliphatic copolyesters were synthesized under different reaction conditions and were studied as plasticizers for poly(vinyl chloride) [11], as biocompatible polymers [12] and as coating materials [13]. Due to its nontoxicity, isorbide was also utilized as a building block in the synthesis of biocompatible PEs for bone tissue engineering. For instance, isorbide-based oligo-L-lactide was prepared as an intermediate to produce porous scaffolds [14]. While in a later work, isorbide-based oligo-D,L-lactide was employed as a chain extender to improve the mechanical properties of biodegradable polyurethanes for bone tissue regeneration [15]. Moreover, isorbide was utilized as a diol in the synthesis of semi-aromatic terephthalate PEs [16] and as a comonomer in the synthesis of co- and terpolyesters including, but not limited to, poly(ethylene terephthalate-co-isorbide terephthalate) [17], poly(1,4-cyclohexanedimethylene-co-isorbide terephthalate) [18] and poly(decamethylene-co-isorbide 2,5-furandicarboxylate) [19].

Owing to its chirality, rigidity and nontoxicity, isorbide was employed as a comonomer in the synthesis of biodegradable and optically active PEAs. Conversely to PEs, limited share of scientific work has been however published on the use of isorbide as a building block in PEAs. In the field of optically active PEAs, Philip and Sreekumar polycondensed isorbide with diacid dichlorides of bismaleamic acid and bis-azoaromatic chromophores to synthesize PEAs for non-linear optical applications. The results showed that the chirality of isorbide improved the PEAs optical properties, whereas its rigidity granted an increase in the PEAs glass transition temperatures [21]. Regarding to their use as biodegradable PEAs, several studies reported on the esterification of isorbide with two equivalents of  $\alpha$ -amino acids and *p*-toluenesulfonic acid monohydrate to produce *O,O'*-bis-( $\alpha$ -aminoacyl)-isorbide [22–24]. In a second step, the amino groups were deprotonated and polymerized with either active diesters of dicarboxylic acids [22, 23] or diacid dichlorides [24]. The series obtained were designed to have degradation products with low cytotoxicity and tunable degradation rates [23, 24].

Since the presence of two different hydroxyl groups with different chemical reactivities in isorbide (*exo* and *endo* hydroxyl groups) makes it a monomer of low reactivity [27], good share of work has been directed toward the development of difunctional derivatives of isorbide [28–31]. One interesting approach to overcome the reactivity limitation is to condense isorbide with bio-based anhydrides to obtain difunctional derivatives with enhanced reactivity [29]. Zenner et al. reported the synthesis of dicarboxylic acid monomer by double esterification reaction of isorbide with succinic anhydride [29]. The monomer was investigated as non-toxic tackifier [32], and was converted to its diisocyanate derivative, which was employed to produce bio-renewable polyurethane [29]. In a following work, Wilbon et al. reported the synthesis isorbide bis(succinic acid) using microwave heating, the monomer was obtained in significantly reduced synthesis time and was polymerized with glycerol to produce bio-based, cross-linked polyester [20].

In this publication, we report the synthesis, characterization, and thermal properties of two series of novel isorbide-based PEs and PEAs. Since our interest lies in the development of isorbide-based building blocks and polymers, we report here facile routes for the double esterification of isorbide with symmetrical cyclic anhydrides (succinic, diglycolic and phthalic), the conversion of these bis(acid ester)s to their diacid dichloride derivatives and their use in polyesters and poly(ester amide)s synthesis. Additionally, this paper discusses the effect of various building blocks on polymer properties such as solubility, thermal stability and glass transition temperature.

## Materials

All chemicals used were of analytical grades and used as received unless otherwise stated. Isorbide was purchased from Sigma-Aldrich. Oxalyl chloride, succinic anhydride, diglycolic anhydride, *trans*-1,4-diaminocyclohexane, potassium hydrogen carbonate, 1,4-dioxane, tetrahydrofuran and HCl solution 35% (w/w) were purchased from Acros, anhydrous chloroform, toluene, 2-propanol and ethyl acetate from VWR. *Cis/trans*-1,4-cyclohexanediol was purchased from Alfa Aesar, phthalic anhydride and 1,6-hexanediol were purchased from Merck-Schuchar, *N,N*-dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) from Daejung, *o*-dichlorobenzene (*o*-DCB) and acetone from Pharmacos. Pyridine was purchased from Riedel-de Haen, and 1,6-hexanediamine from Aldrich. Succinic anhydride and phthalic anhydride were purified by sublimation under vacuum. *Trans*-1,4-diaminocyclohexane and 1,6-hexanediamine were purified by recrystallization from cyclohexane under argon atmosphere.

## Measurements

The inherent viscosity of the dilute polymers solutions were measured with a dilution Ubbelohde glass capillary viscometer (Rheotek, Poulten Selfe & Lee Ltd., Essex, England) in a thermostated water bath at  $25.0 \pm 0.1$  or  $35.0 \pm 0.1$  °C. Dilute polymers solutions were temperature equilibrated for approximately 15 min then the viscosity measurements were repeatedly recorded until reproducible values were obtained. Intrinsic viscosities  $[\eta]$  were calculated by the single point method described by Solomon and Ciuta [33, 34]. The viscosities average molecular weights ( $M_v$ ) were calculated for the PEs series by Mark-Houwink-Sakurada equation, using the coefficients ( $K = 1.28 \times 10^{-4}$  and  $\alpha = 0.78$ ) determined for polyesters with a close molecular structure (Eq. 1) [35]. However, no such parameters were available in the literature for PEAs with similar chemical structures.

$$[\eta] = 1.28 \times 10^{-4} M^{0.78} \quad (1)$$

The infrared (IR) spectra (from 550–4000  $\text{cm}^{-1}$ ) were recorded using a Thermo Nicolet Nexus 670 FTIR spectrophotometer equipped with attenuated total reflection (ATR).  $^1\text{H}$  Nuclear Magnetic Resonance (NMR),  $^{13}\text{C}$  NMR and  $^1\text{H}$ - $^{13}\text{C}$  HMQC-DEPT 135 (HMQC: Heteronuclear Single Quantum Coherence; DEPT: Distortionless Enhancement by Polarization Transfer) spectra were recorded in DMSO- $d_6$  or  $\text{CDCl}_3$  on a 500 MHz ( $^1\text{H}$  NMR) and 125 MHz ( $^{13}\text{C}$  NMR) spectrophotometer (Bruker Avance III). Chemical shifts ( $\delta$ ) were expressed in ppm using tetramethylsilane (TMS) as an internal standard.

The glass transition temperatures ( $T_g$ ) were studied using Netzsch DSC 204 F1 differential scanning calorimeter (Selb Bavaria, Germany).  $T_g$  measurements were performed under dry nitrogen gas using  $8 \pm 3$  mg samples. To eliminate any previous thermal history, the samples were firstly heated from ambient temperature to the 150 °C, maintained at this temperature for 4 min, and rapidly cooled with liquid nitrogen to an appropriate starting temperature. The thermal behavior was then obtained from the second scan by heating the samples at a rate of 10 °C/min, and the  $T_g$  values were taken as the inflection of the step transition. Thermal stabilities of the samples were studied by thermogravimetric analysis (TGA) using a Netzsch STA 409 PG/PC thermal analyzer (Selb Bavaria, Germany). The measurements were conducted at the heating rates 10 or 20 °C/min under dry nitrogen gas purging at a flow of 50 mL/min.

## Experimental

### Synthesis of isosorbide bis(succinic acid) (1)

Monomer **1** was synthesized according to a previously described method [29] with slight modification. A mixture

of isosorbide (3.65 g, 25 mmol) and succinic anhydride (6.25 g, 62.5 mmol, 2.5 eqv.) was fitted in 50 mL round-bottomed flask, the flask was flushed with argon gas for 5 min then quickly sealed with a stopper. The entire reaction vessel was then immersed in an oil bath and heated at 120 °C for 24 h. Upon reaction completion, the excess succinic anhydride was removed by sublimation under reduced pressure. The crude product was then dissolved in 40 mL ethyl acetate, stirred with charcoal, filtered then extracted with distilled water (20 mL  $\times$  3), the organic layer was dried over  $\text{Na}_2\text{SO}_4$ , filtered and the solvent evaporated under reduced pressure. The formed oily product was dried in *vacuo* at 75 °C for 8 h to give the final pure product as a viscous yellowish oil (8.4 g, 97% yield).

### Synthesis of isosorbide bis(diglycolic acid) (2)

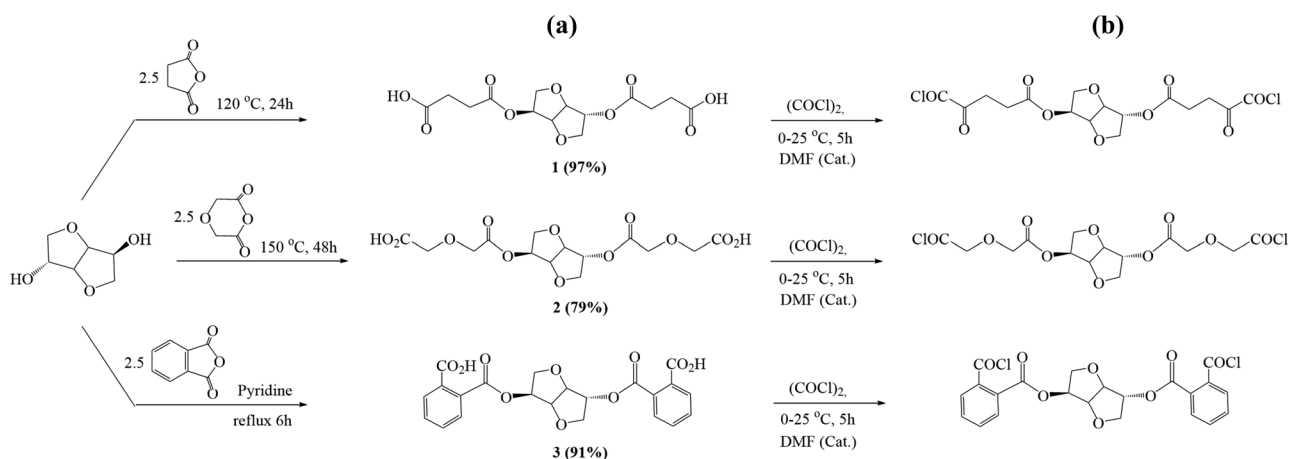
Similarly to **1**, monomer **2** was synthesized in the melt as described below. However, optimization of the reaction conditions and purification approach was carried out to improve the yield. A mixture of isosorbide (3.65 g, 25 mmol) and diglycolic anhydride (7.25 g, 62.6 mmol, 2.5 eqv.) was fitted in 50 mL round-bottomed flask, the flask was flushed with argon gas for 5 min then quickly sealed with a stopper. The entire reaction vessel was then immersed in an oil bath and heated at 150 °C for 48 h. The excess diglycolic anhydride was removed by sublimation under reduced pressure and the crude product was purified by recrystallization 5 times from ethyl acetate/ petroleum ether (3/1, v/v) followed by drying in *vacuo* at 75 °C for 12 h. The pure product was obtained as a viscous yellowish oil (7.44 g, 78.7%).

### Synthesis of isosorbide bis(phthalic acid) (3)

Monomer **3** was synthesized using pyridine as both solvent and catalyst. A solution of isosorbide (3.65 g, 25 mmol) and phthalic anhydride (9.26 g, 62.6 mmol, 2.5 eqv.) in 35 mL of dry pyridine was refluxed for 6 h. The reaction mixture was cooled in ice bath then dropped over 100 mL of ice-cold 2 M HCl solution. The precipitated solid was then filtered, dried and recrystallized twice from 2-propanol /toluene mixture to give the pure product as a white solid ( $T_m$ : 99–101 °C, 10.1 g, 91%).

### Isosorbide bis(acid chloride ester) monomers

The diacid dichloride monomers of **1**, **2** and **3** were synthesized according to a previously described method [36] with slight modification. Oxalyl chloride (100 mmol, 12.7 g, 4 eqv.) was added dropwise to a solution of



**Scheme 1** Synthesis of **a** isosorbide bis(acid ester) monomers **b** diacid dichlorides of isosorbide bis(acid ester) monomers

isosorbide bis(acid ester) derivatives **1**, **2** or **3** (25 mmol), 4 drops dry DMF in an ice-cold anhydrous chloroform (40 mL). Upon dropping completion, the solution was stirred at room temperature for 5 h to reach the reaction completion and the excess oxalyl chloride was stripped in *vacuo* using several portions of chloroform. The isosorbide bis(acid chloride ester) monomers were obtained as a yellow oils and were used without further purification.

### Polyesters synthesis (PE1-6)

PE1-6 were synthesized using a modification of a previously reported method [37]. Under argon gas flow, a solution of isosorbide diacid dichloride derivative (5 mmol) in *o*-dichlorobenzene (7 mL) was added dropwise to a stirred, preheated (80 °C) solution of dihydroxy compound (5 mmol) in *o*-dichlorobenzene (7 mL). Upon the addition completion, the reaction temperature was gradually increased to 130 °C over a period of 1 h, and kept at this temperature for an additional hour. The mixture was then allowed to cool to room temperature, and then diluted with *n*-hexane (70 mL) to precipitate the polymer. The solvent mixture was then decanted and the obtained polyester was dissolved in chloroform and precipitated in tenfold of methanol (v/v). The purified polymer was dried in *vacuo* at 70 °C for 12 h.

### Poly(ester amide)s synthesis (PEA1-4)

PEA1-4 were synthesized similarly to the procedure described in [38]. A solution of isosorbide bis(acid chloride ester) (5 mmol, 1 eqv.) in anhydrous chloroform (20 mL) was added dropwise to a vigorously stirred, ice-cold solution (0–5 °C) of diamine (5 mmol, 1 eqv.) and potassium

hydrogen carbonate (10 mmol, 2 eqv.) in water (15 mL). The reaction mixture was stirred at a high speed in the ice bath for 30 min and at room temperature for one hour. The formed polymers were isolated by filtration, rinsed extensively with water and chloroform, and dried in *vacuo* at 60 °C to constant weights. The crude polymers were further purified by precipitation from DMF to tenfold of ethyl acetate (v/v).

## Results and discussion

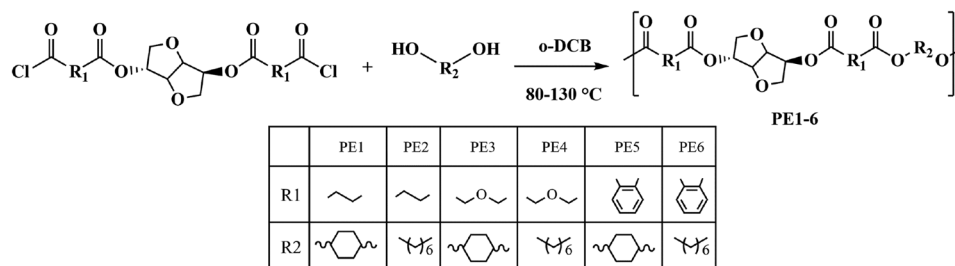
### Monomers and polymers synthesis and spectral characterization

The reactivity difference between the two secondary hydroxyl groups of isosorbide restricted the direct use of this eco-friendly diol in the synthesis of bio-based polymers. One method to overcome this drawback is to improve isosorbide reactivity via chemical derivatization, for this purpose, we report here on the synthesis of three highly reactive isosorbide derivatives and the employment of these difunctionalized derivatives in the synthesis of novel PEs and PEAs.

At first, isosorbide was alcoholized with three symmetrical cyclic anhydrides to obtain three isosorbide bis(acid ester)s (Scheme 1a), these derivatives were synthesized in the melt or in solution and were obtained in high purity and high yields (78.7–97%). It was noticed that monomer **2** has the lowest yield (78.7%) with respect to monomers **1** and **3**, which may originate from the reduced ring strain within the six-membered anhydride ring (diglycolic anhydride) that results in lower reactivity.

In a second step, isosorbide bis(acid ester)s were converted to their diacid dichloride derivatives using oxalyl chloride (Scheme 1b), the highly reactive products obtained from this step were directly used as monomers for

**Scheme 2** Synthesis of polyesters (PE1-6) from Isosorbide bis(acid chloride ester) monomers



copolymers synthesis. It is worth noting that this reaction was performed under mild conditions to avoid ester group hydrolysis. According to the synthetic approaches described in the experimental part and presented in Scheme 2, six novel polyesters (PE1-6) were prepared in *o*-dichlorobenzene by polycondensation reaction of isosorbide bis(acid chloride ester)s monomers with linear or cyclic diols.

Additionally, the monomers were employed in the synthesis of a series of PEAs (PEA1-4) as shown in Scheme 3. The PEAs were synthesized interfacially by the polycondensation reaction of isosorbide bis(acid chloride ester)s monomers with linear or cyclic diamines in the presence of an inorganic base to neutralize the acid produced from the amine-acid chloride reaction. The monomers and polymers chemical compositions were ascertained by FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Whereas other characteristics of the polycondensates were evaluated by inherent viscosity, solubility, TGA and DSC measurements.

Our attempts to produce PEAs from isosorbide bis(phthalic acid) result in the majority of cases, in the production of phthalimide oligomers instead of the long chain polymers. This may have been due to the occurrence of the preferred intramolecular cyclization reaction, which limits the step-growth polycondensation reaction and results in formation of oligomers in low yields [39].

### Spectral characterization of isosorbide bis(acid ester)s

Chemical characterizations of isosorbide bis(acid ester)s structures were performed by FTIR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. Figure 1 illustrates the FTIR spectra of the three isosorbide bis(acid ester)s, the broad bands observed in the

range from 2526 to 3436  $\text{cm}^{-1}$  were assigned to the carboxylic acid stretching vibration. The stretching vibration of the ester group appeared as a strong band in the range from 1723 to 1734  $\text{cm}^{-1}$ .

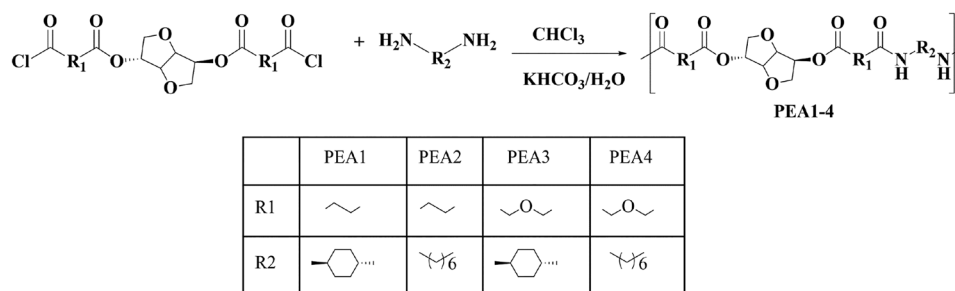
The  $^{13}\text{C}$  NMR spectra confirmed the presence of two types of carbonyl carbons in the derivatives structures. However, due to the non-symmetrical structure of isosorbide, the signals corresponding to the ester and carboxylic acid carbonyl carbons appeared as two pairs of peaks in the chemical shift range from 167 to 174 ppm. Additionally, the carboxylic acid protons ( $-\text{COOH}$ ) appeared in the  $^1\text{H}$  NMR spectra as broad peaks in the chemical shift range from 12.17 to 13.35 ppm.

Figure 2 displays the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of isosorbide bis(phthalic acid) (3) as an example, for this derivative, the peaks of isosorbide protons appeared in the range from 3.81 to 5.30 ppm, while their corresponding carbons signals appeared in  $^{13}\text{C}$  NMR spectrum as six peaks in the range from 70.4 to 85.5 ppm.

The signals for the aromatic phthalate ring protons appeared in range from 7.63 to 7.82 ppm, whereas the signals attributed to its aromatic carbons were observed at the range from 128 to 133 ppm.

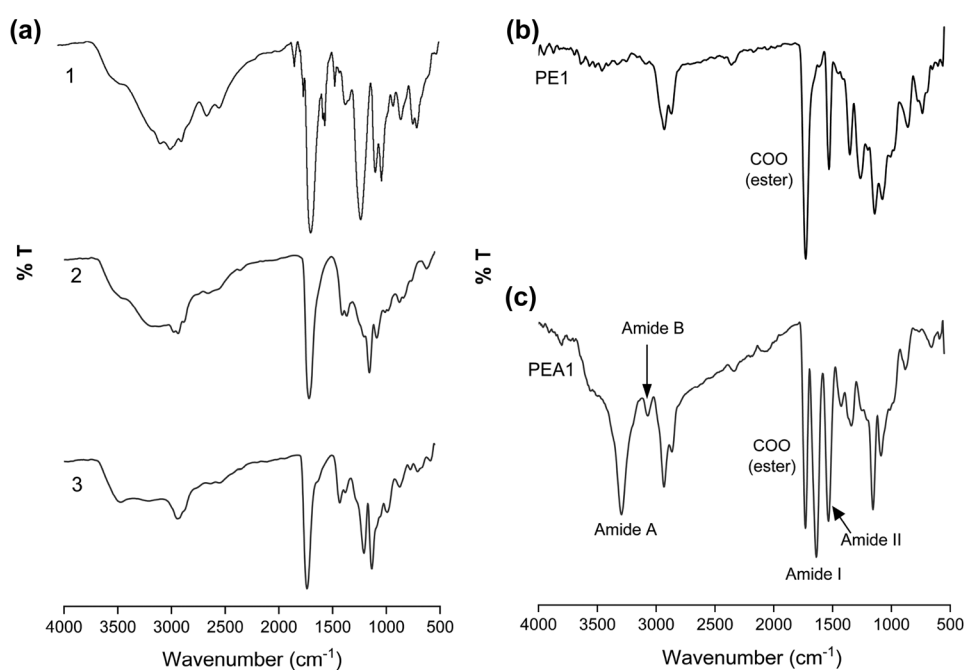
Total assignments of NMR chemical shifts of isosorbide bis(acid ester)s are given in Table S1 (Electronic Supplementary Information, Table S1  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the monomers obtained in  $\text{DMSO}-d_6$ ). The signals of the succinate protons moiety ( $-\text{CH}_2-\text{CH}_2-$ ) in isosorbide bis(succinic acid) (1) appeared at the range of 2.43 to 2.55 ppm, and their associated carbons were observed at 29 ppm. As for isosorbide bis(diglycolic acid) (2) signals, the protons peaks of the diglycolic moiety ( $-\text{CH}_2-\text{O}-\text{CH}_2-$ ) appeared in the range

**Scheme 3** Synthesis of PEAs (PEA1-4) from Isosorbide bis(acid chloride ester) monomers





**Fig. 1** FTIR spectra of **a** monomers 1, 2 and 3 **b** PE1 and **c** PEA1



from 4.04 to 4.38 ppm while their corresponding carbons signals were detected at 67 and 68 ppm.

### Spectral characterization of PEs

Spectral characterization of the PEs structures were achieved by means of NMR and FTIR. The main characteristic absorption bands of the synthesized PEs are summarized in Table S2 (Electronic Supplementary Information, Table S2 Main IR bands of the synthesized PEs and PEAs), whereas Fig. 1 displays the FTIR of PE1 as representative PE and Table 2 lists the yields of the synthesized PEs.

In the PEs FTIR spectra, no obvious absorption was observed in the carboxylic acid stretching region, indicating low contents of the carboxylic acid end group in the polymeric products. Besides, the FTIR spectra of the PEs showed the characteristic absorption bands of the carboxylate group around 1730, 1265 and 1150  $\text{cm}^{-1}$  and the methylene units stretching vibration bands in the range from 3000 to 2850  $\text{cm}^{-1}$ .

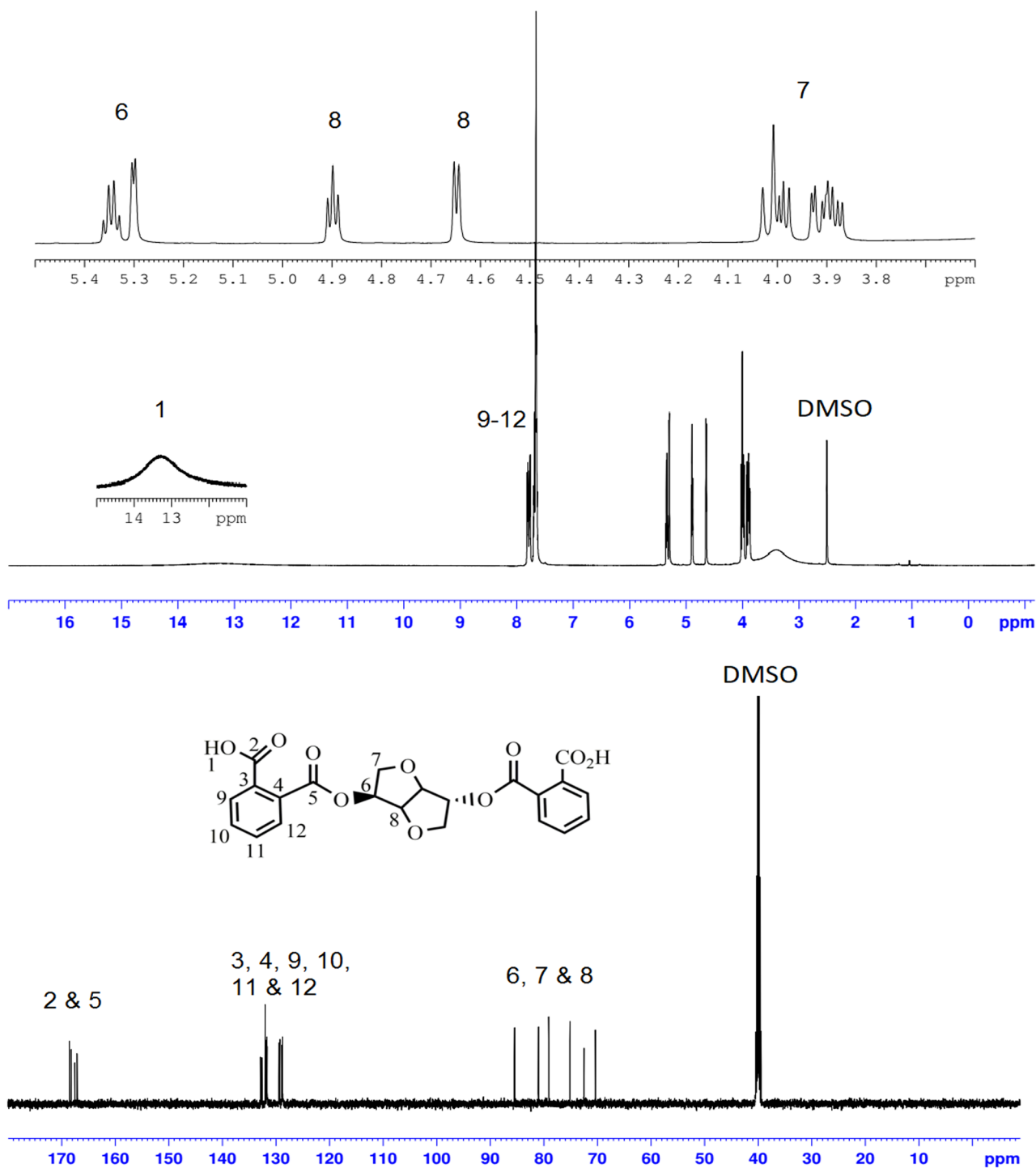
The structures of the PEs were also corroborated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR. The spectra obtained for the PEs contained sets of signals belonging to isosorbide and ester carbonyl groups, which agrees with the data obtained from the FTIR. An assignment of the main  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts of the PEs are given in Table S3 (Electronic Supplementary Information, Table S3 Main spectroscopic data of PEs and PEAs synthesized in this work  $^1\text{H}$  and  $^{13}\text{C}$  NMR data) while Figs. 3 and 4 shows the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of PE1 (as a representative example), respectively.

In the  $^1\text{H}$  NMR spectra obtained for PE1, PE3 and PE5, new signals corresponding to the *cis/trans*-cyclohexylene CH protons were observed in the range from 3.78 to 5.11 ppm, while the methylene protons of the same unit appeared in the range from 1.25 to 2.36 ppm. In  $^{13}\text{C}$  NMR spectra, the signals of the *cis/trans*-cyclohexylene CH carbons appeared in the range from 70.8 to 72.3 ppm, whereas the signals observed in the range from 27.2 to 27.8 ppm were assigned to the methylene carbons of the *cis/trans*-cyclohexylene unit. Likewise, the NMR spectra of PE2, PE4 and PE6 were in consistency with their expected structures. As reported in Table S3, the  $^1\text{H}$  NMR spectra showed the methylene protons signals of the 1,6-hexylene unit in the range from 1.26 to 4.32 ppm. On the other hand, the  $^{13}\text{C}$  NMR showed three peaks corresponding to 1,6-hexylene methylene carbons in the range from 25.3 to 65.4 ppm.

### Spectral characterization of PEAs

The FTIR spectra of PEAs showed the characteristic absorption band of amide A at 3299–3258  $\text{cm}^{-1}$ , amide B at 3079–3060  $\text{cm}^{-1}$ , amide I at 1651–1629  $\text{cm}^{-1}$  and amide II at 1536–1520  $\text{cm}^{-1}$ . Moreover, the ester group ( $-\text{COO}-$ ) absorption band was observed in the range 1749–1723  $\text{cm}^{-1}$ . Figure 1 displays the FTIR of PEA1 as representative PEA, whereas Tables 2 and S2 summarizes the yields and main IR bands of the PEAs synthesized, respectively.

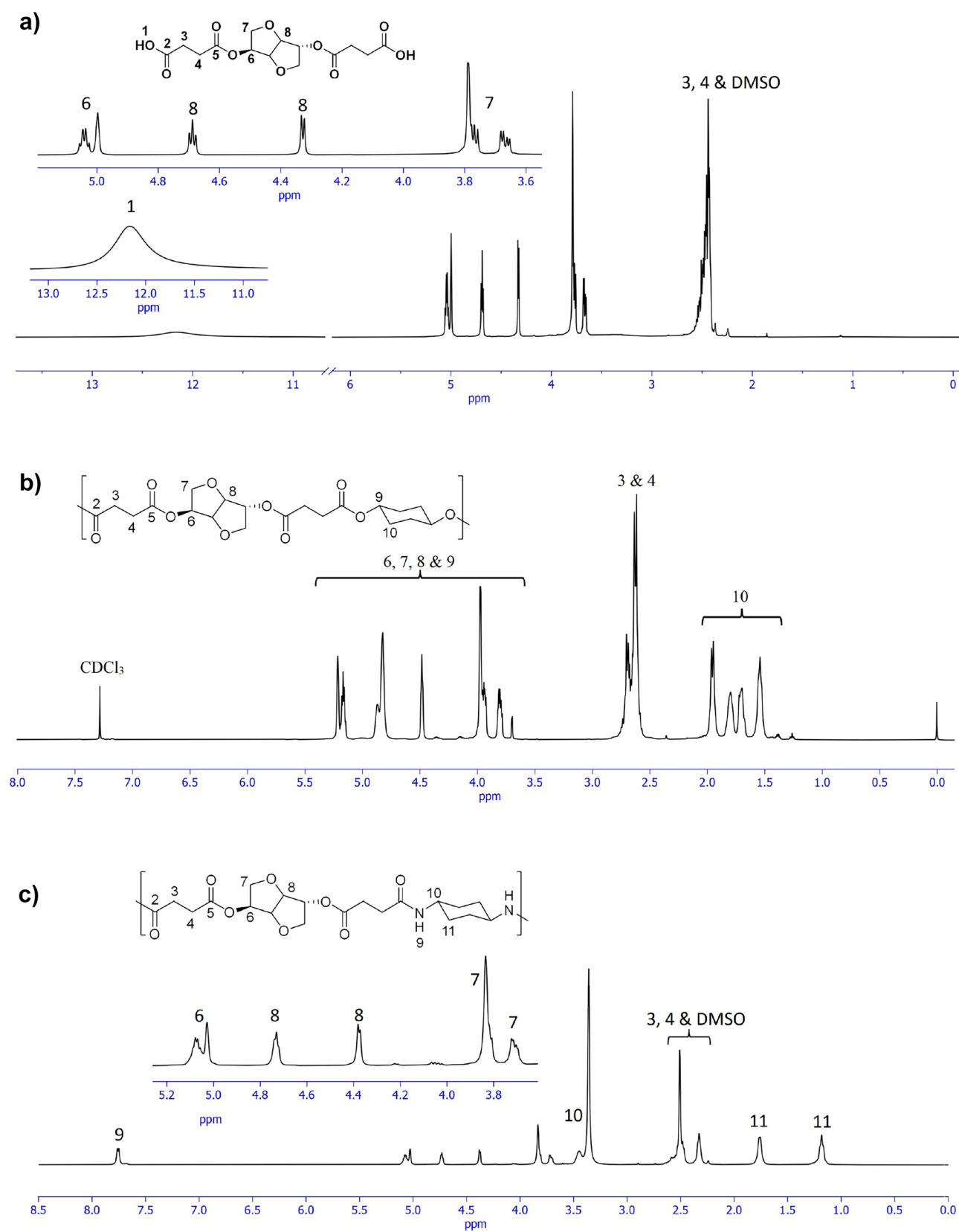
In order to confirm their chemical structures, the synthesized PEAs were also characterized by  $^1\text{H}$ ,  $^{13}\text{C}$  and 2D-NMR spectroscopy. The spectra were found to be in



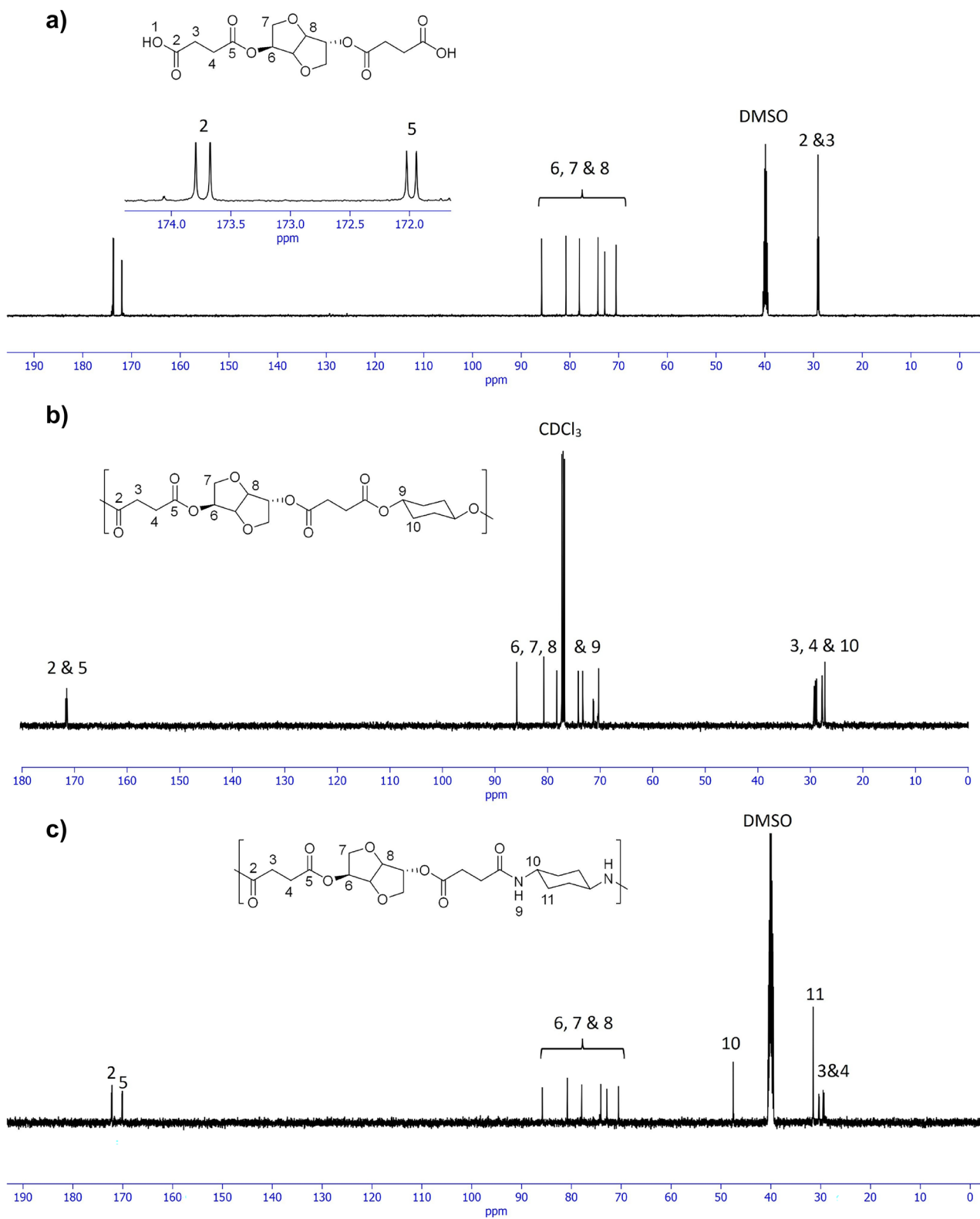
**Fig. 2**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of monomer 3 in  $\text{DMSO-d}_6$

agreement with FTIR data and with the postulated polymer structures. As summarized in Table S3, the formation of the amide group and the appearance of new signals correlated to the diamine units indicated a successful synthesis of the PEAs. The  $^1\text{H}$  NMR spectra of PEA1-4 showed

singlet in the range from 7.74 to 7.84 ppm for the amide proton ( $-\text{CONH}-$ ). Additionally, sets of signals belonging to isosorbide, succinate (in PEA1-2) and diglycolate (in PEA3-4) moieties were found in their expected range. The NMR signals correlated to the methylene protons in the







**Fig. 4**  $^{13}\text{C}$  NMR spectra of **a** monomer 1; **b** PE1 and **c** PEA1

1,6-hexylene unit (in PEA2 and PEA4) were centered at 3.02 (-NH(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH-), 1.37 (-NH(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH-) and 1.19–1.24 ppm (-NH(CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>NH-), while their corresponding methylene carbons resonated around 37, 29 and 26 ppm, respectively.

Figures 3, 4 and 5 show <sup>1</sup>H, <sup>13</sup>C NMR and <sup>1</sup>H-<sup>13</sup>C HMQC-DEPT 135 spectra of PEA1, respectively. The NMR spectra obtained for PEA1 (and similarly PEA3) showed two separated protons peaks in the range from 1.18 to 1.95 ppm, these signals showed HMQC correlation to cyclohexyl methylene carbons signals near 31.5 ppm (Fig. 5), and therefore they were assigned to the axial and equatorial methylene protons of this unit. On the other hand, the <sup>1</sup>H NMR signal near 3.5 ppm were found to be HMQC correlated to the cyclohexyl tertiary carbons near 48 ppm, and therefore assigned to the tertiary protons of *trans*-1,4-cyclohexylene unit.

### Polymers solubility

The polymer solubility was tested in several commonly used organic solvents at room temperature using concentrations in the range of 3 to 5% (w/v). The PEAs were found to be

soluble in polar aprotic solvents such as DMSO, DMF and DMAc and insoluble in diethyl ether, chloroform and ethyl acetate. Clearly, the presence of the intermolecular hydrogen bonding in PEAs results in poor solubility in weakly polar or non-polar solvents. However, high polarity aprotic solvents interrupt this strong intermolecular interaction, and results in higher solubility.

On the other hand, the synthesized PEs showed good solubility in a variety of organic solvents (Table 1), this feature emerges from the lack of strong intermolecular interaction between polymer chains. The results also demonstrated that the solubility depends on the polymer chemical composition. For instance, polyesters containing diglycolate (PE3 and PE4) and phthalate (PE5 and PE6) units showed good solubility in ethyl acetate. Apparently, the presence of the flexible diglycolate and the spacing phthalate segments results in reduced polymer chains packing and enhanced solubility. Additionally, polymer containing *cis-trans* cyclohexane unit (PE3 and PE5) showed good solubility in acetone. This may be attributed to the lower symmetry of the *cis* isomer than the corresponding *trans* isomer, which results in reduced polymer stereoregularity, reduced intermolecular packing and hence higher solubility [40].

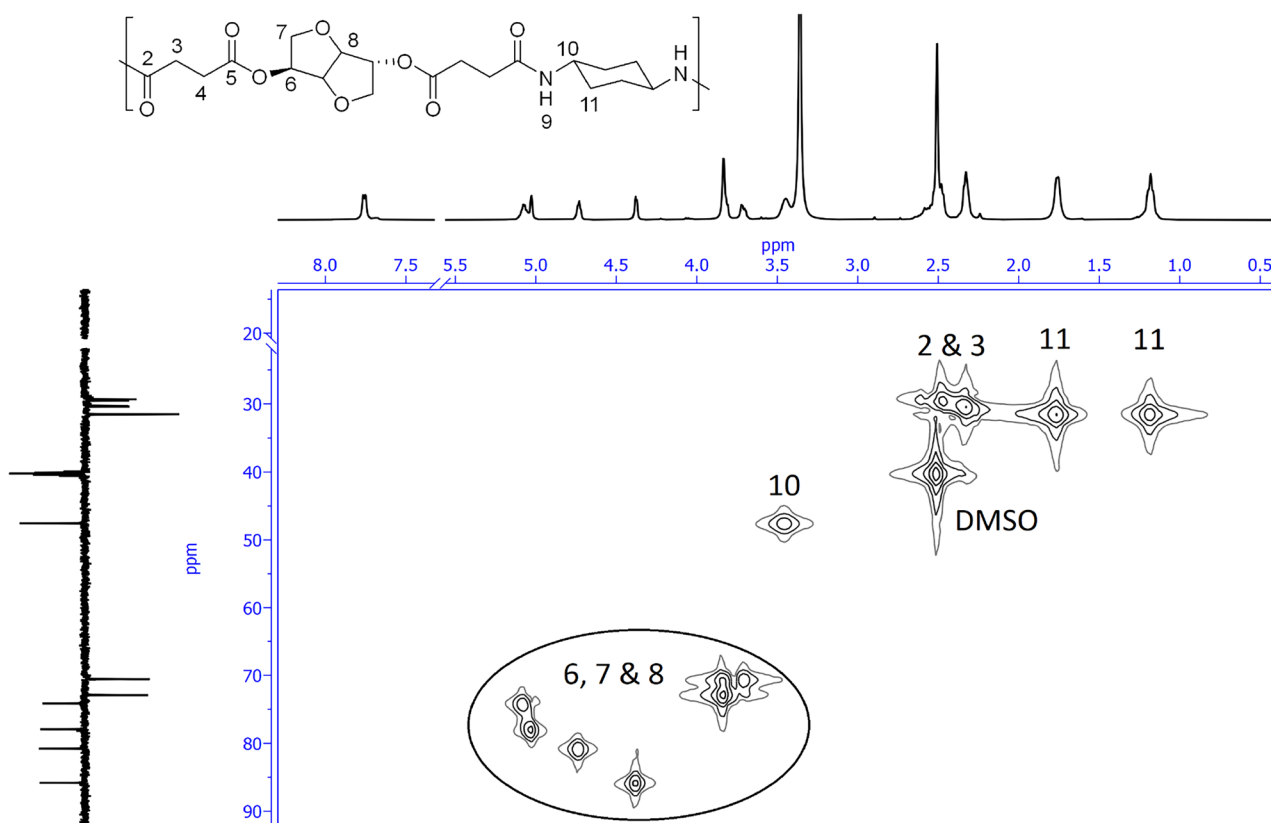


Fig. 5 <sup>1</sup>H-<sup>13</sup>C HMQC-DEPT 135 of PEA1

**Table 1** PEs solubility test

Polymer	DMSO	MeOH	THF	CHCl <sub>3</sub>	Ethyl acetate	1,4-Dioxane	Acetone
PE1	+	-	-	+	-	-	-
PE2	+	-	-	+	-	-	-
PE3	+	-	-	+	+	-	+
PE4	+	-	-	+	+	-	-
PE5	+	-	-	+	+	-	+
PE6	+	-	-	+	+	-	-

(+) Soluble at room temperature, (-) Insoluble at room temperature

## Solution viscosity measurements

The inherent viscosities were measured using Ubbelohde capillary viscometer for diluted polymers solutions of the PEs and PEAs in CHCl<sub>3</sub> at 25.0 ± 0.1 °C and in DMSO at 35.0 ± 0.1 °C, respectively. The PEs had inherent viscosities ( $\eta_{inh}$ ) in the range from 0.40 to 0.58 dL/g and  $M_v$  in the range from 52,000 to 32,000 g/mol (Table 2), which reflect moderate molecular weights of the PEs synthesized. It is noticeable that the PEs derived from monomer **3** had the lowest inherent viscosity and  $M_v$  values when compared with PEs derived from the monomers **1** and **2**. This result is plausible since the polycondensation reaction takes place at the sterically hindered *ortho* position of the aromatic ring in monomer **3**. Moreover, the inherent viscosities and  $M_v$  values of the polymers derived from the primary linear diol (1,6-hexanediol) were slightly higher than those derived from the secondary cycloaliphatic diol (*cis/trans*-1,4-cyclohexanediol) due to the relatively low reactivity of the secondary alcoholic groups. On the other hand, the inherent viscosities and of the PEAs were in the range from

0.23 to 0.25 dL/g suggesting low to moderate molecular weights (Table 2).

## Thermal properties

### Thermal stability: TGA

TGA was evaluated under non-oxidative conditions in the interval from room temperature to 600 °C. The TGA thermograms of the polymers synthesized presenting sample mass loss versus temperature are shown in Fig. 6 and the results are summarized in Table 2. The PEs showed no thermal decomposition below 114 °C (Fig. 6a) and 1% mass loss ( $T_{1\%}$ ) in the temperatures range of 114–223 °C (Table 2), this temperature range associates usually with the loss of adsorbed solvent molecules (*e.g.*, *o*-DCB) or traces of impurities. However, the PEs synthesized showed in general good thermal stabilities with 5% mass loss ( $T_{5\%}$ ) in the temperature range of 162 to 332 °C. The TGA thermograms of 1,6-hexylene-containing PEs (PE2, PE4 and PE6) showed one-stage decomposition with higher  $T_{50\%}$  values when

**Table 2** Thermal stability, glass transition temperature and solution viscosity data of synthesized PEs and PEAs

Polymer	$T_{1\%}$ (°C) <sup>a)</sup>	$T_{5\%}$ (°C) <sup>b)</sup>	$T_{20\%}$ (°C) <sup>c)</sup>	$T_{50\%}$ (°C) <sup>d)</sup>	Residual mass (%) <sup>e)</sup>	$T_g$ (°C)	$\eta_{inh}$ (dL/g)	$M_v$ (g/mol)	Yield (%)
PEA1	124.5	240.1	268.8	327.8	11.44	129.5	0.23	-	70
PEA2	73.7	188.6	270.8	344.6	6.88	53.8	0.25	-	67
PEA3	85.0	238.9	346.8	389.2	16.04	103.7	0.24	-	69
PEA4	81.0	165.8	322.7	361.9	9.47	39.3	0.24	-	58
PE1	209.8	308.4	331.4	346.1	7.69	44.9	0.53	45,500	88
PE2	185.2	332.5	375.4	397.1	7.49	3.0	0.58	52,000	91
PE3	154.4	177.3	333.1	362.8	6.57	36.0	0.52	44,500	78
PE4	205.9	237.6	369.6	392.5	5.33	-13.5	0.52	45,000	81
PE5	222.9	257.8	306.7	330.4	1.97	102.8	0.40	32,000	85
PE6	114.1	162.7	313.7	380.8	0.02	21.1	0.42	34,000	88

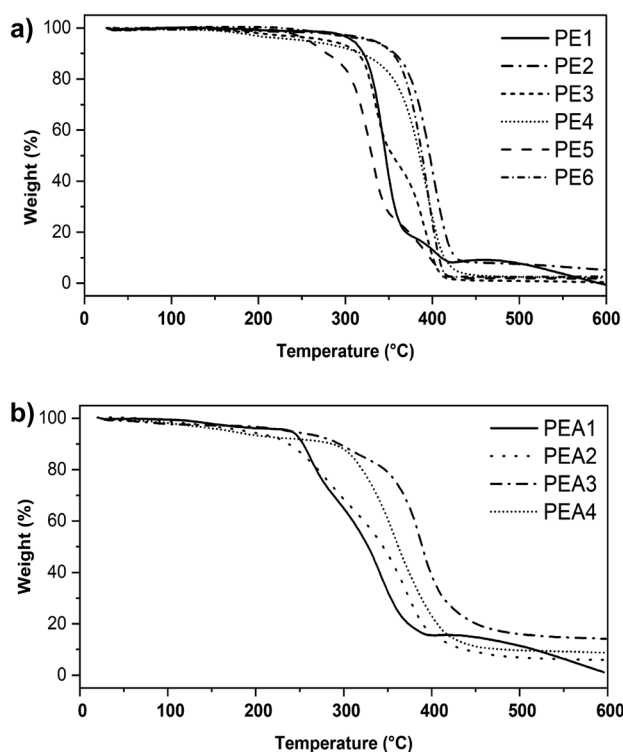
<sup>a)</sup> Decomposition temperature based on 1% weight loss

<sup>b)</sup> Decomposition temperature based on 5% weight loss

<sup>c)</sup> Decomposition temperature based on 20% weight loss

<sup>d)</sup> Decomposition temperature based on 50% weight

<sup>e)</sup> Residual mass at 500 °C



**Fig. 6** TGA thermograms of **a** PEs and **b** PEAs

compared with their analogous *cis/trans*-1,4-cyclohexylene-containing PEs (PE1, PE3 and PE5).

Considering that polyesters thermal decomposition goes mainly through  $\beta$ -hydrogen bond scission [41], *cis/trans*-1,4-cyclohexylene-containing PEs would probably exhibit higher vulnerability to thermal decomposition due to the higher number of  $\beta$ -hydrogens available for elimination. On the other hand, PEs with *cis/trans*-1,4-cyclohexylene unit in the backbones showed a two-stage thermal decomposition (see Fig. 6a), this may be attributed to the difference between the *cis* and *trans* isomers decomposition behavior in the cycloaliphatic unit [42]. Additionally, PEs with *cis/trans*-1,4-cyclohexylene unit showed higher residual mass at 500 °C indicating the formation of less volatile decomposition products. Moreover, the incorporation of the heterocyclic, stiffening isosorbide unit in the PEs structure improved the thermal resistance of the PEs. For instance, poly(hexylene succinate) was reported to have 5% mass loss ( $T_{5\%}$ ) at 321 °C, this value was, however, improved in this work upon the introduction of isosorbide in the polymer backbone to 332.5 [43].

On the other hand, the PEAs showed good thermal stabilities with  $T_{5\%}$  ranging from 166 to 284 °C (Table 2, Fig. 6b). The polymers containing 1,4-cyclohexylene unit (PEA1 and PEA3) in their structure showed a rather higher heat resistance when compared with their 1,6-hexylene-containing PEAs

(PEA2 and PEA4). The rigidity of the 1,4-cyclohexylene ring was reflected in the increase in both  $T_{5\%}$  and the residual mass values at 500 °C, indicating their higher thermal stability and lower decomposition products volatility [44], respectively.

### Thermal transitions: DSC

The glass transition temperature ( $T_g$ ) is a thermal property of fundamental importance for polymers possible applications. Herein, thermal transition properties of the synthesized PEs and PEAs were investigated by DSC. The DSC data of the synthesized materials are given Table 2 and their thermograms are given in Fig. S1 (Electronic Supplementary Information, Fig. S1 DSC thermograms of a) PEs and b) PEAs). *Cis/trans*-1,4-cyclohexylene moiety containing PEs exhibited higher  $T_g$  values compared with their open chain analogues, 1,6-hexylene-containing PEs, this result is highly expected due to the presence of the stiffening cyclohexylene ring in the polymers backbone [45]. Moreover, the presence of the diglycolate unit in the PEs backbone decreased the  $T_g$  values compared with the PEs containing succinate or phthalate units in their backbone (Fig. S1a). This decrease is most attributed to the presence of the diglycolate-ether linkage in the polymer chain, which effectively increases the polymer chain flexibility, escalates the molecular mobility and impedes an efficient macrochains packing [46, 47]. Furthermore, the introduction of the stiffening isosorbide unit in the PEs structure improved the  $T_g$  values compared with poly(butylene succinate) ( $T_g = -15.1$  °C) and Poly(hexylene succinate) ( $T_g = -52.7$  °C) [48].

On the other hand, PEAs are generally characterized by exhibiting high  $T_g$  values; this predominant observation was confirmed by the DSC study in this work. The PEAs synthesized in this series displayed high  $T_g$  values compared with their PEs analogues, this rise in  $T_g$  values is caused by the presence of hydrogen bonding among polymers chains [49]. Furthermore, the incorporation of the *trans*-1,4-cyclohexylene unit in the PEAs (PEA1 and PEA3) structures resulted in a dramatic increase in the  $T_g$  values, this result is expected since the presence of this symmetrical rigid segment in the PEAs structure leads to more efficient chains packing and stronger hydrogen bonding interaction [50]. The DSC thermograms of the PEAs synthesized are presented in Fig. S1, and the  $T_g$  values are reported in Table 2.

## Conclusion

Two series of novel linear bio-based polymeric condensates, belonging to the classes polyesters and poly(ester amide) s based on isosorbide were synthesized and characterized. Isosorbide was first esterified with two equivalents of cyclic

anhydrides to give isosorbide bis(acid ester) monomers, which were successfully transformed to their diacid dichlorides. The reaction of isosorbide with cyclic anhydrides let us overcome the difference in reactivity between the two hydroxyl groups of isosorbide. These monomers were then polycondensed in solution with diols to give polyesters, the polyesters were obtained in high yields (78–91%), showed good thermal stabilities and  $T_g$  values in the range from -13.5 to 102.8 °C. Additionally, a series of novel poly(ester amide)s were synthesized from isosorbide bis(diglycolic acid) or isosorbide bis(succinic acid) and various diamines. The poly(ester amide)s were synthesized interfacially and were obtained in good yields (58–70%). They had good thermal stabilities with 5% mass loss temperature ( $T_{5\%}$ ) in the range from 166 to 240 °C, and  $T_g$  temperatures in the range from 39.3 to 129.5 °C. Thermal properties analysis showed that the polymers synthesized exhibit wide range of thermal properties that can cover broad range of applications.

**Supplementary Information** The online version contains supplementary material available at <https://doi.org/10.1007/s10965-022-03356-0>.

**Acknowledgements** The authors thank The Deanship of Scientific Research of The University of Jordan for the financial support of this work.

## Declarations

**Conflicts of interest** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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