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Synthesis of biosourced polyether-amides from 1,4-3,6-dianhydrohexitols: Characterization by NMR and MALDI–ToF mass spectrometry

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ABSTRACT

New series of polyether-amides were prepared by polycondensation in solution of three diamines based on 1,4-3,6-dianhydrohexitols with two types of diacyl chlorides (sebacoyl and isophtaloyl). Unprecedented diamines based on isomannide and isoidide were elaborated. The corresponding polyether-amides (PeA) were obtained with high yields. They were characterized by different analytical techniques (NMR, MALDI–ToF MS, DSC). The combination of MALDI–ToF MS with NMR spectroscopy allowed us to confirm structure types. DSC measurements revealed an amorphous character for the isophtaloyl family with a high T_g value. The sebacoyl series proved to be semi-crystalline with a high T_m value. Isosorbide-based PeAs demonstrated interesting properties (T_g above 210 °C and T_m above 240 °C) and high viscosity (0.32).

Mots clés:
1,4-3,6-Dianhydrohexitols
Polyéther-amides
Biosourcés
Spectrométrie de masse MALDI–ToF
Polycondensation

RÉSUMÉ

Une nouvelle classe de polyéther-amides a été préparée par polycondensation en solution de trois diamines à partir des 1,4-3,6-dianhydro, avec deux types de chlorures de diacyle (sébacoyle et isophtaloyl). Des diamines inédites à partir de l'isomannide et l'isoidide ont été élaborées. Les polyéther-amides correspondants ont été obtenus avec des rendements élevés. Ils ont été caractérisés par différentes techniques analytiques (RMN, MALDI–TOF MS, DSC). La combinaison des spectrométries de masse MALDI–ToF et RMN nous a permis de confirmer le type des structures obtenues. Les mesures DSC ont révélé un caractère amorphe pour la famille isophtaloyl, avec des valeurs de T_v élevées. La série sébacoyle s'est révélée être semi-cristalline, avec des valeurs de T_f élevées. Les PeA dérivés de l'isosorbide ont révélé des propriétés intéressantes (T_v au-delà de 210 °C et T_f au-delà de 240 °C), ainsi que des viscosités élevées (0,32).

1. Introduction

The increasing demand for biobased materials offering competitive and characteristic properties similar to those of well-established petrochemical analogues is a subject of interest nowadays [1,2]. Among several building blocks, 1,4-3,6-dianhydrohexitols have emerged in the fields of

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polymers chemistry, owing to a multitude of advantages: biodisponibility, non-toxicity, good resistance and chirality. Although these attractive diols have been employed to produce polyesters [3–5], polyethers [6], polyethersulfones [7,8], polycarbonates [9,10] and so on, their use in the polyamide field remains little described. In fact, the tedious transformation of these diols into their corresponding diamines does not make them attractive. Thiem et al. initiated the synthesis of polyamides based on the three diamino dianhydrohexitols, isosorbide (**Is**), isomannide (**Im**), and isoidide (**Id**), with several diacyl chlorides [11]. They exhibited differences in monomer reactivity, and the best results were obtained with **Is** and **Id** analogues. In the same trend, Koning et al. have recently described an elegant synthesis of fully biobased polyamides, starting from the diamino homologue of isoidide and sebacoyl acid [12]. By using solid-state polymerization (SSP), they obtained successfully semi-crystalline materials, as confirmed by CP–MAS NMR studies [13]. In addition to these few works, polyesteramides were also proposed in order to enhance the solubilities and to improve the biocompatibilities of materials for eventual medical purposes [14–16].

Another approach proposed by Loupy et al. consisted in incorporating an aromatic moiety to an **Is-based** diamine monomer to enhance the T_g of the expected polyamides [17,18].

In continuation of anterior works and contributions in this field, we tried to extend the scope of the synthesis to unprecedented diamines based on **Im** and **Id**. These monomers were used to obtain new polyether-amides. We planned to study the effect of the 1,4-3,6-dianhydrohexitols type as well as the nature of the diacylchloride moieties on the inherent viscosities, molecular weights and thermal properties of the resulting polymers. In this context, these polyether-amides were obtained by using a standard method of Nomex synthesis [2]. In order to enhance the biosourced balance composition of these useful materials, sebacoyl chloride was considered in addition to isophtaloyl chloride. The resulting polyether-amides were characterized using different complementary analytical methods (^{1}H and ^{13}C NMR, FTIR, MALDI–ToF mass spectrometry) to determine and confirm all the obtained structure. Viscosimetry and DSC were used in order to study their thermal performances.

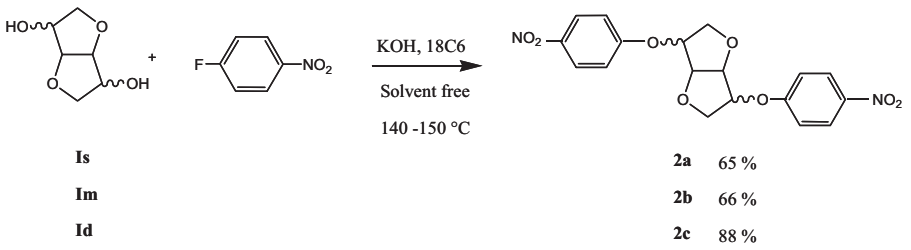
2. Experimental part

The inherent viscosities were measured in a [CH_2Cl_2/TFA = 10/1] mixture with an automated Ubbelohde viscometer thermostated at 20 °C.

The MALDI–ToF mass spectra were recorded with an UltraflexIII, Bruker device, equipped with a smart beam laser®. All the mass spectra were recorded in the reflectron mode with an acceleration voltage of 25 kV. The samples were dissolved in DMSO + TFA solutions, with dithranol as a matrix. ^{1}H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively (Bruker WP 250). The chemical shifts are given in ppm. DSC measurements were conducted from 30 °C to 350 °C at 10 °C/min. Then, the samples were cooled back to 30 °C, after which a second heating scan similar to the first was conducted. The T_g and T_m values were determined from the second DSC heating scan.

2.1. Dinitro compound synthesis

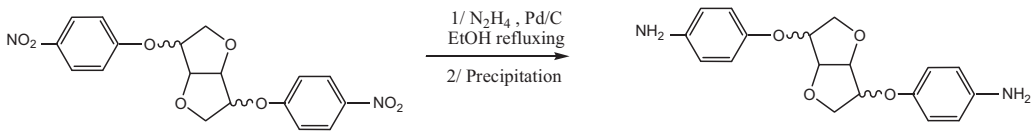
Dianhydrohexitol (10 mmol, 1.46 g), KOH (30 mmol, 1.68 g) 4-fluoronitrobenzene (20 mmol, 2.82 g) and 18 **C 6** (10%, 146 mg) were placed in a cylindrical reactor equipped with a mechanical stirrer. The reaction media was warmed gradually to 140–150 °C (depending on



Is
Im
Id

2a 65 %
2b 66 %
2c 88 %

Scheme 1. Synthesis of dinitro compounds.



2a
2b
2c

DA-Is 75 %
DA-Im 58 %
DA-Id 68 %

Scheme 2. Synthesis of diamine compounds.

dianhydrohexitol) and stirring was maintained during 3 to 4 h. After reaction completion, the crude product was diluted with chloroform and precipitated in cold methanol, affording the dinitrocompound after filtration.

2.2. Diamine synthesis

The process is adapted from the mononitro reduction with a slight modification: the dinitro compound (500 mg) is suspended in EtOH with Pd/C (10%) in two round-bottom necked flasks. The media is warmed to 50 °C then, a hydrazine solution (1 mL in 4 mL of EtOH) is added dropwise during 1 h 30. When addition is completed, the reaction is refluxed for an additional 2 h (TLC control). After completion, the warm crude is filtered on an ice bath and the diamine is recovered as a pure white crystalline solid by precipitation in EtOH.

2.3. Polymer synthesis

Diamine **DA** (1 mmol, 328 mg) and LiCl (2 mmol, 85 mg) were dissolved in NMP (2 mL). The mixture was cooled at −10 °C and a solution of diacyl chloride (1 mmol in 1.5 mL of NMP) was added dropwise. After completion, the media was warmed to room temperature and stirred magnetically. After 18 h, the reaction medium was precipitated in MeOH and the polymer was filtrated and vacuum dried until the weight is kept constant.

3. Results and discussion

3.1. Diamines synthesis

The synthesis of the diamino monomers was optimized compared to the anterior works [17,19]. In fact, the latter could be obtained in gram scale without any chromatographic purification in only two steps. The previous method described for dinitro compound synthesis, which used microwave (MW) irradiation at 170 °C during 30 min. In our context, the first step was carried out in solvent-free conditions and adapted to the classical heating method at 150 °C (Scheme 1). This could be considered as advantageous as a domestic MW was not able to give rise to the desired product, whereas the specially designed monomode MW represent an expensive apparatus, which is not easily accessible.

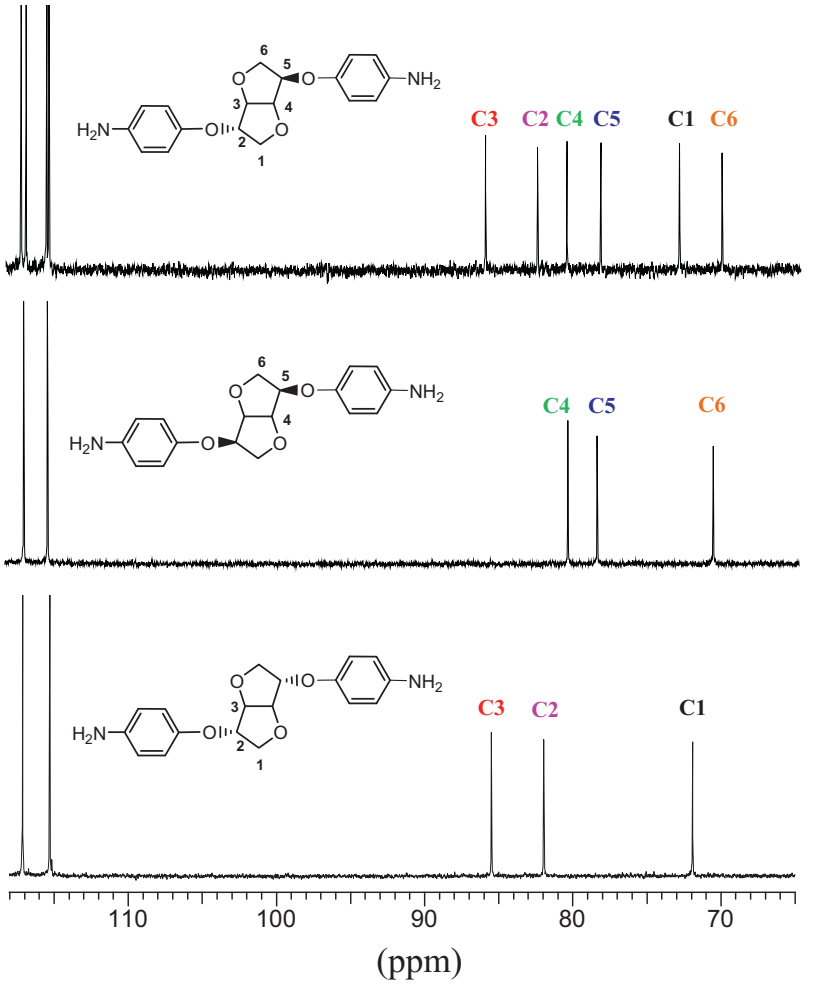


Fig. 1. Comparison of ^{13}C NMR spectra of diamine based on 1,4-3,6-dianhydrohexitols (aliphatic zone).

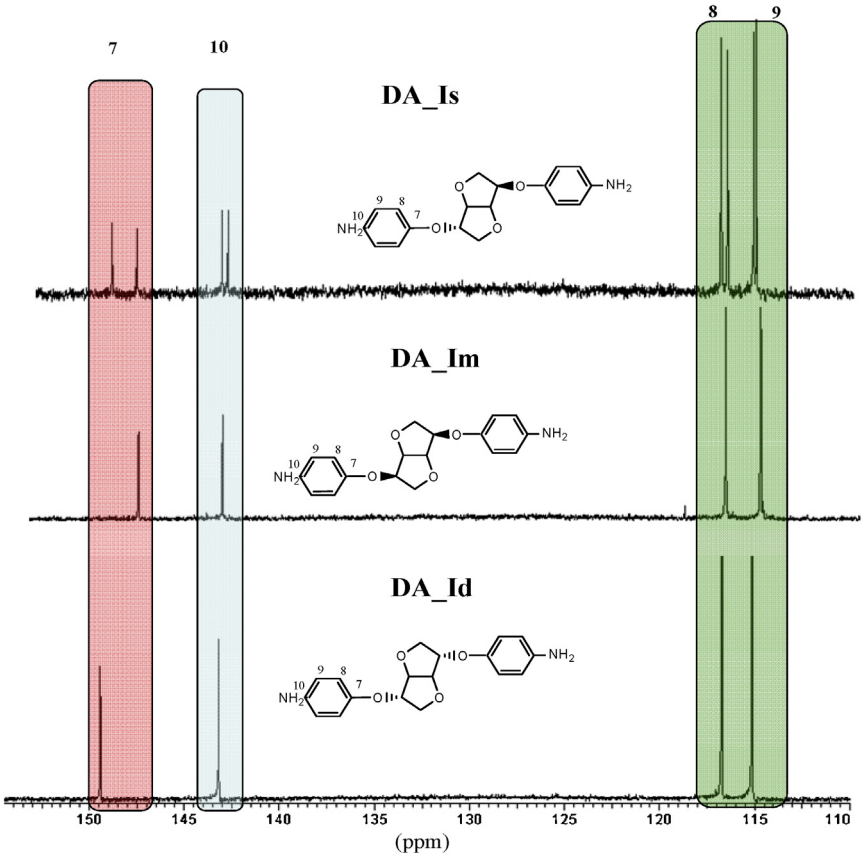


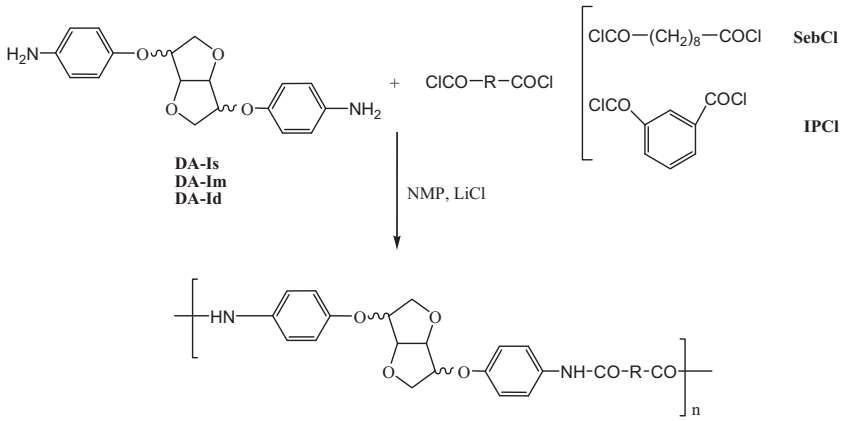
Fig. 2. Comparison of ^{13}C NMR spectra of diamines (aromatic zone).

After 4 h, the dinitro compound was recovered by precipitation in MeOH. The latter was engaged in a Pd/C hydrazine-promoted reduction in EtOH [20]. After reaction completion, pure crystalline diamine could be obtained by precipitation and subsequent recrystallisation in EtOH. The process tolerates small impurities contained in non-purified dinitro starting compounds, as mentioned above. This method was extended to the two additional dianhydrohexitols (**Im** and **Id**) to obtain unprecedented corresponding diamines (Scheme 2).

After mass confirmation by GC–MS analysis, NMR studies were carried out to confirm structures and highlight the characteristic signal of each dinahydrohexitol type.

3.2. NMR studies

Comparing diamines originating from three dianhydrohexitols prompted us to several findings: due to its two hydroxyls stereochemistry, **Is** exhibits six signals.



Scheme 3. Polymer synthesis.

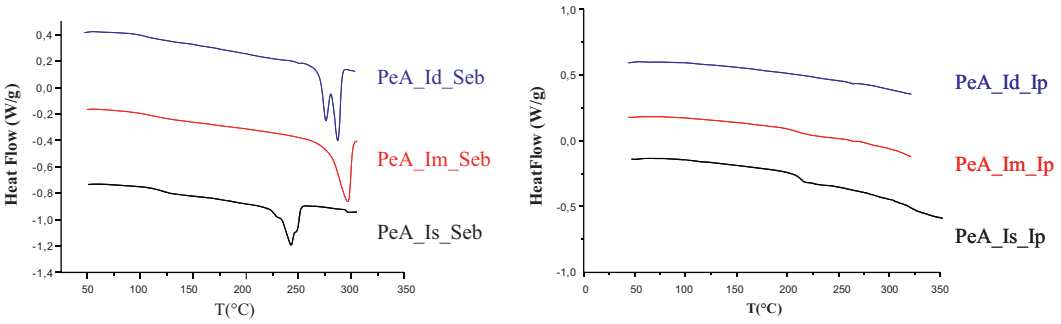


Fig. 3. DSC thermograms of polyether-amides **PeA_Seb** and **PeA_Ip**.

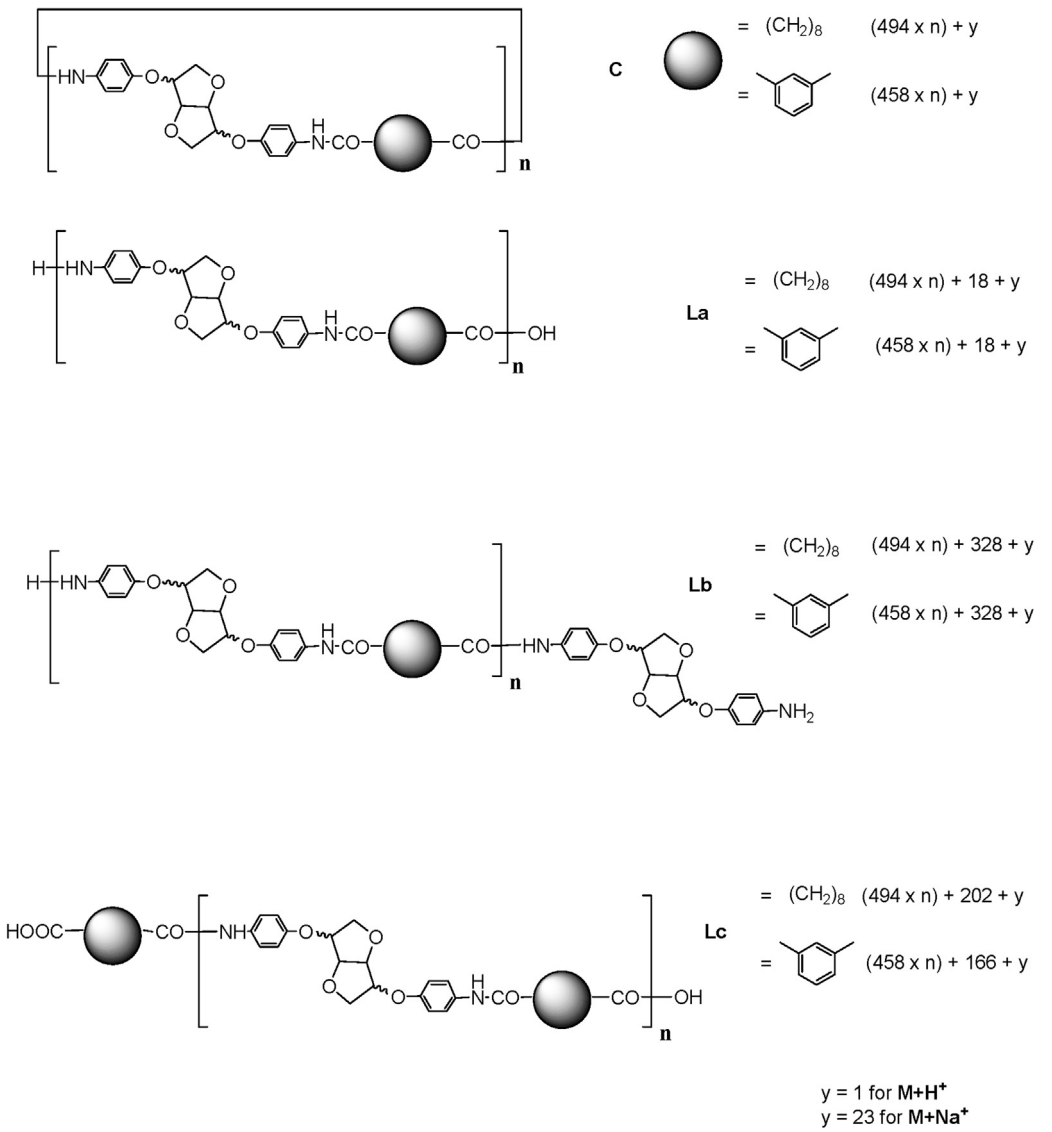


Fig. 4. Different potential structures obtained from the polymerisation reaction.

Table 1
Polymer results and measurements.

Entry	Exp. No	Diamines + diacyl chlorides	Yield (%)[a]	η_{inh} (dL/g)[b]	T_g/T_m
1	**PeA_Is_Ip**	DA-Is + IPCl	93	0.32	217
2	**PeA_Im_Ip**	DA-Im + IPCl	89	0.22	201
3	**PeA_Id_Ip**	DA-Id + IPCl	91	0.19	210
4	**PeA_Is _Seb**	DA-Is + SebCl	98	0.23	129/243
5	**PeA_Im _Seb**	DA-Im + SebCl	88	0.18	108/297
6	**PeA_Id _Seb**[c]	DA-Id + SebCl	93	0.15	112/278–289

[a] Precipitation into methanol.
[b] Measured at 20 °C, with c = 2 g/L in dichloromethane-TFA 95-5
[c] This product showed two T_m values.

In order to identify each signal and proceed to the right attribution, superposition of **Im** and **Id** analogues diamine was undertaken. Each characteristic carbon signal was labelled with a specific colour. We reasoned that when the two hydroxyl groups are in *exo* position (i.e. **Id**), the residue carbons were represented by carbons labelled 1, 2 and 3. Likewise, in **Id** analogue where hydroxyl functions are in *endo* position, the residue carbons are represented by 4, 5 and 6. Superposing them allows us to clearly identify and attribute them in the **Is**-based diamine (Fig. 1). It clearly appears that the stereochemistry of hydroxyls highly influences the carbons' behaviour, the latter shifting to higher values in *exo* configuration. This observation confirms that no epimerisation took place during the synthesis process.

In the aromatic zone, under the influence of the *exo*/*endo* alternation of the signals, the carbons (quaternary) directly attached to the hydroxyl functions split into two signals (**C 7**: 148.1 and 149.3 ppm; Fig. 2). This difference goes by diminishing gradually as the carbon is far from the hydroxyl (**C 10**: 143.5 and 143.2 ppm; **C 8**: 117.1 and 117.2 ppm). The superposition with other diamines shows each peak as originating from the corresponding isomer.

3.3. Polymer synthesis and characterization

The diamine natures as well as the diacyl chloride were varied in order to observe their effect on the properties of the expected polymers.

The method used for the synthesis is derived from Nomex procedures.

First, 1 equiv of LiCl per amine function was used to provide electrophilic assistance and enhance solubility in NMP. After reaction completion at room temperature, the polymers were recovered by precipitation in MeOH in good yields (Scheme 3, Table 1).

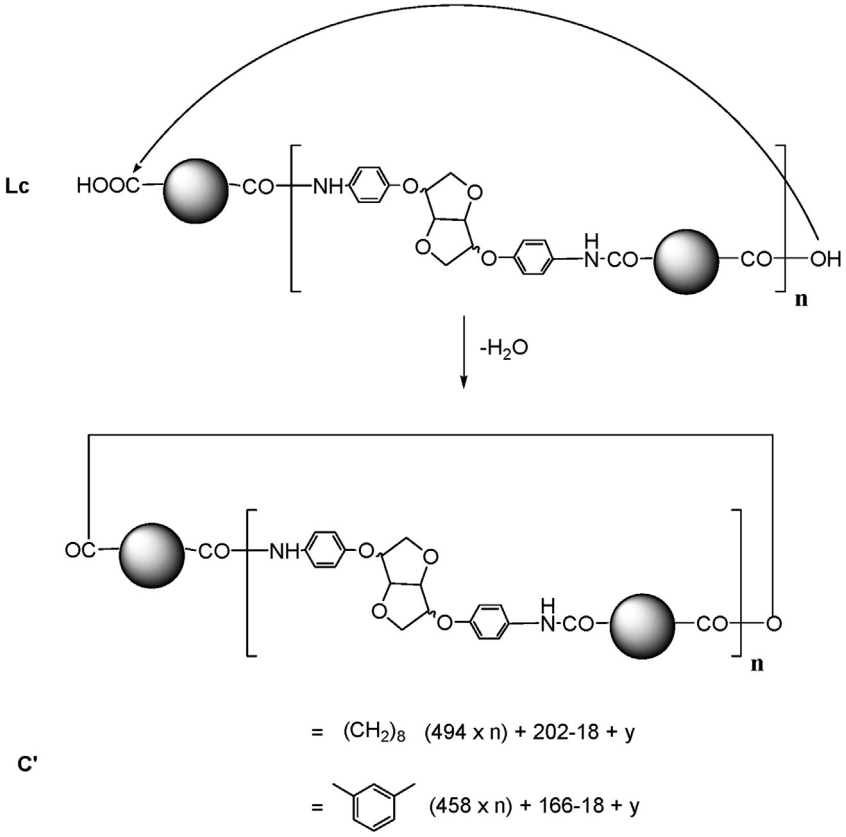
The denomination of monomers and products follows this rule: DA stands for diamines separated by dash and the dianhydrohexitols corresponding isomer, **Is** for isosorbide, **Im** for isomannide and **Id** for isoidide. The corresponding polyether-amides are designed as **PeA** separated by dash, then the dianhydrohexitol nature and the diacylchlorides abbreviation **PeA_Ip** for isophtaloyl and **PeA_Seb** for sebacoyl.

Viscosities and T_g/T_m measurements disclosed in Table 1 and Fig. 3 deserve some comments:

- viscosity values have been improved compared to anterior works upon the RT synthesis method;

Table 2
PEA_Ip family calculated masses.

DP	**C**	**La**	**Lb**	**Lc**	**C′**
H^+ doped					
1	459.1550	477.1656	787.2973	625.1816	607.1711
2	917.3028	935.3134	1245.4451	1083.3294	1065.3189
3	1375.4506	1393.4612	1703.5929	1541.4772	1523.4666
4	1833.5984	1851.6089	2161.7407	1999.6250	1981.6144
5	2291.7462	2309.7567	2619.8885	2457.7728	2439.7622
6	2749.8939	2767.9045	3078.0363	2915.9206	2897.9100
7	3208.0417	3226.0523	3536.1840	3374.0683	3356.0578
8	3666.1895	3684.2001	3994.3318	3832.2162	3814.2056
Na^+ doped					
1	481.1370	499.1475	809.2793	647.1636	629.1530
2	939.2847	957.2953	1267.4271	1105.3114	1087.3008
3	1397.4325	1415.4431	1725.5749	1563.4591	1545.4486
4	1855.5803	1873.5909	2183.7226	2021.6069	2003.5964
5	2313.7281	2331.7387	2641.8704	2479.7547	2461.7441
6	2771.8759	2789.8865	3100.0182	2937.9025	2919.8919
7	3230.0237	3248.0342	3558.1660	3396.0503	3378.0397
8	3688.1715	3706.1821	4016.3138	3854.1981	3836.1875



Scheme 4. Anhydride-type structure formation.

- considering **PeA** derived from the same dianhydrohexitol, the diacyl chloride moiety affects the viscosity values, the highest one being obtained for the isophtaloyl core;
- the highest viscosity was obtained for **Is**-based **PeA** (0.32, for **Ip**; entry 1, and 0.23 for **Seb**);
- as expected, T_g values were lower for the **Seb** moiety than for those with the **Ip** family, regardless of the dianhydrohexitol moiety;
- it is worth noting that **Seb** series revealed semi-crystalline, as shown by DSC experiments;

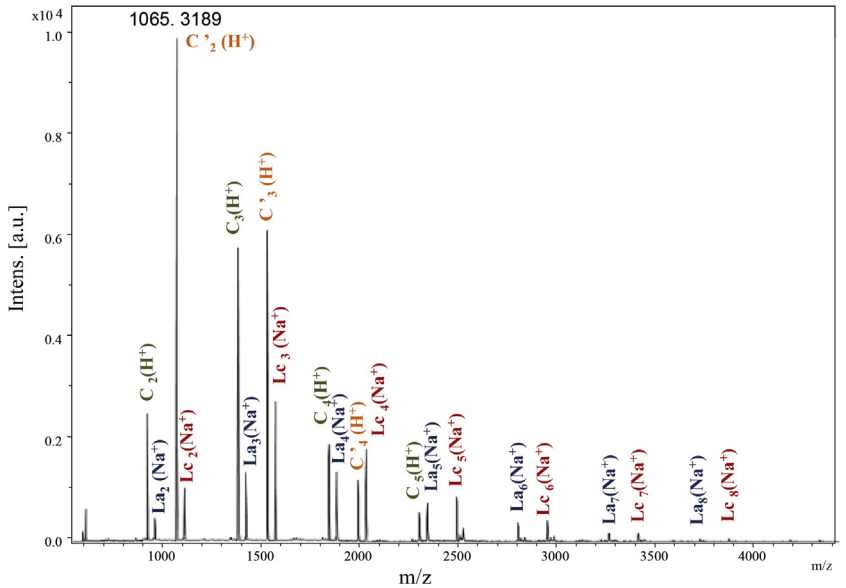


Fig. 5. MALDI–ToF spectrum of **PeA_Is_Ip** (500–4500 Da).

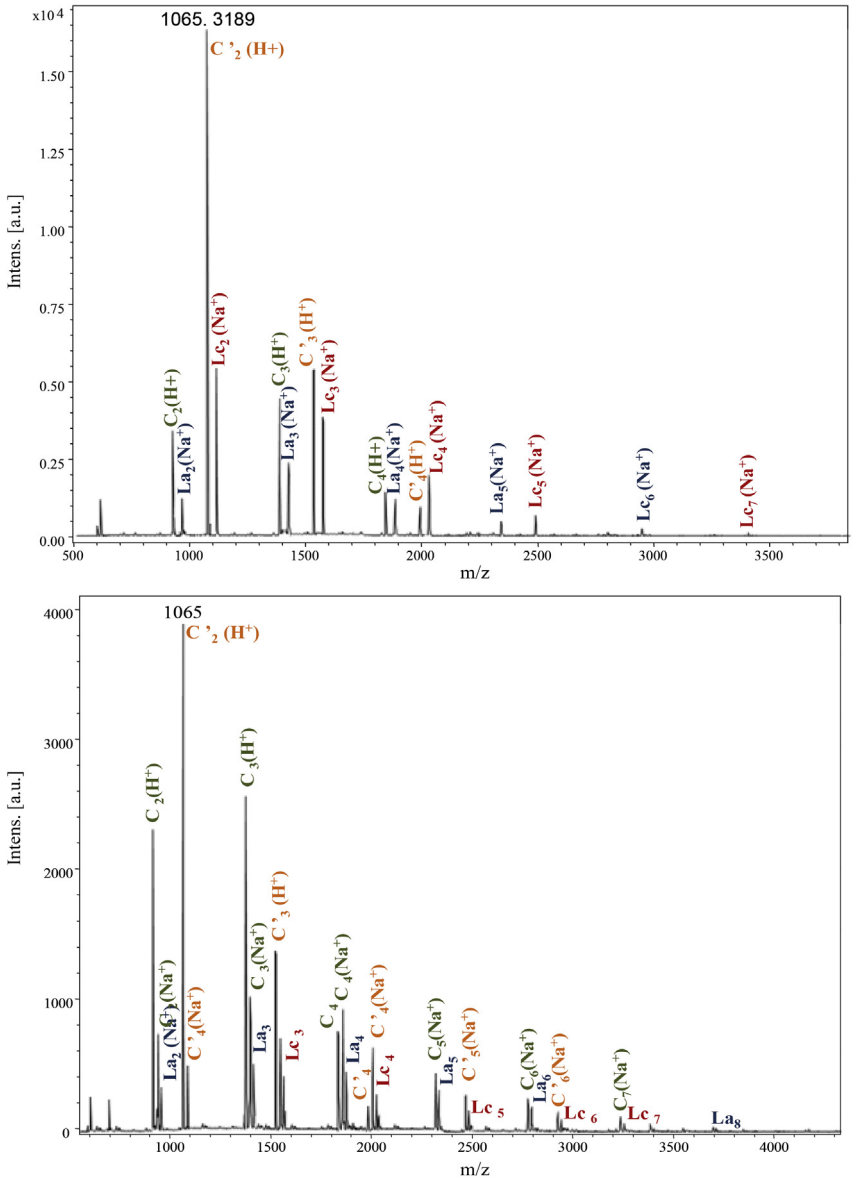


Fig. 6. MALDI–ToF spectra of **PeA_Im_Ip** (500–4000 Da) and PeA_Id_Ip (500–4500 Da).

- thermal properties of **Is**-based polymers were interesting (T_g above 210 °C and T_m above 240 °C);
- the **Id**-based polyether-amide **PeA_Id_Seb** showed two T_m values. This phenomenon, already observed for **Id**-based polyamides, can be explained by the melting of imperfect crystals (first peak), recrystallization upon heating and re-melting of the more perfectly formed crystals (second peak) [21]. The hypothesis of the existence of oligomers, giving rise to heterogeneity, can be considered as well.

3.4. MALDI–TOF-MS studies

Potential structures that could be obtained are depicted in Fig. 4.

3.4.1. Isophtaloyl_family

The investigation of structure type **PeA_Is_Ip** (**Is** moiety) was considered in details. The calculated masses of potential structures are given in Table 2.

In the spectrum enlargement (900–5000) (Fig. 5), the repeating unit 458 Da revealed the predominant presence of the **Lc**-type structure accompanied by **C** and **La** types. The identification and attribution were very tedious, due to the unusual and predominant formation of $[M+H]^+$ adducts accompanied by classical $[M+Na]^+$ and $[M+K]^+$ (in some cases) ionised adducts [22]. Surprisingly, the same value of the repeating unit revealed the presence of an unexpected structure type, represented by the most intense peak of the $[M+H]^+$ type. The latter could be attributed to a cyclic

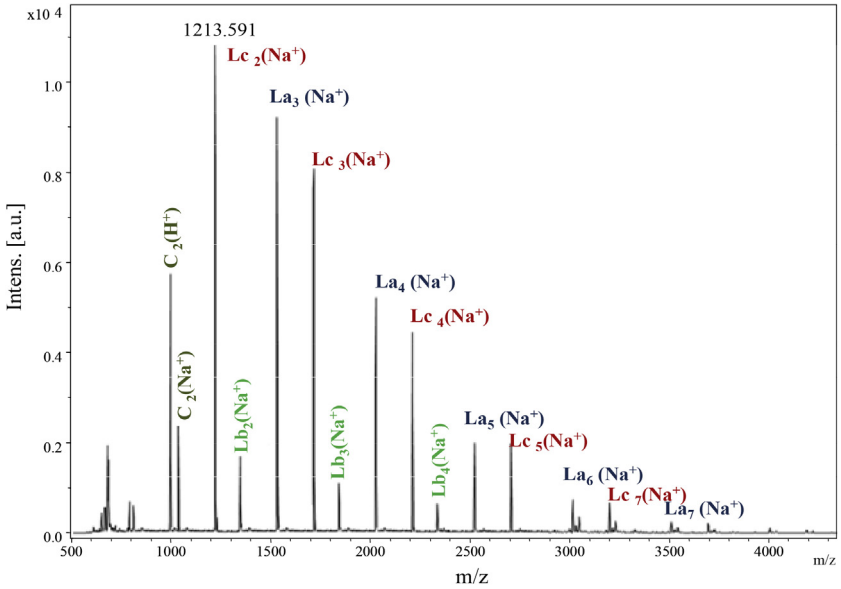


Fig. 7. MALDI–ToF spectrum of **PeA_Is_Seb** (500–4500 Da).

anhydride-type structure originating probably from **Lc** dehydration (noted **C′**, Scheme 4).

The same structure types are observed for the other polyamides **Ip** families originating from **Im** and **Id** moieties (Fig. 6). In the latter case, cyclic structures (C and C′) became predominant.

3.4.2. Sebacoyl family

As for the **Ip** family, we investigated carefully the **PeA_Is_Seb** sample (Fig. 7). The calculated masses of the potential structures are depicted in Table 3.

These samples were partially soluble in DMSO in the preparation step, leading to a pronounced signal/noise ratio. The same type of adducts as with the **Ip** family was observed.

The repeating unit 494 Da revealed the major presence of the **Lc-type** structure, alternating with the **La** type. **C** and **Lb** were in the minority. The cyclic anhydride-type structure **C′**, originating from **Lc** dehydration, is also present, with higher intensities for **Im** and **Id moieties** (Fig. 8). For these samples, adducts ionised with K^+ were also observed.

3.4.3. NMR studies

NMR investigations allowed us to determine and attribute all signals. Comparing ^{1}H NMR spectra of **PeA** originating from three dianhydrohexitols in the **Seb** family prompted us to several findings (Fig. 9):

- the signal at 9.75 ppm confirms the formation of a new amide bond (–NHCO–);

Table 3
PEA_Seb family calculated masses.

DP	C	La	Lb	Lc	C′
H^+ Doped					
1	495.2489	513.2595	823.3912	697.3694	679.3589
2	989.4906	1007.5012	1317.6329	1191.6111	1173.6005
3	1483.7323	1501.7429	1811.8746	1685.8528	1667.8422
4	1977.9740	1995.9845	2306.1163	2180.0945	2162.0839
5	2472.2157	2490.2262	2800.3580	2674.3362	2656.3256
6	2966.4574	2984.4679	3294.5997	3168.5779	3150.5673
7	3460.6990	3478.7096	3788.8413	3662.8195	3644.8090
8	3954.9407	3972.9513	4283.0830	4157.0612	4139.0507
Na^+ Doped					
1	517.2309	535.2414	845.3732	719.3514	701.3408
2	1011.4725	1029.4831	1339.6149	1213.5331	1195.5825
3	1505.7142	1523.7248	1833.8565	1707.8347	1689.8242
4	1999.9559	2017.9665	2328.0982	2202.0764	2184.0659
5	2494.1976	2512.2082	2822.3399	2696.3181	2678.3076
6	2988.4393	3006.4499	3316.5816	3190.5598	3172.5492
7	3482.6810	3500.6915	3810.8233	3684.8015	3666.7909
8	3976.9227	3994.9332	4305.0650	4179.0432	4161.0326

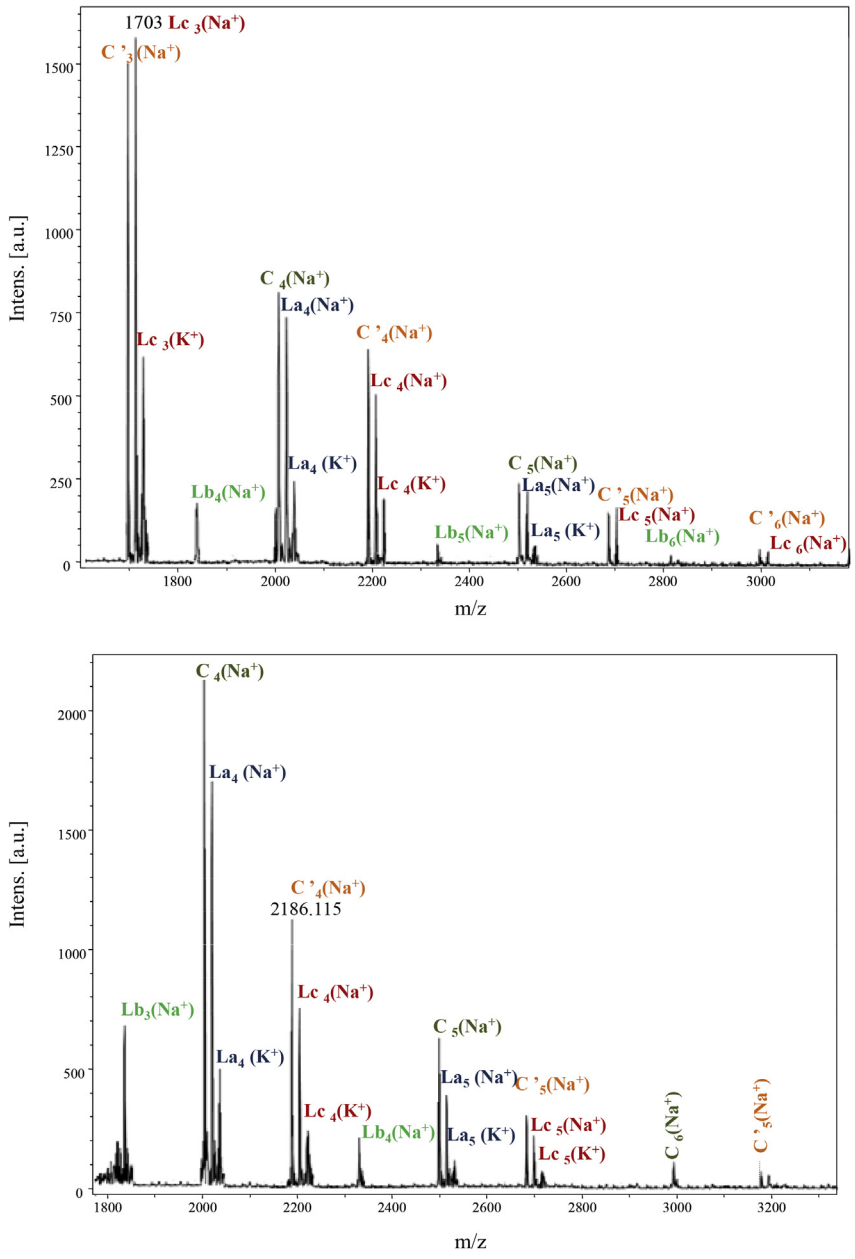


Fig. 8. MALDI–ToF spectra of **PeA_Im_Seb** and **PeA_Id_Seb** (1800–3500 Da).

- nevertheless, the appearance of a doublet clearly indicates that the starting diamine corresponds to the isosorbide moiety. The enlargement of the area from 6 to 10 ppm shows the same bond as a singlet for polymers starting from the two other isomers. This observation confirms that no epimerisation took place during the synthesis process.

In order to investigate and confirm the predominant existing structures, i.e. **Lc**, an NMR study of the **PeA_Is_Seb** sample was considered (Fig. 10).

The absence of an additional small signal related to the **Is** moiety in the aliphatic zone confirms the absence of **Lb**-type structures.

In the aromatic zone, the isophtaloyl typical signals are represented by four carbon types. Additional signals of small intensity related to the isophtalic moiety end-chain confirm the **Lc**-type structure. The NCO bond signal (165 ppm) exhibits a slight split due to **Is stereochemistry**. Careful observations in this region show the existence of an additional small intensity signal (164.7 ppm) proper to NCO functions as the split value remains the same. This observation supposes the existence of an end-chain different from the repeating unit, inducing a different behaviour on the terminal NCO function. An additional singlet (167.3 ppm), potentially of carbonyl type, could be attributed to the carboxylic

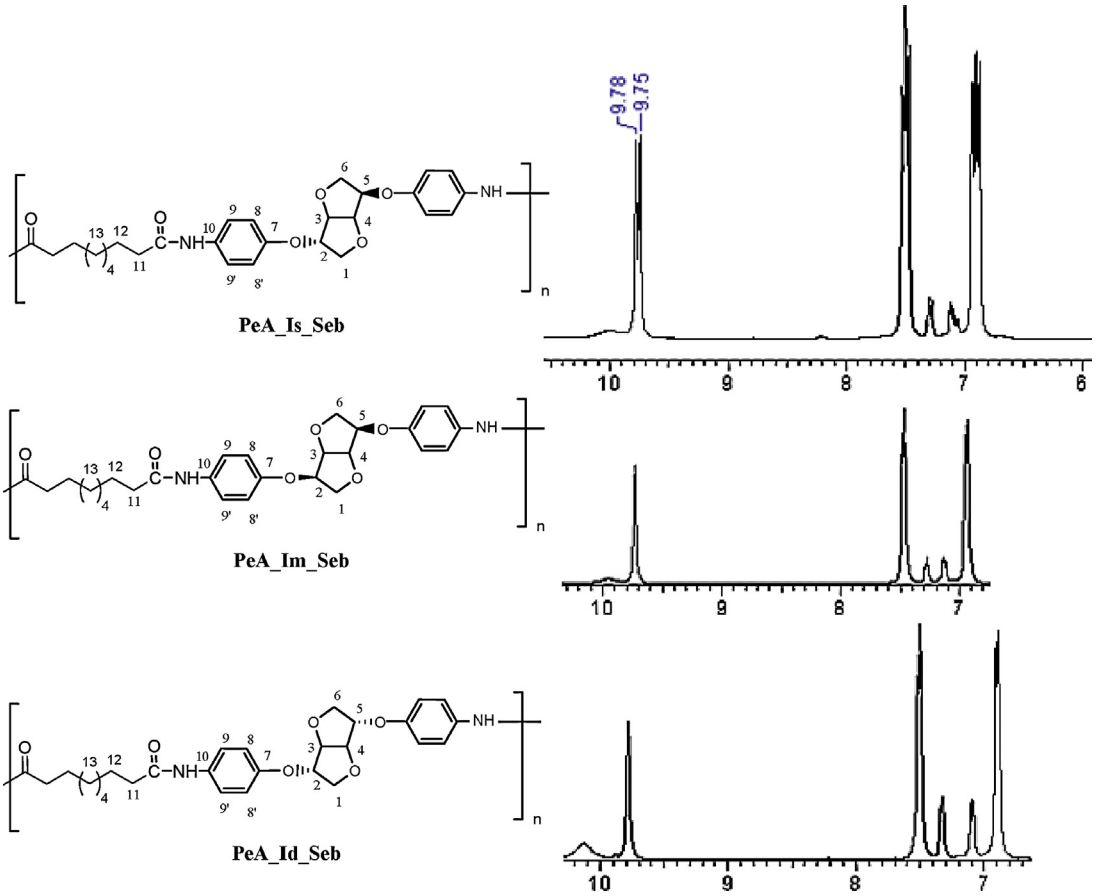


Fig. 9. Comparison of ^{13}C NMR spectra from the **PeA_Seb** family (DMSO D_6).

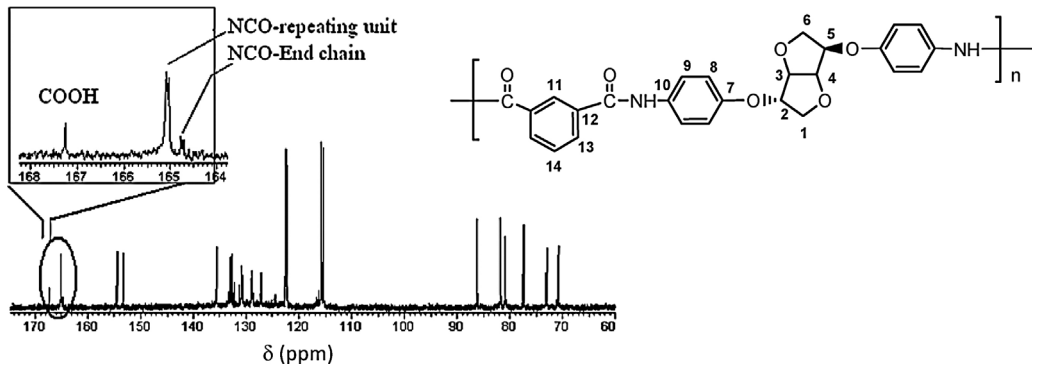


Fig. 10. ^{13}C NMR spectrum of **PeA_Is_Ip** (DMSO D_6).

end-chain type, in concordance with the **Lc**-type structure.

4. Conclusion

In conclusion, we were able to improve the synthesis process of diamines based on 1,4-3,6-dianhydrohexitols and extend the latter to unpublished isomannide and isoidide isomers. The process involved a first solvent-free S_NAr step followed by reduction and isolation of the product by crystallization. These diamines were reacted with diacyl chlorides moieties at room temperature in NMP to obtain biosourced polyether-amides. Isophtaloyl and biosourced sebacoyl chlorides were chosen as diacyl chlorides. We investigated the influence of the dianhydrohexitol moieties as well as of the diacyl moieties on the thermal performances and on the structure type of the polyether-amides as well. The first results showed that the best viscosity values were obtained for the isosorbide moiety for both diacyl chlorides, the highest value being

obtained with isophtaloyl. The same trend is observed for T_g, as the highest value was observed for **PeA_Is_Ip** (isosorbide moiety with isophtaloyl chloride). These results are in agreement with economical expectations, isosorbide being the most commercially available diol. It is worth noting that these thermal performances were similar to those obtained in previous polyamide synthesis in high-temperature conditions.

MALDI–ToF mass spectrometry in association with NMR spectroscopy allowed us to identify the nature of the structures obtained and of the end-chain moieties.

5. Supplementary data

5.1. Dinitro compounds description

5.1.1. 1,4:3,6-Dianhydro-2,5-di-O-(4-nitrophenyl)-D-sorbitol (2a): 65%

^{1}H NMR: (500 MHz, $CDCl_3$): δ (ppm): 4.03–4,18 (m, 4H, $H_1 + H_6$); 4.65–4.66 (d, J = 5 Hz, 1H,H_3,), 4.90–4.94 (m, 2H, $H_2 + H_5$); 5.08–5.10 (m, 1H, H_4.); 7.02 (d, J = 10 Hz,2H, H_8,); 7.04 (d, 15 Hz, 2H, H_8,); 8.21(d, J = 5 Hz, 2H, H_9); 8.23 (d, J = 5 Hz, 2H, H_9). ^{13}C NMR: (125 MHz, $CDCl_3$): δ (ppm): 71.8 (C_6); 73.3 (C_1); 77.9 (C_5); 81.6 (C_4); 81.9 (C_2); 86.2 (C_3); 115.1 (C_8); 115.2 (C_8); 125.9 (C_9); 126.1 (C_9); 142.2 (C_{10}); 161.8 (C_7); 162.8 (C_7). ATR–FTIR: δ (cm^{-1}): 744, 849, 1103, 1244, 1331, 1496, 1587; 2874, 3075.

5.1.2. 1,4:3,6-Dianhydro-2,5-di-O-(4-nitrophenyl)-D-mannitol (2b): 65%

^{1}H NMR: (500 MHz, $CDCl_3$): δ (ppm): 4.09–4.13 (m, 4H, $H_1 + H_6$), 4.88–4.90 (m, 2H, $H_2 + H_5$); 4.94–4.95 (m, 2H, H_3+ H_4). 7.05 (d, J = 5 Hz, 4H, H_8,), 8.22 (d, J = 5 Hz, 4H, H_9,). ^{13}C NMR: (125 MHz, $CDCl_3$): δ (ppm): 71.6 (C_1=C_6); 77.6 (C_2=C_5); 80.9 (C_3=C_4); 115.1 (C_8); 125.9 (C_9); 142.1(C_{10}); 162.7 (C_7). ATR–FTIR: δ (cm^{-1}): 744, 849, 1103, 1244, 1331, 1496, 1587; 2874, 3075.

5.1.3. 1,4:3,6-Dianhydro-2,5-di-O-(4-nitrophenyl)-D-iditol (2c): 88 %

^{1}H NMR: (500 MHz, $CDCl_3$): δ (ppm): 4.13–4.25 (m, 4H, $H_1 + H_6$); 4.80 (m, 2H, $H_3 + H_4$); 4.94 (m, 2H, $H_2 + H_5$); 7.02 (d, J = 10 Hz, 4H, H_8); 8.22(d, J = 10 Hz, 4H, H_9). ^{13}C NMR:(125 MHz, $CDCl_3$): δ (ppm): 72.2 (C_1=C_6); 81.6 (C_2=C_5), 85.7 (C_3=C_4); 115.2 (C_8); 126.0 (C_9); 142.2 (C_{10}); 161.7 (C_7). ATR–FTIR: δ (cm^{-1}): 744, 849, 1103, 1244, 1331, 1496, 1587; 2874, 3075.

5.2. Diamino compounds description

5.2.1. 4,4′-(Diamino)-1,4:3,6-dianhydro-2,5-di-O-phenyl-D-sorbitol (DA-Is): 75%

^{1}H NMR (400 MHz, $CDCl_3$ D_6): δ (ppm): 3.42 (brs,4H,NH_2); 4.11–4.17 (m, 4H,$H_1 + H_6$); 4.60–4.69 (m,2H,$H_3 + H_5$), 4.71–4.71 (m,1H, H_2); 4.86–4.88 (m, 1H, H_4); 6.62–6.65 (m,4H, H_9); 6.75–6.85 (m,4H, H_8). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm): 69.8 (C_6); 72.7 (C1); 77.9 (C_5); 80.0 (C4); 82.1 (C_2); 85.6 (C_3); 114.8 (C_9); 114.9 (C_9); 116.3 (C_8); 116.6 (C_8); 142.8 (C_{10}); 143.1 (C_{10}); 147.6 (C_7); 149.0 (C_7). ATR–FTIR: δ (cm^{-1}): 719, 824, 1094, 1224, 1502, 2896, 3373.

5.2.2. 4,4′-(Diamino)-1,4:3,6-dianhydro-2,5-di-O-phenyl-D-mannitol (DA-Im): 58%

^{1}H NMR (400 MHz, $CDCl_3$ D_6): δ (ppm): 3.46 (brs,4H,NH_2); 3.94–4.12 (m, 2H, H_1); 4.15–4.20 (m, 2H, H_6); 4.62–4.66 (m, 2H, $H_2 + H_5$); 4.74–4.75 (m, 2H, $H_3 + H_4$); 6.60–6.65 (m,4H, H_9), 6.81–6.86 (m,4H, H_8). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm): 70.3 ($C_=C_6$); 78.1 (C_2=C_5); 80.0 (C_4=C_3); 114.7 (C_9); 116.3 (C_8); 142.8 (C_{10}); 149.0 (C_7). ATR–FTIR: δ (cm^{-1}): 719, 824, 1094, 1224, 1502, 2896, 3373.

5.2.3. 4,4′-(Diamino)-1,4:3,6-dianhydro-2,5-di-O-phenyl-D-iditol (DA-Id): 68%

^{1}H NMR (400 MHz, $CDCl_3$ D_6): δ (ppm): 3.43 (brs, 4H,NH_2); 4.04–4.05 (d, J = 20 Hz, 4H, $H_1 + H_6$,); 4.69–4.72 (t, J = 20 Hz, 2H, $H_2 + H_5$,); 4.78(s, 2H, $H_3 + H_4$); 6.61–6.65 (m, 4H, H_9); 6.74–6.79 (m, 4H, H_8). ^{13}C NMR (50 MHz, $CDCl_3$): δ (ppm): 71.5 (C_1=$_6$); 81.6 (C_2=$_5$); 85.1 (C_4=$_3$); 114.9 (C_9); 116.7 (C_8); 143.2 (C_{10}); 147.6 (C_7). ATR–FTIR: δ (cm^{-1}): 719, 824, 1094, 1224, 1502, 2896, 3373.

5.3. Polyether-amides description

5.3.1. PeA_Is_Ip: 93%

^{1}H NMR (400 MHz, DMSO D_6): δ (ppm): 3.83–3.87 (m, 1H, H_1); 3.93–3.96 (m, 1H, H_6); 4.03–4.07 (m, 2H, $H_1 + H_6$); 4.60 (d, J = 4 Hz, 1H, H_3); 4.91(m, 2H, $H_2 + H_5$); 5.01 (m,1H, H_4); 6.99–7.06 (m, 4H, H_9); 7.66–7.76 (m, 5H, $H_8 + H_{14}$); 8.13 (d, J = 7.07 Hz, 2H, H_{13}); 8.55 (s, 1H, H_{11}); 10.4 (s, 2H, NHCO). ^{13}C NMR (100 MHz, DMSO D_6): δ (ppm) 70.5 (C_6); 72.7 (C_1); 77.1 (C_5); 80.6 (C_4); 81.5 (C_2); 85.8 (C_3); 115.1 (C_8); 115.4 (C_8); 121.9 (C_9); 122.1 (C_9); 126.9 (C_{14}); 128.6 (C_{13}); 130.5 (C_{12}); 132.5 (C_{10}); 132.9 (C_{10}); 135.2 (C_{11}); 153.0(C_7); 154.2 (C_7); 164.7 (NCO); 164.8 (NCO); 166.9 (COOH). ATR–FTIR: δ (cm^{-1}): 826, 1090, 1229, 1509, 1652, 3295.

5.3.2. PeA_Im_Ip: 89%

^{1}H NMR (400 MHz, DMSO D_6): δ (ppm): 3.81 (m, 2H, $H_1 + H_6$); 4.07 (m, 2H, $H_1 + H_6$); 4.88 (brs, 4H, $H_3 + H_4$, $H_2 + H_5$); 7.05 (m, 1H, H_9); 7.66–7.76 (m, 5H, $H_8 + H_{14}$); 8.14–8.16 (m, 2H, H_{13}); 8.61 (m, 1H, H_{11}); 10.42 (s, 2H, NHCO). ^{13}C NMR (100 MHz, DMSO D_6): δ (ppm) 70.6 (C_1=C_6); 77.0 (C_2=C_5); 80.2 (C_3=C_4); 115.1 (C_8); 121.9 (C_9); 126.1 (C_{14}); 128.6 (C_{13}); 131.1 (C_{12}); 132.5 (C_{10}); 135.2 (C_{11}); 154.2 (C_7); 164.7 (NCO); 166.9 (COOH).

5.3.3. PeA_Id_Ip: 91%

^{1}H NMR (400 MHz, DMSO D_6): δ (ppm): 3.95–3.98 (m, 2H, H_1 + H6); 4.08–4.11 (m, 2H, $H_1 + H_6$); 4.72 (brs, 2H, $H_3 + H_4$); 4.93 (brs, 2H, $H_2 + H_5$); 7.02 (d, J = 8.59 Hz, 4H, H_9); 7.65–7.70 (m, 1H, H_{14}); 7.78 (d, J = 8.59 Hz, 4H, H_8); 8.14 (d, J = 8.59 Hz,2H, H_{13}); 8.60 (s, 1H, H_{11}); 10.45 (s, 2H, NHCO). ^{13}C NMR (100 MHz, DMSO D_6): δ (ppm) 71.6 (C_1=C_6); 81.0 (C_2=C_5); 85.3 (C_3=C_4); 115.5 (C_8); 122.0 (C_9); 126.8 (C_{14}); 128.6 (C_{13}); 130.6 (C_{12}); 133.0 (C_{10}); 135.1 (C_{11}); 152.9 (C_7); 164.7 (NCO); 166.9 (COOH).

5.3.4. PeA_Is_Seb: 98%

^{1}H NMR (400 MHz, DMSO D_6): δ (ppm): 1.28 (bsr, 8H, H_{13}); 1.56 (brs, 4H, H_{12}); 2.14–2.27 (m, 4H, H_{11}); 3.76–3.79

(m, 1H, H_1); 3.86–3.89 (m, 1H, H_6); 3.97–4.00 (m, 2H, $H_1 + H_6$); 4.53 (m, 1H, H_3); 4.81 (brs, 2H, $H_2 + H_5$); 4.92 (brs, 1H, H_4); 6.89 (d, J = 8.59 Hz, 2H, H_9); 6.90 d, J = 8.34 Hz, 2H, H_9); 7.47(d, J = 8.84 Hz, 2H, H_8); 7.48 (d, J = 8.84 Hz, 2H, H_8); 9.75 (d, J = 13.39 Hz, 2H, NHCO). ^{13}C NMR (100 MHz, DMSO D_6): δ (ppm) 25.2 (C_{13}); 33.7 (C_{12}); 36.8 (C_{11}); 70.3 (C_6); 72.6 (C_1); 77.1 (C_2); 80.4 (C_4); 81.4 (C_5); 85.7 (C_3); 115.0 (C_8); 115.4 (C_8); 120.4 C_9); 120.7 (C_9); 132.9 (C_{10}); 133.3 (C_{10}); 152.2 (C_7); 153.4 (C_7); 170.8 (NCO); 174.6 (COOH). ATR–FTIR: δ (cm^{-1}): 825, 969,1090, 1224, 1504, 1653, 2360, 2855, 2924, 3281.

5.3.5. ***PeA_Im_Seb****: 88%*

^{1}H NMR (400 MHz, DMSO D_6): δ (ppm): 1.28 (brs, 8H, H_{13}); 1.56 (brs, 4H, H_{12}); 2.24 (m, 4H, H_{11}); 3.70–3.72 (m, 2H, $H_1 + H_6$); 4.00 (brs, 2H, $H_1 + H_6$); 4.79 (brs, 4H, $H_2 + H_3 + H_4 + H_5$); 6.93 (d, J = 8.08 Hz, 4H, H_9); 7.47 (d, J = 8.08 Hz, 4H, H_8); 9.72 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO D_6): δ (ppm) 25.1 (C_{13}); 33.6 (C_{12}); 36.2 (C_{11}); 70.5 (C_1=C_6); 77.1 (C_2=C_5); 80.1 (C_3=C_4); 115.1 (C_8); 120.5 (C_9); 132.8 (C_{10}); 153.5 (C_7); 170.8 (NCO); 174.1 (COOH).

5.3.6. ***PeA_Id_Seb****: 93%*

^{1}H NMR (400 MHz, DMSO D_6): δ (ppm): 1.28 (brs, 8H, H_{13}); 1.56 (brs, 4H, H_{12}); 2.15–2.24 (m, 4H, H_{11}); 3.88–3.92 (m, 2H, $H_1 + H_6$); 4.02–4.04 (m, 2H, $H_1 + H_6$); 4.65 (m, 2H, $H_3 + H_4$); 4.84 (brs, 2H, $H_2 + H_5$); 6.89 (d, J = 8 Hz, 4H, H_9); 6.9 (d, J = 8 Hz, 4H, H_9); 7.5 (d, J = 8 Hz, 4H, H_8); 9.77 (s, 1H, NHCO). ^{13}C NMR (100 MHz, DMSO D_6): δ (ppm) 25.2(C_{13}); 33.7 (C_{12}); 36.3 (C_{11}); 71.0 (C_6=C_1); 80.9 (C_2=C_5); 85.2 (C_3=C_4); 115.5 (C_8); 120.6 (C_9); 133.3 (C_{10}); 152.1 (C_7); 170.8 (NCO); 173.8 (COOH).

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