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Synthesis and characterisation of poly(ester-amide)s from aromatic bisoxazoline precursors

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ABSTRACT

A series of novel aliphatic aromatic poly(ester-amide)s (PEA) have been synthesized by condensation reaction of aromatic bisoxazolines with aliphatic dicarboxylic compounds. These polymers have a number average molecular weight of 20,000–25,000. Depending of the aromatic structure of the bisoxazoline precursor, they are either amorphous or semi-crystalline. A good solubility in aprotic solvents was observed for all PEAs.

1. Introduction

Fully aromatic polyamides are well known as high-performance polymer materials with outstanding mechanical properties, good thermal and chemical stabilities [1–3]. However, their applications were restricted in some areas because of their very high melting temperatures, and limited solubility in common organic solvents. On the other hand, aromatic polyesters are recognized as the high performance engineering plastics. However, their thermal–mechanical properties are, in general, not optimal in many end use applications. Another interesting class of polyesters is the aliphatic ones because of their biodegradable character. So combining the key properties of both polyamides, and polyesters appeared as a promising way to access to new polymer materials. In this connection, number research works were focused on the synthesis of various aliphatic poly(ester-amide)s [4–10]. Research works on aromatic poly(ester-amide)s were achieved leading to the development of thermoplastic polymers with high thermal and mechanical properties, and a good solubility in common organic solvents [11–14]. Aromatic aliphatic poly(ester-amide)s were also investigated. For example, Böhme et al. [15] have prepared alternating poly(ester-amide)s by polyaddition reaction of aromatic bisoxazolines with aliphatic dicarboxylic acids.

In addition of thermal and mechanical properties, polymers in many applications must show capacities to fire resistance. Considerable attention has been directed towards this aspect [16,17]. Among the flame-retardant polymers that were developed those containing phosphine oxide moieties were widely investigated [18–21].

Herein, the synthesis and characterisation of a series of new aromatic aliphatic polyesteramides (PEAs) obtained from polymerization of bisoxazoline aromatic compounds with aliphatic linear or cyclic dicarboxylic acid are reported.

2. Experimental

2.1. Materials

Bis(4-carboxyphenyl)phenylphosphine oxide was prepared as describe previously [22].

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Bis(4-carboxyphenyl)ether was washed several times by THF before use. All other reagents were purchased from Aldrich Chemical Co.

The solvents used for polymerization and measurement were used as received.

2.2. Measurements

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at ambient temperature on a 200 and 400 MHz Bruker AM spectrometers, using deuterated dimethylsulfoxide (DMSO-d_6) as a solvent, with tetramethylsilane (TMS) as internal standard.

A TA instruments apparatus (model 2950) was used for thermogravimetric analysis (TGA) of the polymers. Scans were run from 20 to 700 °C at a heating rate of 10 °C/min in an air atmosphere. The glass transition temperatures (T_g) were obtained by differential scanning calorimetry (DSC) on a Mettler Toledo DSC 822e. Scans were run at 5 °C/min in inert atmosphere. The values were reported from a second scan after heating and rapid cooling.

Molecular weights of the polymers were determined by size exclusion chromatography (SEC) on a system equipped with a Waters 515HPLC pump, a differential refractive index detector (Wyatt optilab-rEX). DMF containing 0.05 M LiBr was used as mobile phase. SEC analyses were performed on two PL gel Mixed D columns at 70 °C. The molecular weights were calculated relative to standard polystyrene samples.

2.3. Precursor synthesis

2.3.1. Bis(4-(2-oxazolylphenyl))phenylphosphine oxide(BOOT2P)

2.3.1.1. Bis(4-chlorocarbonylphenyl)phenylphosphine oxide. 5 g (0.0136 mol) of bis(4-carboxyphenyl)phenylphosphine oxide, 19.45 ml (0.272 mol) of thionyl chloride and 1 ml of *N*,*N*-dimethylformamide were placed in a 100-ml two-necked round bottom flask, equipped with a condenser, a nitrogen inlet, and a magnetic stirrer. The reaction mixture was reached to reflux temperature for 2 h. Then, the excess of thionyl chloride was removed by distillation under vacuum.

The same method was used to obtain the bis(4-chlorocarbonylphenyl)ether from the bis(4-carboxyphenyl)ether.

2.3.1.2. Bis(4-(chloroethylamide)phenyl)phenylphosphine oxide. A solution of 5.5 g (0.0136 mol) of bis(4-chlorocarbonylphenyl)phenylphosphine oxide in 25 ml of chloroform placed in additional funnel was added dropwise to a 100-ml three-necked round bottom flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer, and containing a mixture of 3.95 g (0.0341 mol) of 2-chloroethylamine hydrochloride, 3.98 g (0.0709 mol) of KOH and 25 ml of water maintained at 0 °C. After complete addition, the reaction mixture was kept at room temperature overnight. By evaporation of the CH_2Cl_2 the product precipitated in presence of water and then was isolated by filtration.

The same operating conditions were used to obtain the bis((4-chloroethylamide)phenyl)ether.

2.3.1.3. Bis(4-oxazolylphenyl)phenylphosphine oxide. 6.65 g (0.0136 mol) of bis(4-(chloroethylamide)phenyl)phenylphosphine oxide, 3.05 g (0.0544 mol) of KOH and 30 ml of methanol placed in a 100-ml two-necked round bottom flask equipped with a condenser, a nitrogen inlet, and a magnetic stirrer were refluxed for 4 h. The methanol was then evaporated and the solid obtained was washed with 300 ml water to eliminate the formed salt. After filtration, the expected product was dried at 80 °C under vacuum for 6 h. The mp of the compound is 253–254 °C.

RMN ^{31}P (ppm, DMSO-d_6): δ 24.64 ppm (P=O). RMN ^{1}H (ppm, DMSO-d_6): δ 7.5–8.2 (m, 13H, H_{ar}), 3.98 (t, 4H, –CO–HN–**CH**$_2$– oxazoline ring), 4.41 (t, 4H, –**CH**$_2$–O– oxazoline ring).

RMN ^{13}C (ppm, DMSO-d_6) : δ 55 (–CO–HN–**CH**$_2$– oxazoline ring); 68.1 (–**CH**$_2$–O– oxazoline ring); 128.3; 129.3; 131.2; 132.1; 132.4; 132.8; 134.83; 136.8 (C_{ar}); 162.7 (–**CO**–HN– oxazoline ring) .

The bis(4-(2-oxazolylphenyl)ether (BODPE) was synthesized in quite similar conditions. Only the drying step of the isolated product was different: At 50 °C under vacuum overnight. The mp of the compound is 64–65 °C.

RMN ^{1}H (ppm, DMSO-d_6): δ7.11–7.88 (dd, 8H, H_{ar}), 3.91 (t, 4H, –CO–HN–CH_2– oxazoline ring), 4.39 (t, 4H, –CH_2–O– oxazoline ring).

RMN ^{13}C (ppm, DMSO-d_6): δ 55 (–CO–HN–CH_2– oxazoline ring); 67.9 (–CH_2–O– oxazoline ring); 119.1; 123.9; 131.2; 130.4; 159; 163 (–CO–HN– oxazoline ring).

2.3.2. Synthesis of the polymers 1a–1d

In a 50-ml two-necked cylinder flask equipped with a mechanical stirrer, and a nitrogen inlet were placed 1.6 mmol of bisoxazoline, and 1.6 mmol of dicarboxylic acid. The reaction mixture was heated to 150 °C for 1 h, at 180 °C for 1 h and then at 200 °C for 20 h. After cooling the resulting polymer was dissolved in 1 ml of *N*-methylpyrrolidone (NMP) and poured into methanol. The precipitated polymer was collected by filtration washed several times with methanol and dried at 80 °C under vacuum for 48 h.

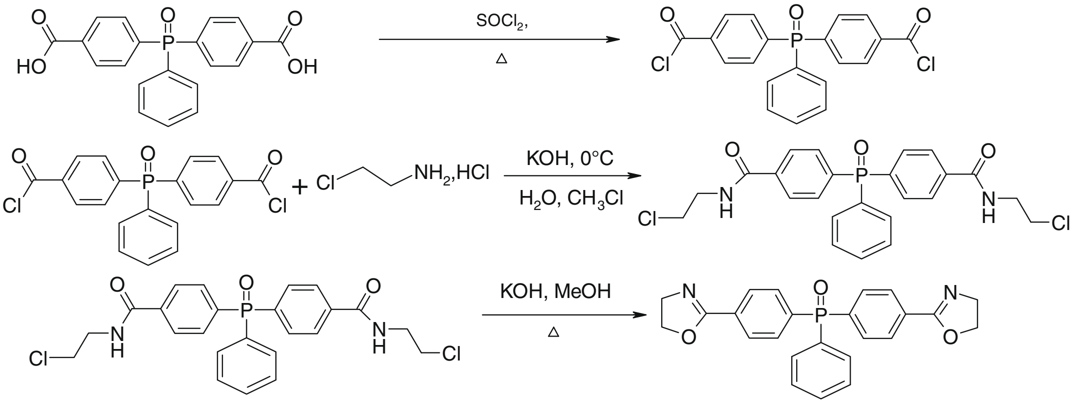
2.3.3. Synthesis of the polymers 2a–2d

In a 50-ml two-necked cylinder flask equipped with a mechanical stirrer, and a nitrogen inlet were introduced 0.016 mol of bisoxazoline, and 0.016 mol of dicarboxylic acid along with 18 ml of NMP. The solution was then heated at 150 °C for 1 h, at 180 °C for 1 h and at 200 °C for 5 h. After cooling the reaction mixture was poured into methanol. The precipitated polymer was collected by filtration washed several times with methanol and dried at 80 °C for 48 h.

3. Results and discussion

3.1. Bisoxazoline precursor synthesis

As illustrated in Scheme 1, the synthesis of both BOOT2P and BODPE bisoxazoline compounds involved three distinguished steps: First, the dicarboxylic acid compound was transformed into acid chloride counterpart by



Scheme 1. Synthetic route for bisoxazoline BOOT2P.

reaction with thionyl chloride. The second step was concerned with the reaction of the acid chloride compound with the 2-chloroethylamine hydrochloride to give the chloro amide derivative. The last one corresponds to the cyclization of the chloroethylamide group into oxazoline ring using basic medium.

This synthetic route allowed obtaining both BOOT2P and BODPE bisoxazoline compounds with an overall yield of 50% and 79%, respectively.

3.2. Poly(ester-amide) synthesis

The synthesis of PEAs from bis(2-oxazoline)s and dicarboxylic acids is known for about 50 years [23–26], but surprisingly only little is known about their preparation and properties.

Initially, the purpose was to prepare all the PEAs by melt polymerization. Hence, the reactions between the bisoxazolines and the different dicarboxylic acid monomers retained in this study were investigated by DSC in order to determine the temperature range in which the reactions happen. For example, the thermogram shown in Fig. 1 lets appear an exothermic peak from 125 to 200 °C corresponding to the reaction between the two reagents. For all the couples (oxazoline/dicarboxylic acid) studied a quite similar peak was observed in the same range of temperatures. As a consequence, the same temperature schedule was used for melt polymerization. It worth also to mention, that for all the reactions only one wide endotherm peak corresponding to the melting of the two reagents was observed and not two peaks as it was expected. For the reaction between BOOT2P (mp at 253–254 °C) and the suberic acid (mp at 141 °C) one endothermic peak was observed from 99 to 114 °C (see Fig. 1).

The triarylphosphine oxide containing PEAs were synthesized by melted polymerization. The polymerization temperature was increased progressively until to reach 200 °C in order to maintain the reaction mixture in liquid state. After 20 h at 200 °C highly viscous reaction mixture was observed. Similar operating conditions were tried for the polymerization of BODPE and the dicarboxylic acid monomers. Much to our surprise, the reaction mixture

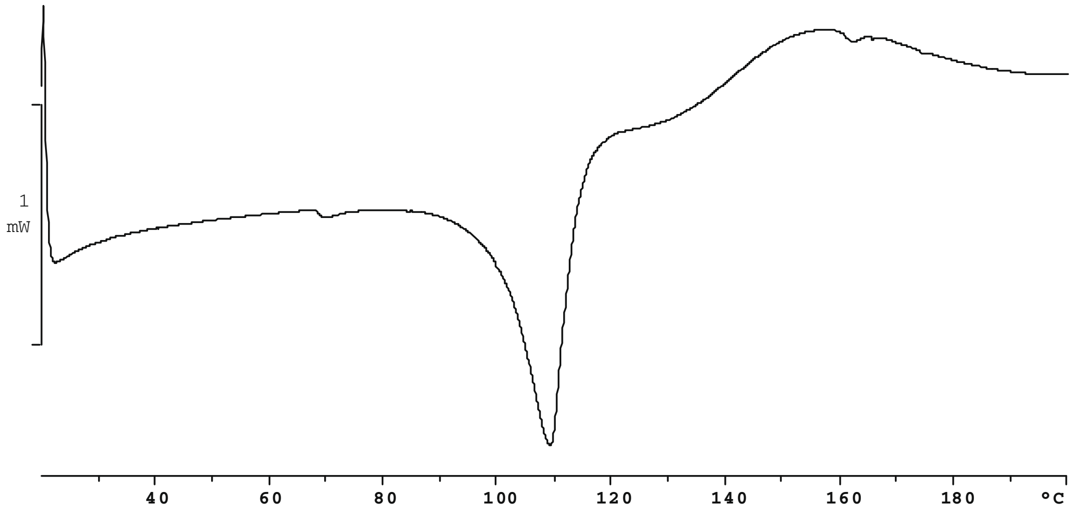
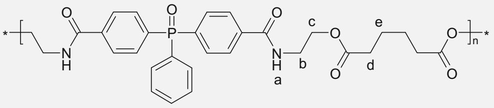
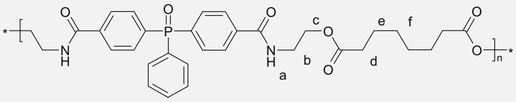
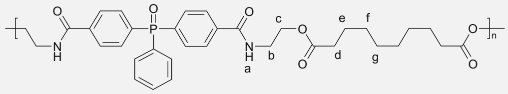
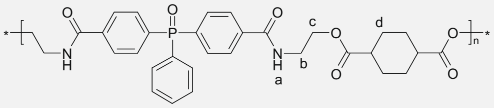
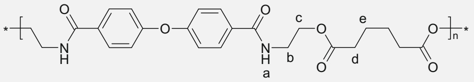
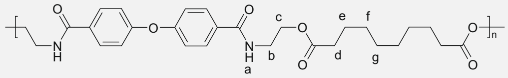
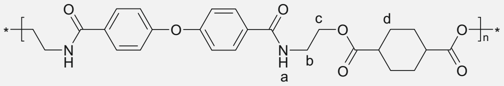
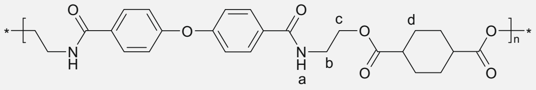


Fig. 1. DSC trace for the BOOT2P monomer/suberic acid system.

Table 1
^1H and ^{31}P NMR data for the PEAs.

PEA	^1H δ (ppm)	^{31}P δ (ppm)
BOOT2P/ ADA 	8.74 (t, 2H, H_a), 7–8.5 (m, $13H_{ar}$) 4.12 (t, 4H, H_c), 3.5 (q, 4H, H_b) 2.24 (t, 4H, H_d), 1.48 (s, 4H, H_e)	24.93
BOOT2P/ SUA 	8.86 (t, 2H, H_a), 7–8.5 (m, $13H_{ar}$) 4.14 (t, 4H, H_c), 3.5 (q, 4H, H_b) 2.16 (t, 4H, H_d), 1.42 (m, 4H, H_e) 1.42 (s, 4H, H_f)	24.93
BOOT2P/ SEA 	8.74 (t, 2H, H_a), 7–8.5 (m, $13H_{ar}$) 4.14 (t, 4H, H_c), 3,5 (q, 4H, H_b) 2.21 (t, 4H, H_d), 1.43 (m, 4H, H_e) 1.15 (m, 8H, $H_{f,g}$)	24.93
BOOT2P/ CYDA 	8.74 (t, 2H, H_a), 7–8.5 (m, $13H_{ar}$) 4.14 (t, 4H, H_c), 3.5 (q, 4H, H_b) 1.62 (m, 8H, $H_{f,g}$)	24.93
BODPE/ ADA 	8.52 (t, 2H, H_a), 7–7.9 (dd, $8H_{ar}$) 4.13 (t, 4H, H_c), 3.49 (q, 4H, H_b) 2.27 (t, 4H, H_d), 1.5 (s, 4H, H_e)	
BODPE/ SUA 	8.52 (t, 2H, H_a), 7–7.9 (dd, $8H_{ar}$) 4.13 (t, 4H, H_c), 3.5 (q, 4H, H_b) 2.24 (t, 4H, H_d), 1.46 (m, 4H, H_e) 1.19 (s, 4H, H_f)	
BODPE / SEA 	8.52 (t, 2H, H_a), 7–7.9 (dd, $8H_{ar}$) 4.13 (t, 4H, H_c), 3.5 (q, 4H, H_b) 2.25 (t, 4H, H_d), 1.46 (m, 4H, H_e) 1.16 (m, 8H, $H_{f,g}$)	
BODPE / CYDA 	8.74 (t, 2H, H_a), 7–8.5 (m, $13H_{ar}$) 4.14 (t, 4H, H_c), 3.5 (q, 4H, H_b) 1.62 (m, 8H, $H_{f,g}$)	

ADA, adipic acid; SEA, sebacic acid; SUA, subaric acid; CYDA, 1,4-cyclohexane dicarboxylic acid.

turned solid rapidly before to reach 200 °C and very low molecular weight polymers resulted. As a consequence, a solvent namely NMP was used. In these conditions, 5 h at 200 °C were sufficient to get high molecular weight PEAs.

The chemical structure of PEAs was confirmed by ^1H NMR analysis and also by ^{31}P NMR analysis for PEAs based on BOOT2P. Table 1 summaries the chemical shifts of proton and phosphorous nuclei of the different PEAs. As illustrated in Fig. 2 the reaction between oxazoline ring and the carboxylic acid function is confirmed by the chemical shifts of oxazoline ring protons which appear initially at 4.4 and 3.9 ppm, and move to 4.1 and 3.5 ppm.

3.3. Steric exclusion chromatography (SEC)

The solubility of polymers in DMF allowed molecular weight determination using SEC. Table 2 lists molecular weights and polydispersities of polymers. The data show that the polymerization both in melt for the BOOT2P/dicarboxylic acid systems and in solution for the BODPE/dicarboxylic systems produced PEAs with fairly good molecular weights. The polydispersity values were around 2 which is typical for polycondensation reaction.

3.4. Thermal analyses

The thermal behaviour of PEAs was investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The results are mentioned in Table 3. The DSC thermogram of triphenylphosphine oxide containing PEAs show only one inflection point corresponding to the glass transition temperature and means these polymers seem amorphous in character (see Fig. 3).

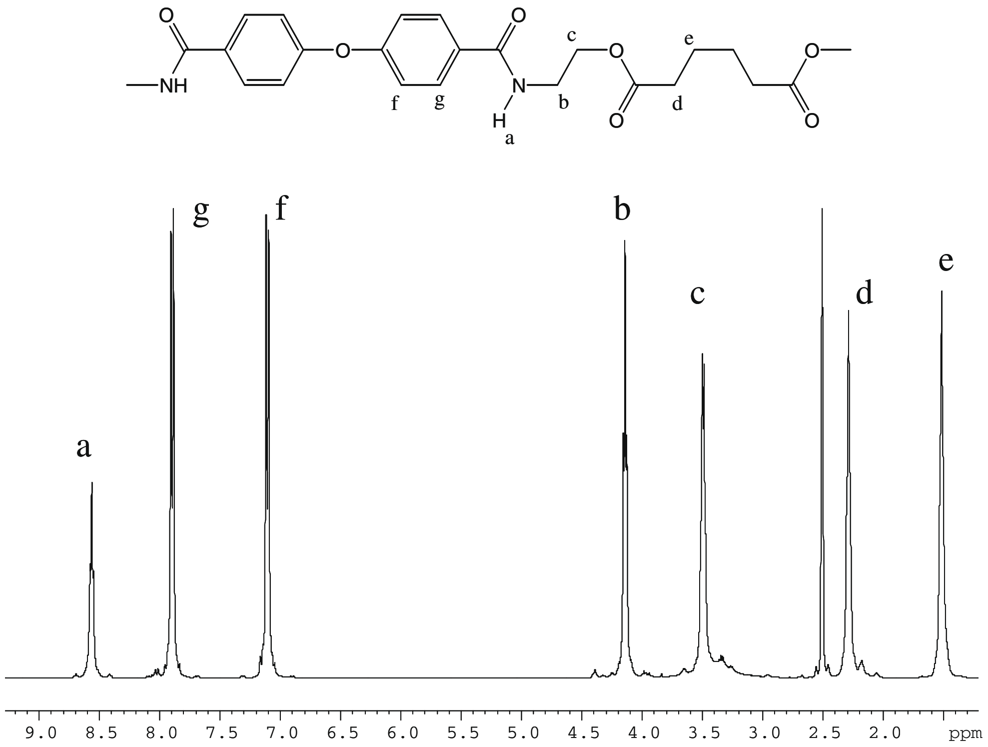


Fig. 2. ^{1}H NMR spectrum of PEA 2a.

Table 2
Molecular weight values of the polymers.

PEA	Bisoxazoline/carboxylic acid	M_n	M_w	Ip
1a	BOOT2P/ADA	24,800	40,600	1.6
1b	BOOT2P/SUA	23,200	41,700	1.8
1c	BOOT2P/SEA	24,600	45,600	1.85
1d	BOOT2P/CYDA	22,900	38,600	1.7
2a	BODPE/ADA	23,300	39,300	1.7
2b	BODPE/SUA	24,000	39,900	1.7
2c	BODPE/SEA	71,800	187,900	2.6
2d	BODPE/CYDA	23,900	38,300	1.6

For those based on BODPE precursor and the linear aliphatic dicarboxylic acid reagents, the thermograms show in addition of an inflection point, one exothermic peak followed by one endothermic peak. One example of such thermogram is reported in Fig. 4 and corresponds to the polymer PEA 2a. Based on these DSC analysis the PEAs should be considered as semi-crystalline.

Table 3
Thermal data for poly(ester-amide)s.

PEA	T_g (°C)	T_{exo} (°C) DSC	T_m (°C) DSC	5% weight loss TGA	T_{onset} in °C TGA
1a	103	–	–	315	215
1b	79	–	–	310	206
1c	70	–	–	311	201
1d	136	–	–	322	239
2a	57	142	196	296	202
2b	40	127	196	303	198
2c	40	105	193	304	198
2d	88	–	–	302	219

T_{exo}, temperature of the maximum exothermic peak; T_m, melting temperature of polymer; T_{onset}, onset temperature of weight loss in air.

The results of TGA measurements show a distinct variation in the thermo oxidative stability between the two series of PEAs. Those incorporating triphenylphosphine oxide units display thermo oxidative stabilities (5% weight loss > 310 °C) higher that the PEAs (2a–2d).

3.5. Solubility

The solubility of PEAs was investigated in different common organic solvents, at ambient temperature and at a concentration of 10%. The results are reported in Table 4. All the PEAs were found to be soluble in aprotic polar solvents. The poly(ester-amide)s containing the longest and most flexible, aliphatic bridging chains (1b, 1c, 2b and 2c) displayed a slightly better solubility in the common organic solvents such as chloroform, tetrahydrofuran and dichloromethane. Clearly, the aliphatic chain within the polymer backbone must contain up to 6 carbon atoms in order to modify significantly the solubility properties.

4. Conclusion

Poly(ester-amide)s were successfully prepared from aromatic bisoxazolines and aliphatic dicarboxylic acid compounds. When the triphenylphosphine oxide containing polymers are all amorphous those obtained by polymerization of the BODPE oxazoline with the aliphatic

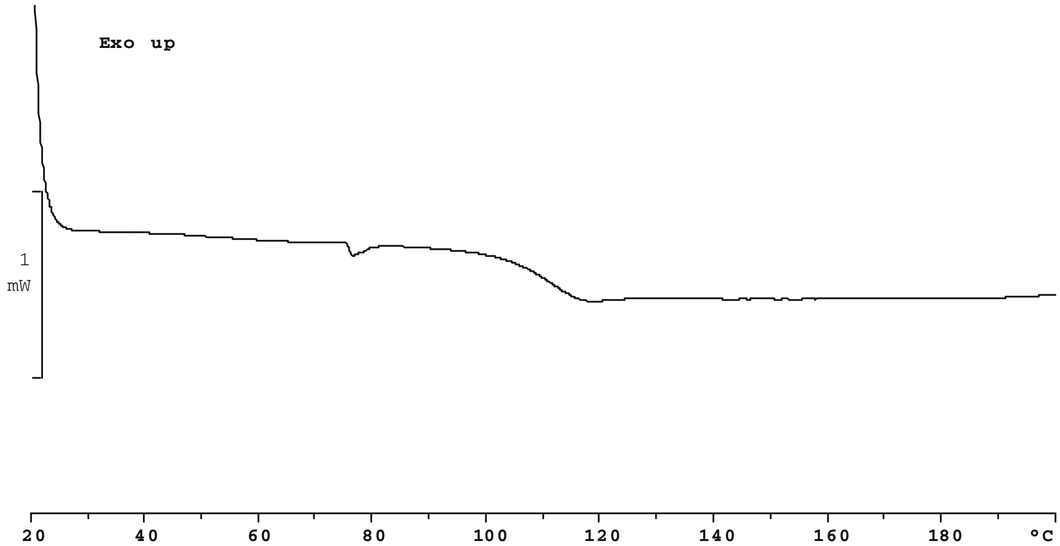


Fig. 3. DSC trace of PEA 1a.

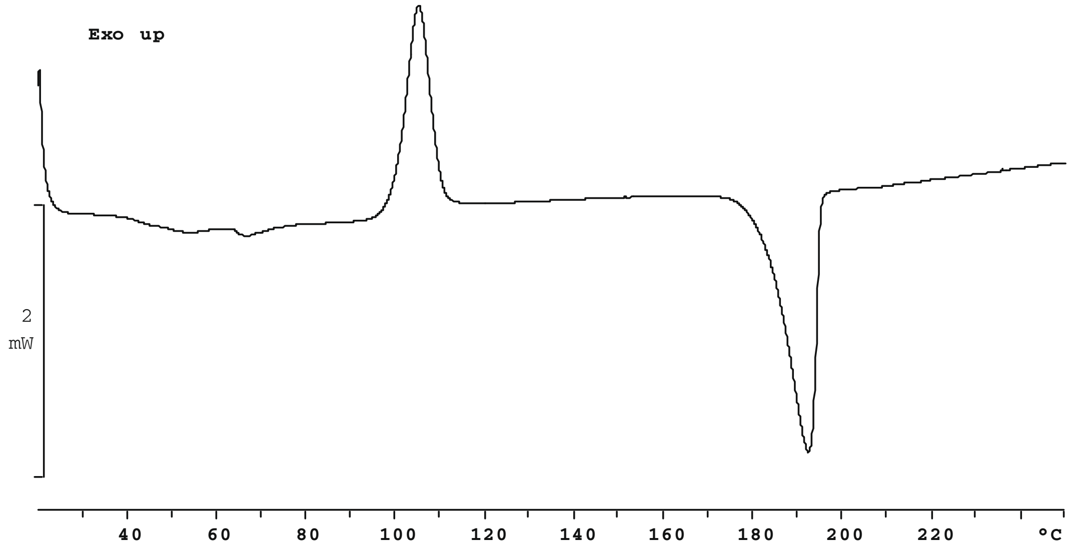


Fig. 4. DSC trace of PEA 2b.

Table 4
Solubility properties of polymers at ambient temperature.

Solvent	Poly(ester-amide)							
	1a	1b	1c	1d	2a	2b	2c	2d
Chloroform	–	+	+	–	–	+	+	–
Tetrahydrofuran	–	+	+	–	–	+	+	–
Dichloromethane	–	+	+	–	–	+	+	–
Acetone	–	–	–	–	–	±	±	–
Methanol	–	–	–	–	–	–	–	–
1-Methyl-2-pyrrolidone	+	+	+	+	+	+	+	+
N,*N*-dimethylacetamide	+	+	+	+	+	+	+	+
N,*N*-dimethylformamide	+	+	+	+	+	+	+	+
Dimethylsulfoxide	+	+	+	+	+	+	+	+
γ-Butyrolactone	–	–	–	–	±	±	±	–

(+) soluble; (–) insoluble; (±) slightly soluble.

linear dicarboxylic acid compounds are semi-crystalline. The data obtained from TGA analysis (temperature for 5% weight loss under air) show that these PEAs display a fairly good thermal stability.

Acknowledgments

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