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Synthesis and characterization of poly(4-oxyalkylenoxy benzoate)s of different chain length

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Abstract: Three different monomers starting from p-(4-hydroxy)benzoic acid and 3-chloro-1-propanol, 4-chloro-1-butanol and 6-chloro-1-hexanol, respectively, were synthesized and extensively characterized by means of ^{1}H and ^{13}C NMR, MALDI-TOF MS and elemental analysis. Subsequently, poly(4-oxyalkylenoxy benzoate)s polymers with different chain length were prepared in bulk starting from the mentioned above monomers, employing $Ti(OBu)_4$ as catalyst, according to the usual two-stage polymerization procedure. The polymers were characterized in terms of chemical structure, molecular mass and thermal behaviour. T_g, T_m and the ability to crystallize were found to be affected by the number of methylene groups per repeat unit and the results were explained mainly on the basis of the increment of the chain flexibility.

Introduction

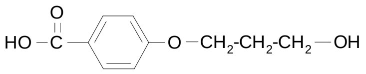
Poly(4-oxyethoxy benzoate) (PHEBA) is a polymer with a rather stiff chain, which in the past found application as fiber, being manufactured in Japan under the commercial name "A-Tell". Several patents have been published concerning its synthesis and physical properties, with a special attention devoted to those concerning fiber (Yoshizawa, [1]; Mihara, [2]; Rimura et al. [3]; Rimura et al. [4]. In particular, a patent claimed the moderate Young's modulus, excellent elastic recovery, weathering resistance, dyeing properties and resistance to chemicals of PHEBA [2]. Moreover, PHEBA fiber has been described to have a silk-like hand and drape, good wrinkle resistance and easy care properties (Mihara [2]). Recently, we described its synthesis and molecular and thermal characterization (Lotti, [5]). Subsequently, taking in mind that both the crystallization rate and morphology are crucial factors during the processing and manufacturing of polymeric materials, the crystallization kinetics and the morphology of PHEBA were also investigated (Finelli, [6], Nuñez, [7]). Lastly, random copolymers of PHEBA with poly(ε-caprolactone) have been synthesized and the effect of composition on the thermal properties and the kinetic and thermodynamic parameters was investigated (Finelli, [8]).

In this view, it appeared interesting to carry on the research by synthesizing novel more flexible aromatic polyesters belonging to the same class of PHEBA with different chain length, starting from the appropriate monomers prepared in our laboratories. Herein, the results concerning the synthesis of both the monomers and the corresponding polymers are described. Moreover, the data of a detailed investigation of the thermal properties of these new polyesters are reported. All polymer were characterized by (1H and 13C)-NMR tool, and especially by MALDI-TOF mass spectrometry technique which is capable of detecting individual and intact polymer molecules even in a complex mixture, including species present in minor amounts in a polymer sample [Montaudo, 9-11].

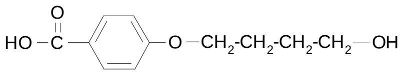
Results and discussion

Monomers

A preliminary study was carried out to optimize the experimental conditions to obtain the monomers **1**, **2** and **3** (Chart 1) in high yield.



(1)



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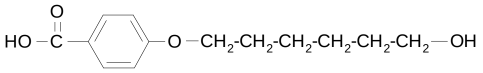


(3)

CHART 1

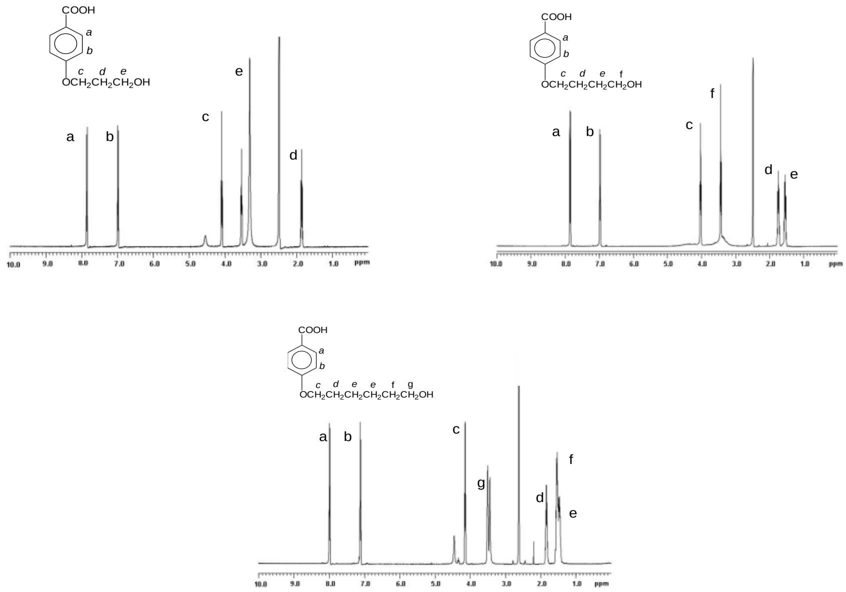


Fig. 1. ^{1}H-NMR spectrum of the monomers in Dimethyl sulfoxide-d_6, at room temperature (10 mg/mL).

First of all, several runs were made to establish the correct molar ratio between the p-(4-hydroxybenzoic) acid (HBA) and the corresponding chloro-alcohol derivates, which was found to be 1:1.1 for the first synthesis, 1:1.5 for the second and 1:1.3 for the third one. In the first step the accurate control stoichiometry, time and reaction temperature was important. To reach high yields it was also necessary to acidify the solution with sulfuric acid, which was added very slowly keeping the solution continuously under stirring, at a controlled temperature of 30 °C.

The solubility of the monomer samples was checked in various solvents at different temperatures: the best solvent for *p-(4-hydroxypropoxy)benzoic acid (HPBA)* (**1**) and for *p-(4-hydroxybutoxy)benzoic acid (HBBA)* (**2**) was found to be acetonitrile, while for *p-(4-hydroxyhesoxy)benzoic acid (HExaBA)* (**3**) acetone.

Elemental analysis, carried out in all cases, support the formulation of the synthesised compounds (see Experimental Part).

The chemical structure was characterized by ^{1}H-NMR analysis. ^{1}H-NMR spectra of all monomers synthesized were found to be consistent with the expected structure. The spectra are shown in Figure 1 together with the chemical shift assignments. In all cases the expected pattern of the phenyl group (two doublets at 7.88 and at 7.01 ppm for monomer **1** and **2,** respectively, and two doublets at 8.09 and 7.14 ppm for monomer **3**, assigned to aromatic protons) and of the aliphatic chain assigned to methylene protons (two triplets at 4.06 and 3.29 ppm for monomer **1**, two triplets at 4.06 and 3.43 ppm for monomer **2** and three triplets at 4.10, 3.55 and 1.39 ppm for monomer **3**; two multiplets at 1.73 and 1.50 ppm for monomer **2** and at 1.78 and 1.48 ppm for monomer **3**) was found. The small differences in the chemical shifts observed for the same chemical groups have to be attributed to the different chemical surrounding which create different resonance signals.

Polymers

At room temperature all the polyesters synthesized are semicrystalline solids. The solubility of the polymers was checked in various solvents: all the samples were found to be fully soluble at room temperature only in chloroform/trifluoroacetic acid ($CHCl_3/CF_3COOH$) (80/20 v/v), 1,1,1,3,3,3-hexafluoro-2-propanol or in a mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol ($CH_2Cl_2/CHCl_3$/HFIP) (75/20/5 v/v/v). Poly(4-oxyalkylenoxy benzoate) polymers were carefully purified by means of the following procedure: after dissolution in chloroform/trifluoroacetic acid (80/20 v/v), and precipitation in methanol, they were recovered by filtration and again dissolved and reprecipitated twice.

Tab. 1. Molecular and thermogravimetric characterization data.

Polymer	M_n	T_{id} (°C)	T_{max} (°C)
PHEBA	9500	412	446
PHPBA	9200	390	415
PHBBA	8600	389	421
PHExaBA	10100	393	417

Finally, the samples were kept in a vacuum oven at room temperature overnight, in order to remove the residual solvent. The polymers synthesized are listed in Table 1, which also collects the number-average molecular weights (M_n) data obtained by GPC technique.

(^{1}H and ^{13}C)- NMR spectra of all polyesters synthesized are shown in Figure 2, and the corresponding chemical shift assignments are reported in Table 2. In all cases, the spectra were found to be consistent with the expected structure.

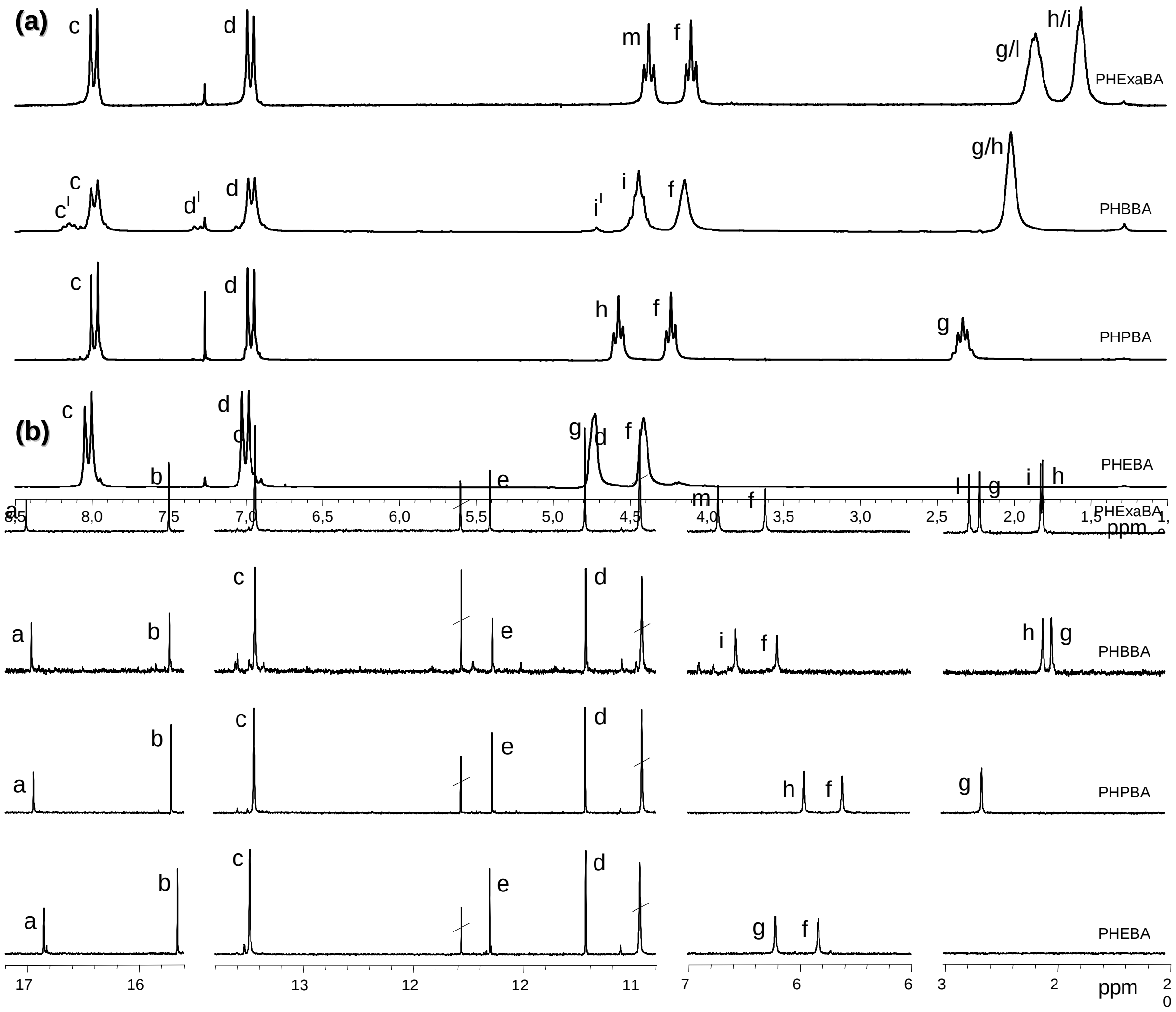
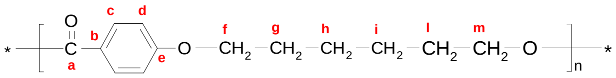
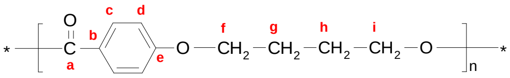
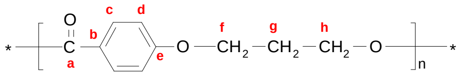
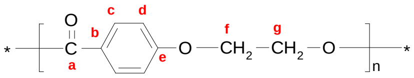


Fig. 2. ^{1}H NMR **(a)** and ^{13}C NMR **(b)** spectra of the PHEBA, PHPBA, PHBBA and PHExaBA samples recorded using chloroform-d/trifluoroacetic acid-d mixture (80:20 v/v) as a solvent.

Figure 3 shows the MALDI-TOF mass spectra of the PHEBA, PHPBA, PHBBA and PHExaBA polymers. MALDI-TOF mass spectra of PHEBA, PHPBA and PHExaBA polymers shows well resolved mass peak series from 1400 up to 10000 Da, while the mass spectrum of PHBBA sample present signals until 6000 Da. All peaks correspond to sodiated ions of the the poly(4-oxylachylenoxy benzoate) oligomers and their pertinent assignments are summarized in Table 3, which also reports the mass of the representative families of homologous peaks present in the insets in Figure 3. The most intense peaks in Figure 3 belong to the linear oligomers terminated with carboxyl and hydroxyl groups (species B_n, G_n, I_n, L_n, N_n, O_n in Figure 3 and in Table 3). Sodiated salts of these carboxyl terminated oligomers were also observed in Figure 3 (species C_n, H_n, M_n and P_n, in Figure 3 and in Table 3).

Tab. 2. Chemical shifts and assignments of the signals observed in the ^{1}H and ^{13}C NMR spectra to the poly(4-oxylachylenoxy benzoate)s studied.

Polymer	Structure of repeat unity	Shift (ppm) ^{1}H	Shift (ppm) ^{13}C
PHExaBA		- - **c** = 8,121 **d** = 7,101 - **f** = 4,212 **g** = 1,969 **h** = 1,675 **i** = 1,675 **l** = 1,969 **m** = 4,487	**a** = 170,070 **b** = 163,678 **c** = 132,188 **d** = 114,740 **e** = 121,523 **f** = 66,559 **g** = 28,460 **h** = 25,675 **i** = 25,767 **l** = 28,923 **m** = 68,670
PHBBA		- - **c** = 8,008 **d** = 6,986 - **f** = 4,146 **g** = 2,021 **h** = 2,021 **i** = 4,442	**a** = 169,823 **b** = 163,645 **c** = 132,185 **d** = 114,642 **e** = 121,416 **f** = 66,035 **g** = 25,298 **h** = 25,673 **i** = 67,893
PHPBA		- - **c** = 8,000 **d** = 6,983 - **f** = 4,217 **g** = 2,327 **h** = 4,569	**a** = 169,737 **b** = 163,575 **c** = 132,237 **d** = 114,642 **e** = 121,429 **f** = 63,113 **g** = 28,378 **h** = 64,827
PHEBA		- - **c** = 8,048 **d** = 7,026 - **f** = 4,412 **g** = 4,727	**a** = 169,273 **b** = 163,285 **c** = 132,435 **d** = 114.735 **e** = 121,547 **f** = 64,177 **g** = 66,111

These species were formed during the preparation of the matrix/polymer mixture for MALDI analysis, as well observed in the MALDI analysis of other polyesters [Montaudo, 9–11]. Weak intense peak families corresponding to the cyclic oligomers (mass series A_n) are also present in the MALDI spectra in Figure 3.

All MALDI-TOF mass spectra in Figure 3, beside to the expected polyester chains Bn (Scheme 1) also show other families of peaks corresponding to the macromolecular species with one or more benzoate units along the chains (species G_n, I_n, L_n, N_n and O_n in Figure 3 and in Table 3). These families of unexpected oligomers can be generated by reaction of monomers (1, 2, 3 and HEBA) with *p*-hydroxy benzoic (HBA) acid present as impurities in the monomers synthesized. These impurities were not observed by ^{1}H-NMR analysis of the monomers (see Figure 1) probably because their amount is below the sensitivity of NMR instrument.

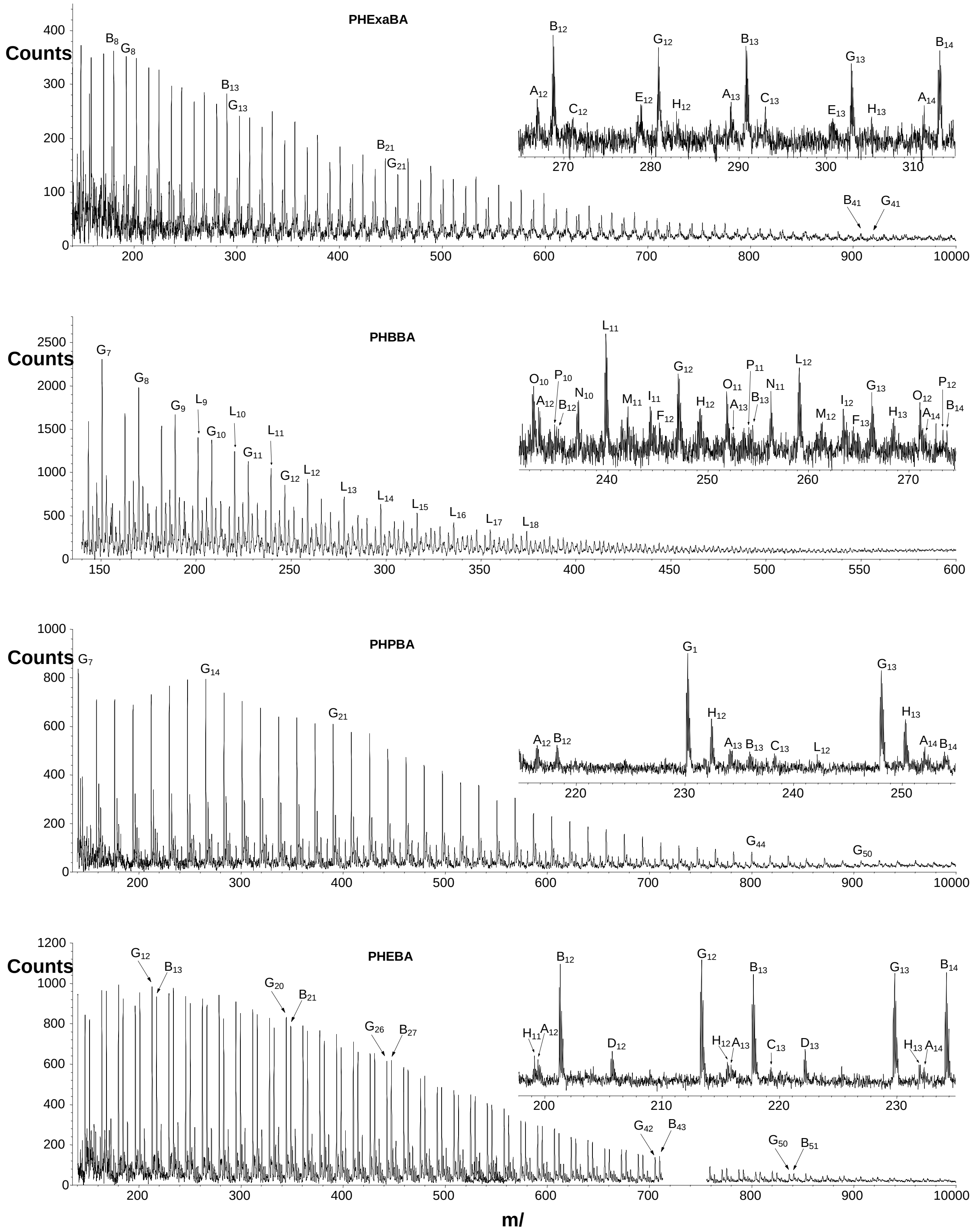


Fig. 3. MALDI-TOF mass spectra of the PHEBA, PHPBA, PHBBA and PHExaBA polymers. The insets report an enlarged section of the corresponding spectrum.

In the mass spectra of PHEBA and PHExaBA polymers the intensity of the peak series G_n is similar to that of peaks B_n, while in the spectra of the polyesters PHPBA and PHBBA the intensity of peak series L_n, G_n and P_n corresponding to the linear oligomers containing one, two or three benzoate units (see Table 3), respectively, is higher with respect to that of the peaks B_n (see Figure 3). Cyclic oligomers containing one benzoate units (species F_n in Figure 3 and in Table 3) were also observed in the MALDI mass spectrum of the PHBBA. Therefore, according with MALDI data we believe that the amount of HBA is higher in the monomers 1 and 2 with respect to that present in the monomers 3 and HEBA.

MALDI-TOF mass spectrum of the PHBBA polymer also shows two families of peaks (labelled as I_n and N_n in Figure 3) that we have assigned to the PHBBA oligomers containing one 4-oxyethoxy benzoate (HEBA) units in the chains (see assignments in Table 3). The presence of these units was also confirmed by ^{1}H NMR analysis of the PHBBA sample. In fact, the ^{1}H-NMR reported in Figure 2a beside to the peak resonance due to the protons of the PHBBA units shows a weak signal at 4.72 ppm (labelled as $i^{/}$) that we have assigned to the methylene protons belong to the HEBA units in the chains. Using the integrated area of the peaks *i* and $i^{/}$ in the ^{1}H-NMR spectrum of the PHBBA polymer, we have calculated that this polymer contains 4% mol of HEBA units. These impurity can be formed by reaction of HBA with 2-chloro ethanol present as impurity in the commercial 4-choro-1-butanol used for the synthesis of the HBBA (monomer 2). ^{1}H-NMR spectrum in Figure 2a also shows weak multiplet signals in the range 8.25-8.10 ppm and 7.40-7.25 ppm that we have assigned to the aromatic protons *c'* and *d'*, respectively, of the benzoate units in the PHBBA chains.

Finally, MALDI TOF mass spectra of PHEBA and PHExaBA show also another two species of mass peak correspondingly at the D_n and E_n family, respectively. The family of peaks D_n corresponds to the oligomers having a dioxyethylene unit (see Table 3), while the series of peaks E_n belong to the oligomers containing a dioxyexyl unit (see Table 3). Therefore the MALDI TOF MS analysis permit the complete characterization of the chemical composition of the polyesters studied.

The polyesters were afterwards examined by thermogravimetric (TGA) analysis and differential scanning calorimetry (DSC). The investigation on the thermal stability was carried out both in air and under nitrogen atmosphere.

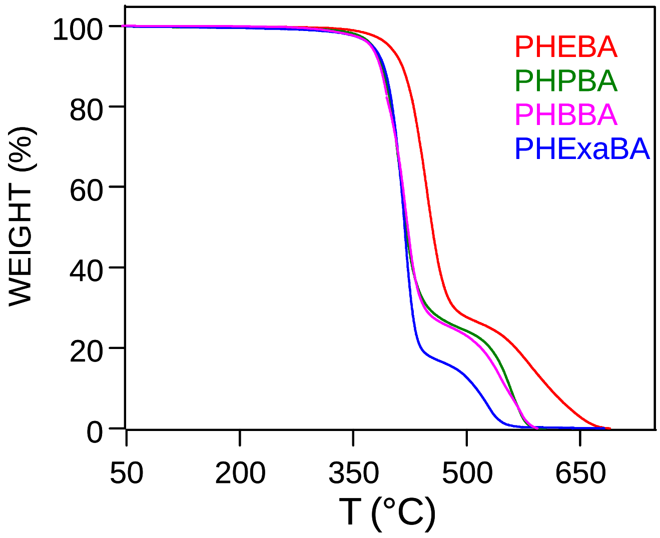
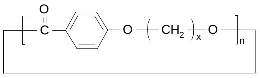
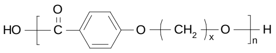
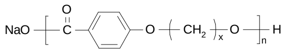
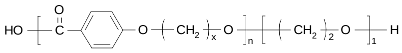
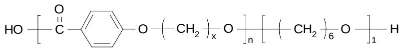
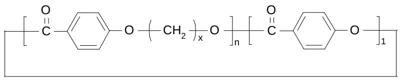
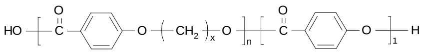
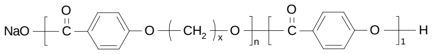
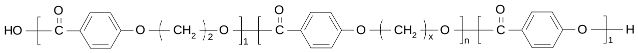
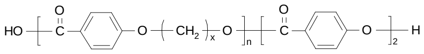
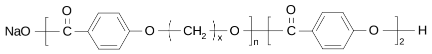
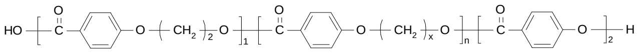
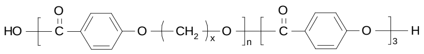
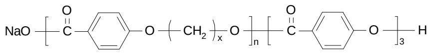


Fig. 4. Thermogravimetric curves in air (10 °C/min).

Tab. 3. Assignments of the Mass Peaks Signals present in the enlarged sections of the MALDI-TOF spectra showed in Figure 3.

Structure	Species	n	PHEBA	PHPBA	PHBBA	PHExaBA
	A_n	1 2 1 3 1	1993 2157 2321	2161 2339 2517	2329 2521 2713	2666 2886 3107
	B_n	1 2 1 3	2011 2175 2339	2179 2357 -	2347 2539 -	2684 2904 3125
	C_n	1 2 1 3 1	- 2033 2197	- 2201 -	-	2706 2926 -
	D_n	1 2 1 3	2055 2219	-	-	-
	E_n	1 2 1 3	-	-	-	2784 3004
	F_n	1 2 1 3	-	-	2450 2641	-
	G_n	1 2 1 3	2131 2295	2299 2477	2468 2660	2804 3024
	H_n	1 1 1 2 1	1989 2153 2317	- 2321 2500	- 2490 2682	- 2826 3047
	I_n	1 1 1 2	-	-	2416 2608	-
	L_n	1 1 1 2	-	- 2419	2396 2588	-
	M_n	1 1 1 2	-	-	2418 2610	-
	N_n	1 0 1 1	-	-	2367 2559	-
	O_n	1 0 1 1 1	-	-	2323 2515 2707	-
	P_n	1 0 1 1 1	-	-	2345 2537 2729	-

In Table 1 are collected the temperature of initial decomposition (T_{id}) and the temperature corresponding to the maximum weight loss rate (T_{max}) as obtained by thermogravimetric analysis in air. Similar results were observed by means of TGA measurements carried out under nitrogen atmosphere. In all cases the weight loss takes place practically in one-step and is 100% (see Figure 4). All the samples are characterized by good thermal stability, the temperature of initial decomposition T_{id} ranging from 390 to 412°C. However, a dependence of the thermal stability on the aliphatic chain length was observed: as a matter of fact, the thermal stability was found to decrease as the number of methylene groups per repeat unit was increased.

Calorimetric data were obtained on samples with the same thermal history: all polymers were quenched from the melt and the second heating scan was recorded. The DSC traces of such samples are reported in Figure 5 and the data obtained in Table 4.

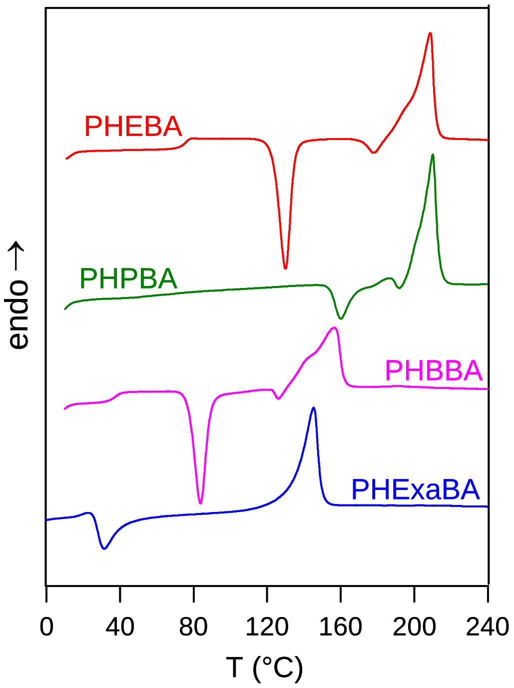


Fig. 5. Calorimetric curves of poly(4-oxyalkylenoxy benzoate)s polymers after melt quenching.

As it can be seen in Figure 5, all calorimetric traces are characterized by an endothermal baseline deviation associated with the glass transition followed by an exothermal “cold crystallization” peak and a melting endotherm at higher temperature. With respect to PHPBA and PHExaBA, the enthalpy associated with the crystallization phenomenon is lower than that of fusion endotherm, indicating that these samples cannot be frozen into a completely amorphous state by quenching. Nevertheless, a portion of amorphous material, once T_g is exceeded, acquires enough mobility to rearrange and crystallize. On the contrary, in the case of PHEBA and PHBBA polyesters, the enthalpy of crystallization very well compares with the corresponding heat of fusion, indicating that these polymers are completely amorphous.

Tab. 4. Calorimetric characterization data.

Polymer	T_g (°C)	Δc_p (J/°C·g)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PHEBA	75	0.47	129	48	209	49
PHPBA	59	0.13	160	14	210	57
PHBBA	37	0.48	84	43	156	45
PHExaBA	18	0.23	31	26	145	49

As is well known, a partially crystalline material usually exhibits a different glass transition behaviour than the completely amorphous analogs. In fact, although some conflicting results are reported in the literature (Boyer, [12]), crystallinity usually acts like cross linking and raises T_g through its restrictive effect on the segmental motion of amorphous polymer chains. Therefore, to study the influence of chemical structure on the glass transition, the phenomenon should be examined in the total absence of crystallinity. Rapid cooling (quenching) from the melt is the method commonly used to prevent crystallization and to obtain polymers in a completely amorphous condition. Unfortunately, as can be seen in Fig. 6 and from the data collected in Table 4, such procedure was not always efficacious; in fact, PHPBA and PHExaBA cannot be frozen in a completely amorphous glassy state due to their high rate of crystallization. Nevertheless, the values of glass transition temperature collected in Table 4 show a clear dependence on aliphatic chain length, T_g consistently decreasing as the number of CH_2 groups per repeat unit is increased. The observed trend can be explained on the basis of an increment of chain flexibility: as a matter of fact, the higher is the number of methylene groups in the polymeric chain the lower the concentration of the stiffer ester groups (O-CO-). As a consequence, the polymeric chain is more flexible and thus the polymer has a lower T_g.

As far as the T_m trend is concerned, the melting temperature exhibits an odd-even effect. It would be expected that polymers containing longer aliphatic chains are more flexible, thus crystallizing more readily and melting at lower temperature. The different behaviour observed for the poly(4-oxyalkylenoxy benzoate)s polymers analyzed suggests that the chain flexibility is not the only parameter that has to be taken into consideration to explain the melting phenomenon. In particular, it can be noted that the polyester with an odd number of methylene groups per repeat units, i.e. PHPBA (with three CH_2 groups per repeat units), has the highest melting point. Therefore, in addition to the chain flexibility, the characteristics of the crystal structure and the chain conformation have to be also considered. In order to investigate these results more deeply, further experiments by using X-ray diffractometry are currently being carried out. Comparing the melting temperatures of the polyesters with an even number of CH_2 groups per repeat unit, i.e. PHEBA, PHBBA and PHExaBA, one can see that T_m value decreases as the chain length is increased, as expected on the basis of an increment of the chain flexibility.

Lastly, the calorimetric results indicate a different phase behaviour of poly(4-oxyalkylenoxy benzoate)s polymers: the polymer with an odd number of methylene groups per repeat unit (PHPBA) and that with the longest chain length (PHExaBA) are partially crystalline, whereas the PHEBA and PHBBA are completely amorphous after melt quenching. Such phase behaviour proves that PHPBA and PHExaBA are characterized by high crystallization rate. In the case of PHPBA, latter is probably correlated to the nature of the crystalline phase; as far as PHExaBA is concerned, the increased crystallization rate with respect to PHEBA and PHBBA, can be explained on the basis of the higher chain flexibility which characterizes the polyester with the longest chain length.

Conclusions

The results obtained showed the possibility of easily synthesizing in bulk, by the usual two-stage polycondensation procedure, novel polyesters characterized by different chain length starting from monomers prepared in our laboratories.

The data concerning the thermal characterization display that the number of methylene groups per repeat unit lead to significant variations in the final properties of poly(4-oxyalkylenoxy benzoate)s polymers. In particular:

- the thermal stability of the polyesters keeps good, even though slightly decreasing with the number of methylene groups per repeat unit;
- the glass transition temperature decreases as the number of methylene groups in the repeat unit is increased, due to an increment of macromolecular chain flexibility;
- the melting point shows an odd-even fluctuation, due to several factors, like chain flexibility, chain conformations and crystal structure;
- the ability to crystallize increases as the number of methylene groups is increased, due to an increment of macromolecular chain flexibility.

Experimental part

Materials

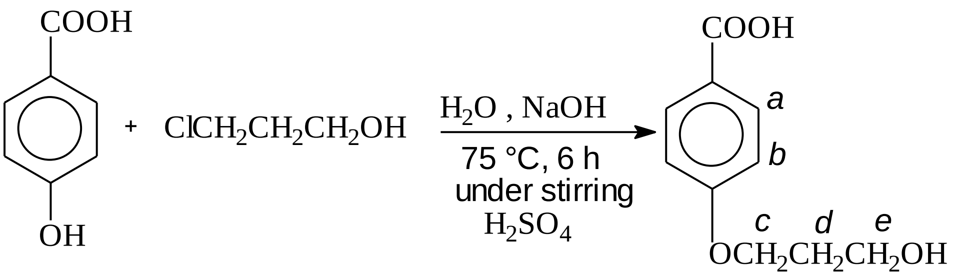
p-(4-Hydroxybenzoic) acid (HBA), 3-chloro-1-propanol (ClP), 4-chloro-1-butanol (ClB), 6-chloro-1-hexanol (ClEs), sodium hydroxide 98% pellets, sulfuric acid 99.99%, aceto nitrile, chloroform, trifluoro acetic acid, methanol, acetone, titanium tetrabutoxide ($Ti(OBu)_4$), dichloromethane, 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP), dimethyl sulfoxide-d_6 (DMSO-d), chloroform-d ($CDCl_3$), trifluoroacetic acid-d (CF_3COOD) (Aldrich) are reagent grade products; all of them were used as supplied, except $Ti(OBu)_4$ which was distilled before use.

Synthesis of monomers

The three monomers were synthesized according to the following experimental procedure:

-Synthesis (a): p-(4-hydroxypropoxy)benzoic acid (HPBA) (**1**)

45 g of p-(4-hydroxybenzoic) acid (HBA, 0.32 mol) were dissolved in 225 ml of a water solution of NaOH (27.45 g, 0.69 mol), and subsequently 34.03 g of 3-chloro-1-propanol (ClP, 0.36 mol) was added dropwise at 50 °C for about 45 min, giving rise to the following reaction:



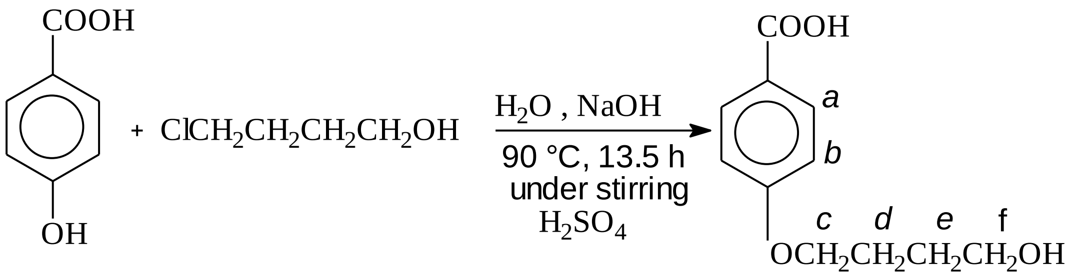
(1)

The mixture was stirred at 75 °C for 6 h. Then 15.75 ml of H_2SO_4 were added at 30 °C, under continuous stirring, to afford 54 g of **1** (86%) as white powder, after filtration and washing with water. After two recrystallization from acetonitrile, 50 g of **1** (80%) as white crystals were obtained.

Elemental analysis calculated for $C_{10}H_{12}O_4$: C, 61.22; H, 6.16; O, 32.62 %. Found: C, 60.49; H, 6.39; O, 33.12%.

-Synthesis (b): p-(4-hydroxybutoxy)benzoic acid (HBBA) (**2**)

45 g of p-(4-hydroxybenzoic) acid (HBA, 0.32 mol) were dissolved in 225 ml of a water solution of NaOH (32.5 g, 0.81 mol), and subsequently 52.93 g of 4-chloro-1-butanol (ClB, 0.49 mol) was added dropwise at 50 °C for about 45 min, giving rise to the following reaction:



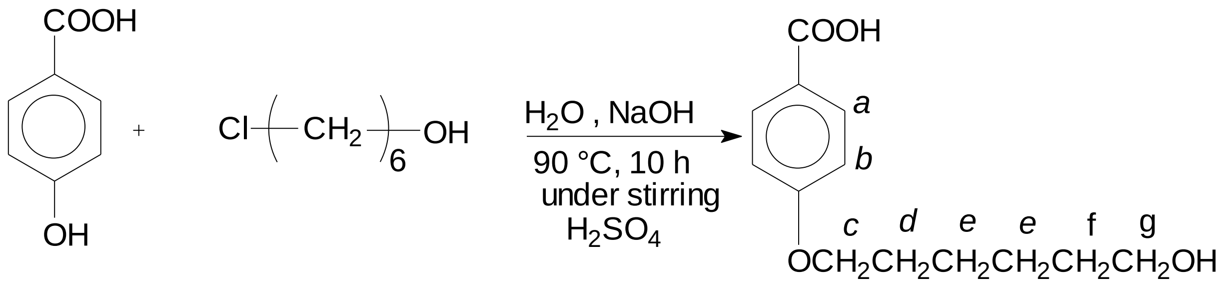
(2)

The mixture was stirred at 90 °C for 13.5 h. Then 15.75 ml of H_2SO_4 were added at 30 °C, under continuous stirring, to afford 55 g of **2** (80.5%) as white powder, after filtration and washing with water. After two recrystallizations, one in distilled water and one in acetonitrile, 35 g of **2** (51%) as white crystals were obtained.

Elemental analysis calculated for $C_{11}H_{14}O_4$: C, 62.55; H, 6.68; O, 30.77 %. Found: C, 62.54; H, 6.66; O, 30.8%.

-Synthesis (c): p-(4-hydroxyhesoxy)benzoic acid (HExaBA) (**3**):

45 g of p-(4-hydroxybenzoic) acid (HBA, 0.32 mol) were dissolved in 225 ml of a water solution of NaOH (27.45 g, 0.69 mol), and subsequently 56.65 g of 3-chloro-1-hexanol (ClEs, 0.42 mol) was added dropwise at 50 °C for about 45 min, giving rise to the following reaction:



(3)

The mixture was stirred at 90 °C for 10 h. Then 15.75 ml of H_2SO_4 were added at 30 °C, under continuous stirring, to afford 62.5 g of **3** (82 %) as white powder, after filtration and washing with water. After two recrystallizations in acetone, 59.5 g of **3** (78 %) as white crystals were obtained.

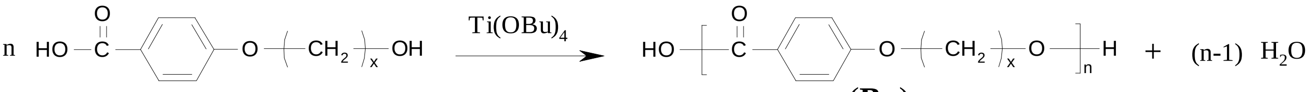
Elemental analysis calculated for $C_{13}H_{18}O_4$: C, 65.53; H, 7.61; O, 26.86 %. Found: C, 65.12; H, 7.61; O, 27.27 %.

Synthesis of polymers

Poly(oxyalkylenoxy benzoate)s polymers (P-HPBA, P-HBBA and P-HExaBA) were synthesized in bulk, starting from the appropriate monomer (**1**, **2** or **3)**, using $Ti(OBu)_4$ as catalyst (Scheme 1). After some preliminary syntheses carried out in order to optimize catalyst concentrations, an amount of 0.6 g of catalyst/kg of polymer was employed in all the syntheses.

The syntheses were carried out in a 200 mL stirred glass reactor, with a thermostated silicon oil bath; temperature and torque were continuously recorded during the polymerization. The polymers were prepared according to the usual two-stage polymerization procedure. In the first stage, at atmospheric pressure and under pure nitrogen flow, the temperature was raised to 180-200 °C and maintained there for about 1 h, until 90 % of water was distilled off. In the second stage the pressure was reduced (to about 0.3 mbar), in order to facilitate the removal of the water and the temperature was kept at 240 °C until a torque constant value was measured (about 10 hours). All the polymer samples were purified twice by dissolving in chloroform/Trifluoroacetic acid (80/20 v/v) and precipitated on methanol solution, in order to remove all catalyst and oligomer residuals.

Scheme 1



(Bn)

where x=3 for PHPBA, x=4 for PHBBA and x=6 for PHExaBA samples.

NMR spectroscopy

The chemical structures of the monomers and the polymers were determined by means of ^{1}H-NMR spectroscopy. The samples under investigations were dissolved in dimethyl sulfoxide-d_6 (10 mg/mL) in the case of monomers and in a mixture of chloroform-d/trifluoroacetic acid-d (80:20 v/v) (15 mg/mL) in the case of polymers with 0.03% (v/v) tetramethylsilane added as an internal standard. The measurements were carried out at room temperature with a relaxation delay of 0 s, an acquisition time of 1 s up to 100 repetitions, employing a Varian INOVA 400 MHz instrument.

MALDI-TOF mass spectrometry

MALDI-TOF mass spectra were recorded both in linear mode and in reflection mode, using a Voyager-DE STR (Perseptive Biosystem) mass spectrometer instrument, equipped with a nitrogen laser emitting at 337 nm, with a 3 ns pulse width, and working in positive ion mode. The accelerating voltage was 20-25 KV, the grid voltage and delay time (delayed extraction, time lag), were optimized for each sample to achieve the higher mass resolution, expressed as the molar mass of a given ion divided by the full width at half maximum (FWHM). The laser irradiance was maintained slightly above the threshold. 2-(4-Hydroxylphenylazo)-benzoic acid (HABA) 0.1 M in hexafluoro-2-propanol (HFIP) solvent, was used as matrix. The concentration of tailored polymers poly(oxyalkylenoxy benzoate)s was 5-6 mg/ml in HFIP. 10 μl of polymer solution were mixed with 10 or 30 μl of HABA solution. 1 μl of each sample/matrix mixture was spotted on the MALDI sample holder and slowly dried to allow matrix crystallization.

The better MALDI spectra reported here were recorded in reflectron mode, and present a mass resolution of 5000-6000 FWHM. The accuracy of mass determination was about 110 ppm in the mass range 1400-3300 Da and 170 ppm in the mass range 3300-5200 Da.

GPC analysis

Molecular weight data were obtained by gel permeation chromatography at 30 °C using a 1100 HP Series system with an UV spectrophotometer (at 254 nm wavelength) as detector, equipped with PL gel 5μ MiniMIX-C column (250/4.6 length/i.d., in mm). A mixture of dichloromethane/chloroform/1,1,1,3,3,3-hexafluoro-2-propanol (CH_2Cl_2/$CHCl_3$/HFIP) (75/20/5 v/v/v) was used as diluent with a 0.3 mL/min flow, and sample concentrations of about 2 mg/mL were applied. A molecular weight calibration curve was obtained with several monodisperse polystyrene standards in the range of molecular weight 2,000-100,000.

Thermal analysis

Thermogravimetric analysis was carried out both in air and under nitrogen atmosphere using a Perkin Elmer TGA7 apparatus (gas flow: 40 mL/min) at 10 °C/min heating rate up to 900 °C. The procedure suggested by the supplier was followed for the temperature calibration of equipment. This method is based on the change of the magnetic properties of two metal samples (Nickel and Perkalloy) at their Curie points (354.0 and 596.0 °C, respectively). The T_{onset} at which the weight loss starts was taken as temperature of initial decomposition (T_{id}).

Calorimetric measurements were carried out by means of a Perkin Elmer DSC7 instrument equipped with a liquid sub ambient accessory and calibrated with high purity standards (indium and cyclohexane). The external block temperature control was set at -40 °C. Weighed samples (c.a. 10 mg) were encapsulated in aluminum pans and heated to about 40 °C above fusion temperature at a rate of 20 °C/min (first scan), held there for 3 min, and then rapidly quenched to -10 °C. Finally, they were reheated from -10°C to a temperature well above the fusion temperature of the sample at a heating rate of 20°C/min (second scan). The glass-transition temperature T_g was taken as the midpoint of the heat capacity increment Δc_p associated with the glass-to-rubber transition. The melting temperature (T_m) and the crystallization temperature (T_c) were determined as the peak value of the endothermal and exothermal phenomena in the DSC curve, respectively. The specific heat increment Δc_p, associated with the glass transition of the amorphous phase, was calculated from the vertical distance between the two extrapolated baselines at the glass transition temperature. The heat of fusion (ΔH_m) and the heat of crystallization (ΔH_c) of the crystal phase were calculated from the area of the DSC endotherm and exotherm, respectively.

Repeated measurements on each sample showed excellent reproducibility.

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