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Side-chain polyesters and polyester hydrochlorides based on terephthalic acid

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Abstract

Side-chain polyesters and polyester hydrochlorides were synthesized from α-(bis(2-hydroxyethyl)amino)-ω-(4′-methoxy biphenyl-4-oxy) alkanes with different spacer lengths (Cn-diol, $n = 6, 8, 10$) and terephthaloyl chloride. Since N-substituted diethanolamine acts as a stronger acid acceptor than triethylamine or pyridine, polyester hydrochlorides are formed during polyesterification instead of polyesters. Polyesters can be prepared from a chloroform solution of polyester hydrochlorides by extraction of HCl. During the polyesterification, linear polymers as well as cyclic oligomers are formed. All polymers were analyzed by ^{1}H NMR, size exclusion chromatography (SEC), differential scanning calorimetry (DSC), X-ray spectroscopy (XND) and polarizing optical microscopy (POM). Polyesters and polyester hydrochlorides differ greatly in solubility and thermal properties. Although no liquid crystalline phase transitions were detected for either kind of polymer, an ordered structure was observed in XRD experiments for both polymers and was ascribed to a crystal smectic E phase.

Keywords: Polymer chemistry; Polymer synthesis; Polyester hydrochlorides

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1. Introduction

Polyesters containing long side-chains have received increasing attention over the past two decades. There are two main types of side-chain polyesters:

(i) aliphatic and aromatic polyesters with alkyl side-chains, which do not form liquid crystalline phase [1–3].
(ii) side-chain liquid crystalline (SCLC) polyesters with a mesogenic group in the side-chain [4–13].

Side-chain polyesters have been synthesized by direct polyesterification of acid anhydrides [4] or acid halides and diols [5–7], or by trans-esterification of mesogenic esters with diols [8–13]. The preparation of polyesters using acid halides and diols usually follows a relatively simple procedure. An acid halide is added to a solution of diol in a mixture of solvent and acid acceptor, preferably pyridine or triethylamine (TEA), and the reaction is completed in a few hours. The formed polyester is precipitated by alcohol [5–7].

Liquid crystalline diols, namely α-(bis(2-hydroxyethyl)-amino)-ω-(4′-methoxy biphenyl-4-oxy) alkanes with different spacer lengths (Cn-diol, $n = 6, 8, 10$ CH$_2$ units), as well as their analogues, have already been proven to induce liquid crystalline properties in polyurethanes [14–19]. Hard segmented polyurethanes with short side-chains ($n \leq 4$) were amorphous and did not exhibit LC properties. Polyurethanes with longer side-chains were thermotropic liquid crystals with a high tendency towards crystallization of the polyurethane backbone.

The aim of this work was to synthesize low molar mass polyesters from Cn-diols, which would then be further used to synthesize segmented liquid crystalline polyurethanes. Because of the small number of urethane groups, hydrogen bonding of the polyurethane main chains would be reduced, leading to a reduced possibility of crystallization of the main chain.

We began by synthesizing polyesters using Cn-diols and adipoyl chloride, with 1,2-dichloroethane as a solvent and pyridine as an acid acceptor. However, these polyesters did not exhibit LC properties [20]. By using terephthaloyl chloride instead of adipoyl chloride, polyesters with a more

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rigid backbone are more likely to be formed, thus favoring liquid crystalline properties. Therefore, we decided to prepare a series of polyesters based on C*n*-diols and terephthalic acid. However, the nitrogen atom in the C*n*-diol acted as a stronger acid acceptor than either triethylamine or pyridine, and, consequently, the hydrochloride evolved during the polyesterification reacted with the C*n*-diol rather than with the pyridine or triethylamine. Using the usual reaction procedure, as described above, polyester hydrochlorides were formed instead of polyesters. However, subsequent extraction of the hydrochlorides with water yielded the expected polyesters.

Other N-substituted diethanolamine derivatives with various mesogenic groups have also been used for the synthesis of side-chain polyesters [21–24]. Only one polyester was prepared with various acid halides and 2,2′-[4-[(4-nitrophenyl)azo] phenyl] iminobisethanol (Disperse Red 19) using pyridine as an acid acceptor [22]. The authors did not observe any formation of polyester hydrochlorides in that case, probably due to the resonance assisted stabilization of the nitrogen lone pair.

2. Experimental

The synthesis of C*n*-diols is described elsewhere [16]. Polyester hydrochlorides, as well as polyesters, can be obtained by two kinds of procedures, one direct (Procedures 1 and 3) and one indirect (Procedures 2 and 4). The reaction is depicted in Scheme 1.

2.1. Synthesis of polyester hydrochloride

Procedure 1. The C*n*-diol (3.3 mmol) was dissolved in a mixture of 10 ml 1,2-dichloroethane and 1 ml pyridine or trietylamine (TEA) under an inert (N_2) atmosphere. The reaction vessel was then sealed with a rubber septum. Terephthaloyl chloride (TC) was weighed (3.0 mmol) in a syringe, dissolved in 1,2-dichloroethane (15 ml), and injected through the rubber septum. The mixture was heated to 70 °C and kept at this temperature for 4 h. The polyester hydrochloride (Pes-*n*H, $n = 6, 8, 10$ CH_2 units in the side-chain) was precipitated by adding 70 ml of ethanol. The mixture was cooled to room temperature and filtered. Pes-8H and Pes-10H were dissolved in 10 ml of hot dichloroethane and precipitated by 70 ml of methanol. Pes-6H, which was not soluble in dichloroethane, was only washed with methanol.

Procedure 2. Linear Pes-*n* of 0.25 g was dissolved in 5 ml THF and 1 ml of concentrated HCl was slowly added during stirring. Precipitates of Pes-*n*Hs were filtered off, washed with HCl (10 wt%), and dried under vacuum.

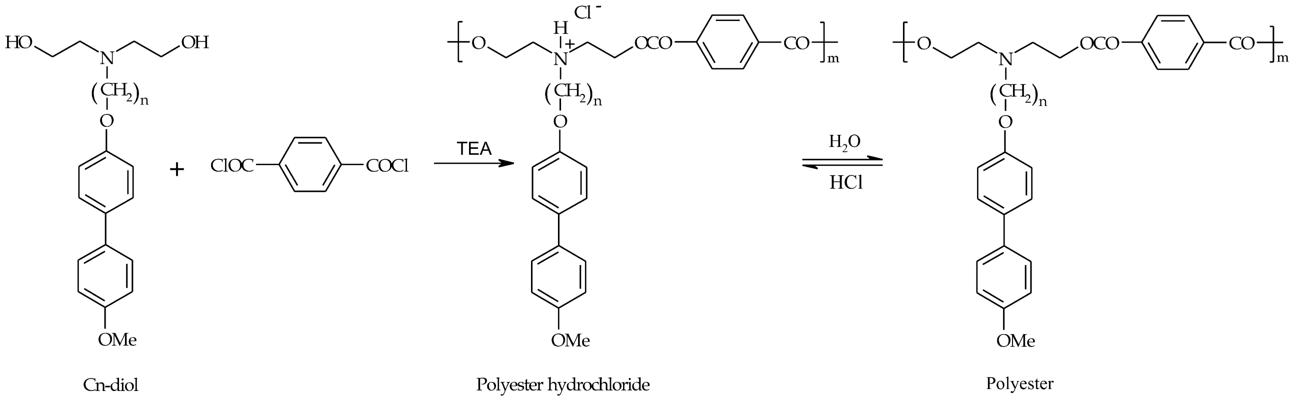
2.2. Synthesis of polyesters (Pes-n)

Procedure 3. The reaction was conducted as in procedure 1. Instead of ethanol, 70 ml of water was added to the reaction mixture. The water was changed five times (every 30 min), then the mixture was mixed at room temperature overnight. The dichloroethane solution was dried on a rotatory evaporator. The polyester was dissolved in 10 ml chloroform and precipitated with 75 ml ethanol.

Procedure 4. Polyester hydrochloride was dissolved in chloroform, then water was added and the mixture was mixed with a magnetic stirrer. The water was changed several times. Since Pes-6H is only slightly soluble in chloroform individual particles were floating on the phase boundary. When all the HCl was removed the particles fully dissolved.

2.3. Characterization

^1H NMR and ^{13}C NMR spectra were recorded at 25 °C on a Varian Unity Inova-300 spectrometer using $CDCl_3$ or DMSO-d_6 as the solvent and TMS as the internal standard. Average molar masses and molar mass distributions were determined relative to polystyrene standards by size exclusion chromatography on a modular Perkin–Elmer liquid chromatograph equipped with a DAD detector working at a wavelength of 254 nm. A PL Mixed D column



Scheme 1. The synthesis of polyester hydrochlorides and polyesters from α-(bis(2-hydroxy ethyl)amino)-ω-(4′-methoxybiphenyl-4-oxy) alkanes and terephthaloyl chloride in 1,2-dichloroethane; $n = 6, 8, 10$.

with a precolumn and THF as an eluent with a flow rate of 1 ml/min were used. Differential scanning calorimetry analysis was performed on a Perkin–Elmer Pyris 1 calorimeter. Heating and cooling rates were 10 K/min. X-ray diffraction patterns were taken on a Philips 17-10 using Cu Kα radiation ($\lambda = 1.54$ Å) in 0.04° steps from 2 to 35° (in 2θ) with 2 s per step. Optical textures were obtained using a Carl Zeiss polarizing optical microscope Stemi SV6 equipped with an MC 80 microscope camera and a Mettler Toledo FP82 hot stage.

3. Results and discussion

3.1. Synthesis

Synthesis of Pes-nH (*Procedure* 1). After the addition of TC to the 1,2-dichloroethane solution of C*n*-diol a precipitate was formed, which dissolved on heating to 70 °C, except in the case of Pes-6H. The reaction mixture after completion of the reaction was transparent for Pes-8H and Pes-10H, whereas a precipitate had formed for Pes-6H. The yield of Pes-*n*H was approximately 75%.

Knowing that the nitrogen atom of C*n*-diol is a stronger acid acceptor than TEA, the reaction was also conducted without TEA. Pes-*n*H were obtained with similar yields, showing that the presence of an acid acceptor is not necessary for this particular reaction.

Synthesis of Pes-n (*Procedure* 3). Observations during the reaction were the same as those noted above. Water was added at the end of the reaction to extract TEA and HCl. The yield of the polyester was 80–90%. However, when we tried to synthesize Pes-*n* without TEA a stable dispersion was formed after the addition of water and the polyester could not be isolated.

Molar masses of the synthesized polyesters are relatively low ($M_w = 3300–6600$ g/mol) and depend on the molar ratio of the reactants. The polydispersity indexes are from 1.72.1.

All Pes-*n* are soluble in solvents of different polarity, namely dimethylformamide, dimethylsulfoxide, acetone, tetrahydrofuran, chloroform, dichloroethane, and toluene, while Pes-*n*Hs are, due to their ionic character, soluble in high polarity solvents such as dimethylformamide and dimethylsulfoxide. Pes-8H and Pes-10H are also soluble in hot dichloroethane and chloroform, while Pes-6H is only slightly soluble in these solvents.

3.2. NMR spectroscopy

The structure of Pes-*n* and Pes-*n*H was determined by ^{1}H and ^{1}H COSY NMR spectroscopy. The representative spectra of Pes-10H (solvent DMSO-d_6) and Pes-10 (solvent $CDCl_3$), obtained from parent Pes-10H are shown in Fig. 1. The spectra of other polymers differ from these only in the intensity of the signal of the $-CH_2-$ groups at 1.2–1.6 ppm.

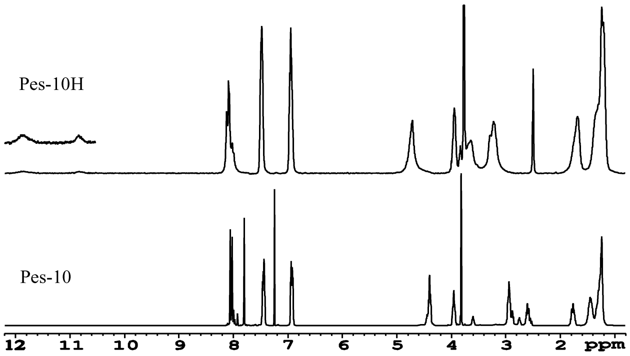


Fig. 1. ^{1}H NMR spectra of polyester (Pes-10) and the parent polyester hydrochloride (Pes-10H).

The signals of Pes-*n* are assigned as follows: 8.0 ppm (aromatic ring of terephthalic acid in a linear polyester), 7.8 ppm (aromatic ring of terephthalic acid in a cyclic ester), 6.9 and 7.4 ppm (biphenyl), 4.4 ppm ($-CH_2-O-CO-$), 4.0 ppm (biphenyl$-O-CH_2-$), 3.8 ppm ($-O-CH_3$), 3.6 ppm ($-CH_2-OH$ end groups), 2.5–3 ppm ($-CH_2-N-(CH_2-CH_2)_2-$, small signals belonging to the end groups), and 1.2–1.8 ppm (inner $-CH_2-$ groups of the spacer).

In the spectra of Pes-10H there are two broad signals for the N^+-H at 10.7 and 11.8 ppm. The signal at 10.7 ppm was ascribed to the end group, since its intensity decreased with increasing molar mass; the signal for N^+-H in C*n*-diol–HCls around 10 ppm supports this assignment [25]. The intensities of the N^+-H signals are 0.3–0.7H, indicating a partial loss of HCl during the purification procedure. However, the intensity is 0.9H for the polymer synthesized by procedure 2. Other signals are assigned as follows: 8.1–8.2 ppm (aromatic ring of terephthalic acid), 6.9 and 7.4 ppm (biphenyl) 4.7 ppm ($-CH_2-O-CO-$), 3.9 ppm (biphenyl$-O-CH_2-$), 3.8 ppm ($-O-CH_3$), 3.7 ppm ($-N^+-CH_2-CH_2-O-CO$), 3.3 ppm ($-N^+-CH_2$-side-chain), 1.7 ppm (overlapping peaks of $-N^+-CH_2-CH_2$-side-chain (1.76 ppm) and biphenyl$-O-CH_2-CH_2-$ (1.64 ppm), and 1.2 ppm (inner $-CH_2-$ groups of spacer). There are also signals for the end groups in the 3–4 ppm range that are overlapped with the above signals.

3.3. Thermal properties of Pes-n

DSC curves of Pes-*n* (Fig. 2) show melting of polyesters at temperatures between 60 and 100 °C followed by small endothermic fluctuations up to 180 °C. The crystallization is observed on cooling as a broad exotherm, which starts above 130 °C with peak temperature approximately 20–30 °C below melting temperature. The second heating scan is similar to the first one. The position of the melting peak is shifted for 1–2 °C but the position of the last peak remains the same. According to the DSC measurements these polyesters could be liquid crystalline with melting and isotropization temperatures decreasing with increasing numbers of CH_2 units in the side-chains. When heating

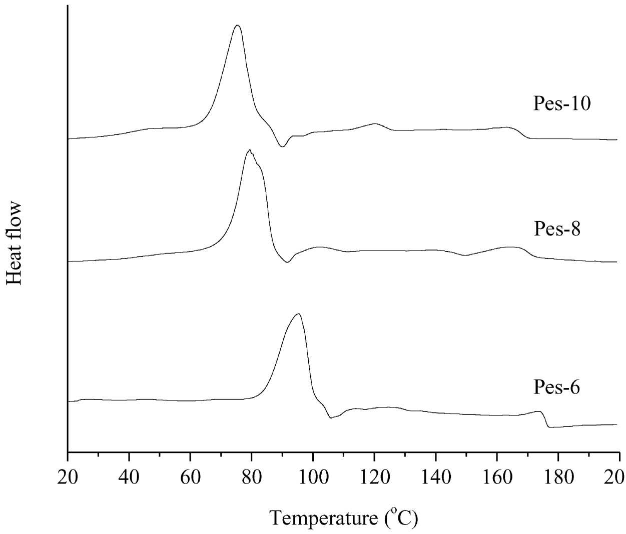


Fig. 2. DSC curves of side-chain polyesters (Pes-*n*).

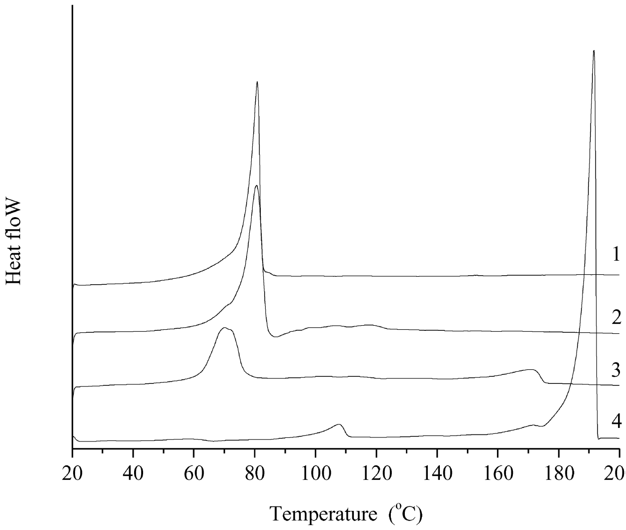


Fig. 3. DSC curves of Pes-10 fractions: 1—first, 2—second, 3—third, and 4—fourth fraction.

the polyesters under a polarizing optical microscope, melting was observed at temperatures determined by the DSC. The melt was viscous and the droplets formed did not coalesce. The melt started to flow and the droplets coalesced at 115 °C (Pes-6) and 125 °C (Pes-8 and Pes-10). A sanded texture, which turned to an isotropic liquid at temperatures above 170 °C was observed. The sanded texture slowly developed again upon cooling the isotropic melt. The same behavior (formation of a viscous melt (LC_1) that starts to flow at higher temperature (LC_2) and the formation of a sanded texture turning into an isotropic melt) has been already observed for liquid crystalline C*n*-diol hydrochlorides [25]. Therefore, we believed that these polyesters too were liquid crystalline.

However, the analysis of polyester fractions separated by column chromatography using chloroform (fractions 1 and 2) and then a chloroform/methanol (9/1) mixture (fraction 3) as an eluent revealed that endothermic fluctuations of Pes-*n* above 100 °C were due to the presence of cyclic oligomers. As an example, the DSC curves of the three fractions of Pes-10 are shown in Fig. 3. The first fraction with a M_w of 9380 g/mol melts at 83.0 °C and exhibits no liquid crystalline properties. The second fraction with a M_w of 6280 g/mol melts at 80.6 °C. Small endothermic transitions were observed at 101 and 124 °C. The third fraction with a M_w of 2950 g/mol melted at 70 °C and exhibited a small transition in the temperature region 100–120 °C, as well as a strong endothermic transition at 160–180 °C. Fraction 3 was again fractionated by column chromatography using $CHCl_3$. The resulting fraction 4, which represents only 12% of fraction 3, exhibits a small endothermic peak at 108 °C and an intensive melting peak at 191 °C, whereas its molar mass distribution is bimodal. Peak molar masses are 1340 and 2030 g/mol and their area ratio is 3:2. ^{1}H NMR shows no OH groups in fraction 4 and the ratio of diol to terephthalate is 1:1, indicating the presence of cyclic oligomers. It is known that cyclic esters are formed during the reaction of various glycols with terephthaloyl chloride at concentrations up to 15 times lower than we used [26,27]. It was found out that mostly monoesters were formed at lower solution concentrations, while at higher concentrations mostly dimers were obtained [27]. Cyclic esters have also been synthesized by trans-esterification of linear polyesters in boiling chlorobenzene solution [28]. According to our reaction conditions (relatively high solution concentration, low temperature) and the molar mass of fraction 4, it seems most probable that a cyclic dimer ($M_w = 1340$) was formed which melts at approximately 190 °C. Higher cyclic polyesters ($M_w = 2030$ g/mol) melt at somewhat lower temperatures; i.e. between 90 and 130 °C, as shown in the DSC curves of fractions 2 and 4. The melting temperature of cyclic oligomers in fraction 4 is 20 °C higher than in fraction 3, indicating that the melting temperature depends greatly on the presence of linear molecules. The melting temperatures of linear polyesters also seem to be influenced by the presence of cyclic oligomers. Further separation of cyclic oligomers and their analysis is in progress.

Linear Pes-*n* were obtained by the above-mentioned fractionation. The melting temperatures and melting enthalpies of the collected fractions of linear Pes-*n* having molar masses (M_w) in the range of 3100–9380 g/mol are summarized in Table 1. The melting temperature increases with increasing molar mass and decreases when the number of CH_2 units in the side-chain increases from 6 to 8, however, the melting point of Pes-10 is higher than PES-8. The melting enthalpies of Pes-6 and Pes-8 are practically the same, while that of Pes-10 is about 30% higher.

3.4. Thermal properties of Pes-*n*H

DSC curves of Pes-*n*Hs synthesized by procedure 1 exhibit multiple and not well-resolved peaks at the temperatures up to 210 °C where degradation starts

Table 1
Molar mass averages and thermal properties of collected fractions of linear Pes-*n*

Sample	M_w (g/mol)	M_n (g/mol)	M_w/M_n	T_m (°C)	ΔH_m (J/g)
Pes-6	7510	5790	1.30	92.0	31.9
	6360	4160	1.53	89.5	32.4
	3340	2500	1.34	79.0	33.7
Pes-8	6000	4340	1.38	80.2	30.1
	5300	4380	1.21	81.8	31.4
	3130	2380	1.32	72.3	33.5
Pes-10	9380	6980	1.34	83.7	41.1
	6280	3990	1.58	83.5	42.5
	3380	2100	1.61	74.2	45.5

(Fig. 4). Multiple peaks were ascribed to the presence of both linear polyester hydrochlorides as well as cyclic oligomeric hydrochlorides, both of which melt in a broad temperature range.

The melting of all Pes-*n*Hs was also followed by polarizing optical microscopy. The first droplets of melt were observed at 137 °C (Pes-10H), 160 °C (Pes-8H) and 180 °C (Pes-6H). A sanded texture was formed, which turned to an isotropic liquid at 200 °C (Pes-8H and Pes-10H) or 225 °C (Pes-6H). We did not observe any textures characteristic of liquid crystalline transitions, which confirmed that fluctuations in the DSC curves were a consequence of the presence of cyclic oligomers.

The thermal properties of linear Pes-*n*Hs were determined for the hydrochlorides synthesized by procedure 2, i.e. by adding concentrated hydrochloric acid to the THF solution of linear polyesters having molar masses $M_w = 6000-9380$ g/mol. The ^{1}H NMR spectrum of linear Pes-10H differs from the one in Fig. 1 only in the absence of signals belonging to cyclic oligomers (no shoulder at 8.0 ppm). The intensity of the N^+-H signals is 0.9H.

The melting curves of linear Pes-*n*Hs taken in the first heating scan are shown in Fig. 5. All three Pes-*n*Hs exhibit small transitions at temperatures below 100 °C. For Pes-6H and Pes-8H the transitions look like melting or recrystallization and were not observed on the second heating scan. Pes-10H exhibits a glass transition temperature, which was also observed in the second heating scan at 59 °C. The melting temperature of Pes-6H is 185 °C, whereas the melting of Pes-8H proceeds in two steps with peak temperatures at 155 and 172 °C. The lower melting point represents the melting of a small molar mass polymer. Namely, for Pes-8H prepared from the linear fraction of Pes-8 with molar mass M_w of 3130 g/mol melting proceeds in only one step with a peak temperature of 158 °C. Pes-10H exhibits cold crystallization just before melting at 182 °C.

In the second heating scan the DSC curves showed melting peaks at much lower temperatures (171 °C—Pes-6H, 148 °C—Pes-8H, 159 °C—Pes-10H) than in the first heating scan. Lowering of the melting point is probably a consequence of irregularities in the polymer chain, which might have formed due to thermal degradation of the polymer. Weight loss was calculated from the difference in the mass of the DSC pan before and after measurements (two heating scans up to 200 °C). The weight loss increases with increasing number of CH_2 units in the side-chain (1.6%—Pes-6H, 1.8%—Pes-8H and 4.6%—Pes-10H), which is in agreement with the observations concerning C*n*-diol hydrochlorides [25].

The melting of Pes-*n*H proceeds at approximately 100 °C higher than the melting of the parent Pes-*n*. The melting temperature decreases with increasing numbers of CH_2 units in the side-chain from 6 to 8. The melting point of Pes-10H is again somewhat higher than Pes-8H as was also observed in Pes-*n*.

3.5. X-ray spectroscopy

X-ray diffractograms of Pes-*n* (containing cyclic

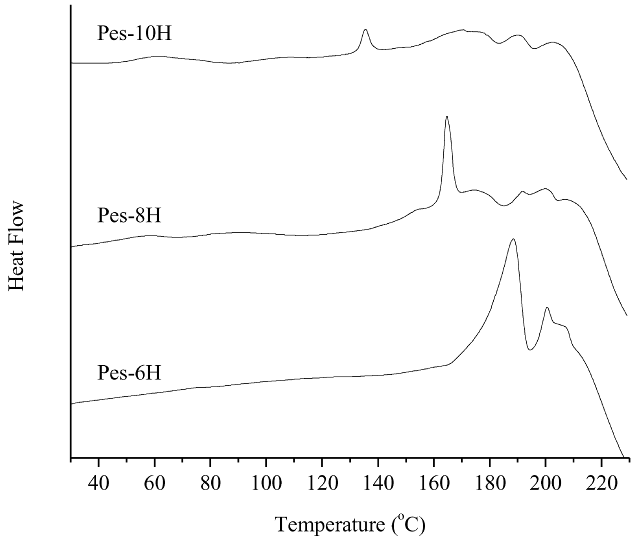


Fig. 4. DSC curves of polyester hydrochlorides synthesized by procedure 1.

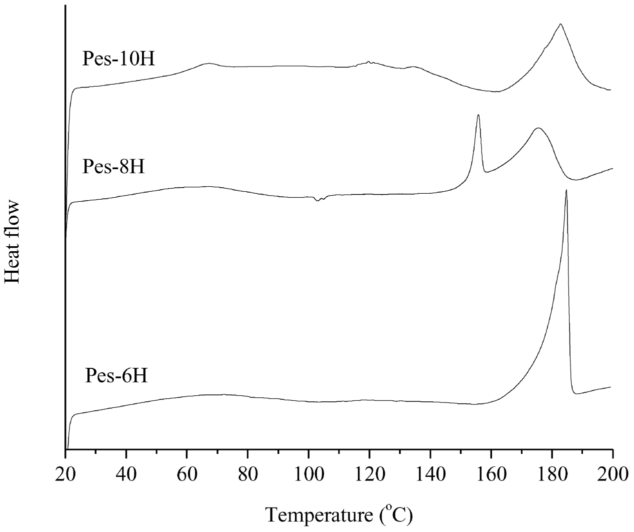


Fig. 5. DSC curves of linear polyester hydrochlorides (Pes-*n*H).

oligomers) taken at room temperature are shown in Fig. 6. In the small and middle-angle regions there are small Bragg reflections of the second, third, and higher orders, corresponding to the layer spacing (*d*) 3.32 nm (PES-6), 3.71 nm (PES-8), and 4.17 nm (PES-10). In the wide-angle region there are three Bragg reflections indicative of a smectic E phase as demonstrated for polyacrylates having the same mesogenic unit in their side-chains [29].

The X-ray diffractograms of Pes-6H and the parent linear Pes-6 are shown in Fig. 7. The diffractogram of linear Pes-6 is slightly different from the one in Fig. 6. All diffractions in linear PES-6 are shifted towards higher angles, i.e. smaller layer spacings (3.23 nm). It seems that the presence of cyclic oligomers increases the layer thickness.

The diffractogram of the polyester hydrochloride is similar to that of the polyester, although the diffractions are much weaker and not well resolved. In the small and middle-angle regions there are small Bragg reflections of the second and third order, corresponding to the layer spacing 3.37 nm. In the wide-angle region there is a shift of one reflection from 23.44° (0.39 nm) to 22.72° (0.40 nm). This reflection is most probably related to the interchain distance of the main chains. Due to the attachment of HCl to the nitrogen atom in the main chain the interchain distance is increased.

4. Conclusion

In the course of polyesterification of α-(bis(2-hydroxyethyl)amino)-ω-(4′-methoxy biphenyl-4-oxy) alkanes (6, 8, 10 CH_2 units) with terephthaloyl chloride the hydrochloride thus formed preferably reacts with the nitrogen atom in the polyester chain rather than with the triethylamine. Therefore, polyester hydrochlorides are formed instead of polyesters. The strength of the interaction between HCl and the nitrogen atom in polyester hydrochloride is weak and polyesters can be obtained from polyester hydrochlorides by extraction of HCl with water, and, vice versa, polyester hydrochlorides can be formed by adding HCl to a THF solution of the polyester. This feature makes reversible surface modification of these kinds of polyesters possible.

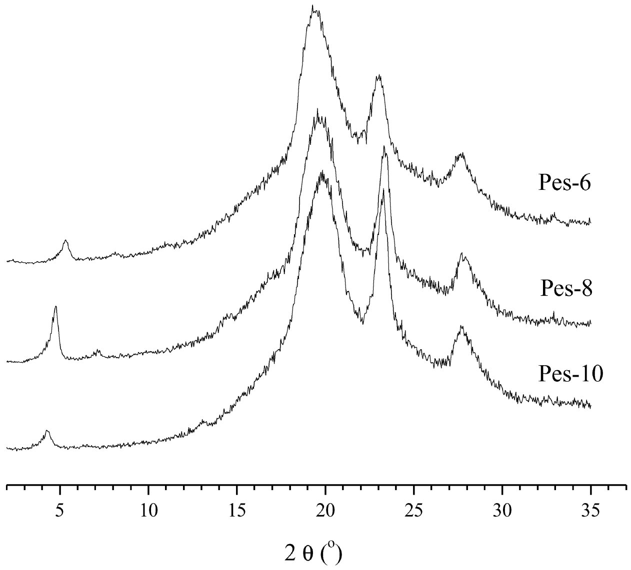


Fig. 6. X-ray diffractograms of Pes-*n* taken at room temperature.

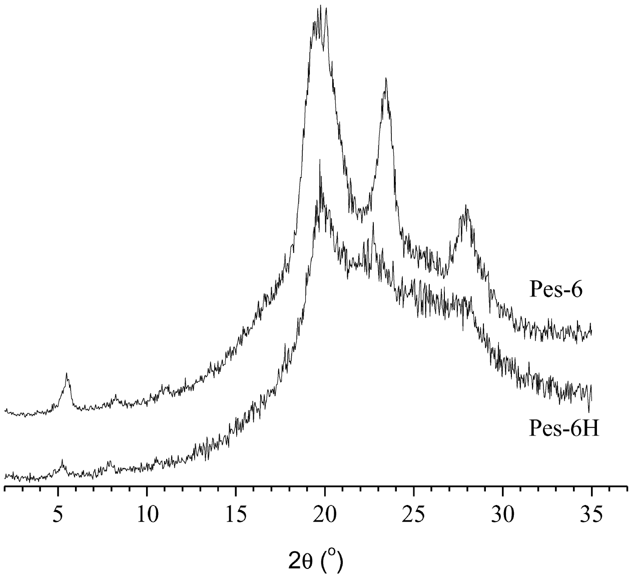


Fig. 7. X-ray diffractograms of Pes-6 and Pes-6H taken at room temperature.

Polyesters consist of linear polymers as well as cyclic oligomers, which exhibit higher melting temperatures than the linear polymers. Linear polyesters melt in the temperature range from 60 to 100 °C, while linear polyester hydrochlorides melt at the temperatures up to 200 °C, where they start to degrade.

Although no liquid crystalline phase transitions of polyesters and polyester hydrochlorides were found, an ordered structure was observed by XRD experiments and it was ascribed to a crystal smectic E phase.

Acknowledgements

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