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# Side-chain polyesters derived from adipoyl chloride and α-(bis(2-hydroxyethyl)amino)-ω-(4'- methoxybiphenyl-4-oxy) alkanes

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## Summary

A series of polyesters derived from adipoyl chloride and α-(bis(2-hydroxy ethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy)alkanes with different spacer lengths (Cn-diol, n=6,8,10) have been synthesized and characterized by NMR spectroscopy, SEC, DSC, and X-ray spectroscopy. All polyesters have a narrow distribution of molar masses (1.3-1.5), melting temperature of 55-62°C, and they melt in a narrow temperature range of 7-11°C. Although no liquid crystalline phase transitions were found, an ordered structure was observed by XRD experiments and was ascribed to a crystal smectic phase.

## Introduction

Polyesters containing long side-chains have received increasing attention over the past two decades. There are two main types of side-chain polyesters. The first type is a group of the aliphatic and aromatic polyesters with alkyl side-chains [1-3] which do not form liquid crystalline phase. The second type is a group of side-chain liquid crystalline (SCLC) polyesters [4-16]. The LC properties of the later depend on the polymer chemical structure, *i.e.* type of the main chain, and the type, length and number of side chains. Side chains can be aliphatic [15,16] but mostly they have a mesogenic group bonded to a main chain via aliphatic spacer [4-14]. A main chain might be rigid rod or flexible. Rigid rod polyesters with aliphatic side chains form sanidic layer structure [15,16]. It has been observed that polyesters having one or two side chains per unit form liquid crystals while those, having four side-chains per unit, do not [16].

The SCLC polyesters with flexible main chain have attracted considerable attention as a potential medium for reversible optical data storage and holography [4-8].

The aim of the present work was to synthesize novel, low molar mass SCLC polyesters which could be further used to prepare SCLC polyurethanes. Since LC diols, namely α-(bis(2-hydroxyethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy) alkanes with different spacer lengths (Cn-diol, n=6,8,10), as well as their analogues, have already been proven to induce liquid crystalline properties in polyurethanes [17-22] we used them for the preparation of the SCLC polyesters. However, by using adipoyl chloride with four methylene units, instead of hexamethylene diisocyanate (HDI) with six methylene units as in polyurethane, the liquid crystalline properties were lost. This was unexpected because adipoyl chloride has previously been used for the synthesis of liquid crystalline polyesters [23-25].

## Experimental

### *Materials*

4,4’ dihydroxybiphenyl, dimethyl sulfate, dibromo alkanes, diethanolamine, adipoyl chloride, $K_2CO_3$ (Aldrich), and NaOH (Kemika, Zagreb) were used as received. Solvents 1,2-dichloroethane and pyridine (Aldrich) were dried over $CaH_2$ prior to their use.

### *Synthesis of α-(bis(2-hydroxy ethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy)alkane (Cn-diol, n=6,8,10)*

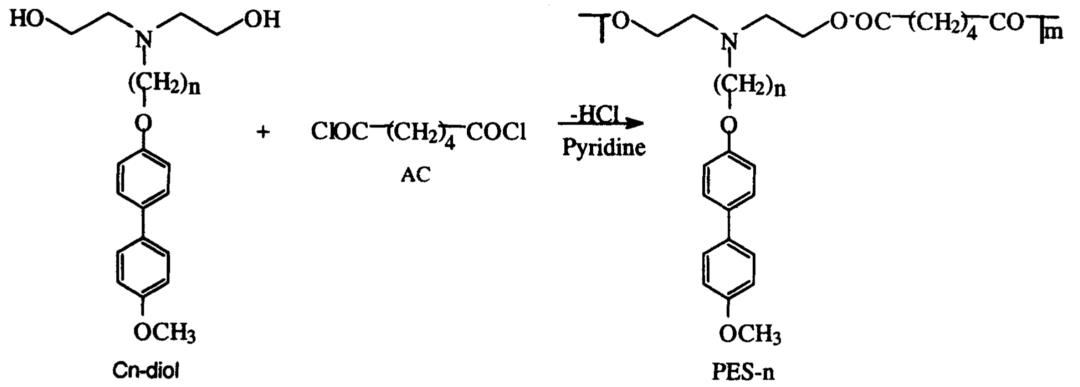
The synthesis of Cn-diols is described elsewhere [17].

### *Synthesis of polymers*

The Cn-diol (3.3 mmol) was dissolved in a mixture of 15 ml 1,2-dichloroethane and 1 ml pyridine under an inert ($N_2$) atmosphere. The reaction vessel was then sealed with a rubber septum and adipoyl chloride (AC) was added by syringe. The Cn-diol : AC molar ratios (X) were 1:0.8, 1:0.9 and 1:0.98 (X=80, 90, 98). The mixture was heated to 70°C and kept at this temperature for 4 hours. 75 ml of water was then added to react with any unreacted AC and to extract pyridine hydrochloride and pyridine. The water was changed five times (every 30 minutes), then the mixture was mixed at room temperature overnight. The dichloroethane solution was dried on a rotatory evaporator. Samples were purified by dissolution in 100 ml boiled ethanol. The polyesters (designation: PES-n-X, n=6,8,10, X=80, 90, 98) remained at the bottom of the flask as viscous liquids. Ethanol was removed and purification was repeated twice using 50 ml ethanol. The polyesters were dried *in vacuo* at 55°C. The reaction is depicted in Scheme 1.

### *Characterization*

$^1H$ and $^{13}C$ NMR spectra were recorded at 25°C on a Varian VXR-300 spectrometer using $CDCl_3$ as the solvent and TMS as the internal standard. Average molar masses



**Scheme 1: The reaction of α-(bis(2-hydroxy ethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy) alkane with adipoyl chloride; n=6, 8, 10.**

and molar mass distributions were determined relative to polystyrene standards by size exclusion chromatography (SEC) on a modular Perkin-Elmer liquid chromatograph equipped with a DAD detector working at a wavelength of 254 nm. A PL Mixed E column with a precolumn and THF as an eluent with a flow rate of 1 ml/min were used. Differential scanning calorimetry (DSC) analysis was performed on a Perkin-Elmer Pyris 1 calorimeter. The samples were heated twice and subsequently cooled in the temperature range from 25 °C to 90°C. Heating and cooling rates were 10°K/min. After the heating or cooling cycle the samples were maintained for 3 min at 90°C or 25°C, respectively. X-ray diffraction patterns were taken on a Siemens D-5000 diffractometer using Cu $K_\alpha$radiation ($\lambda$=1.54Å) in 0.04° steps from 2-35° (in 2θ) with 2 s per step.

## Results and discussion

All polyesters (PES-n) are soluble in the following solvents: dimethylformamide, dimethylsulfoxide, acetone, tetrahydrofuran, chloroform, dichloroethane, and toluene. They are insoluble in hexane. The yields of polyesters depend on the molar ratio of the reactants as shown in Table 1.

**Table 1: The yield of PES-n in dependence on reactants molar ratio.**

| Ratio of reactants Cn-diol:Acl | PES-6 Yield (%) | PES-8 Yield (%) | PES-10 Yield (%) |
|---|---|---|---|
| 1 : 0.8 | 41.5 | 42.1 | 47.3 |
| 1 : 0.9 | 51.5 | 59.3 | 63.6 |
| 1 : 0.98 | 60.1 | 64.1 | 70.9 |

$^1$H and $^{13}$C NMR spectra confirm the predicted structures of all the synthesized polyesters. $^{13}$C spectrum of PES-8-90 is shown as a representative example in Figure 1. The signals are assigned as follows: 173 ppm (-COO-), 114-159 ppm (biphenyl), 68 ppm (biphenyl-O-$CH_2$-), 62 ppm (-O-CO-$CH_2$-), 50-60 ppm (-$CH_2$-N-($CH_2$-$CH_2$)- and -O-$CH_3$ (55.2ppm)), 20-40 ppm (-$CH_2$- groups of adipic acid and inner -$CH_2$- groups of spacer).

Molar masses of the synthesized polyesters are relatively low (3300-5250 g/mol) and depend on the molar ratio of the reactants. SEC chromatograms of PES-10 are shown in Figure 2. The molar mass distributions are narrow, from 1.3 to 1.5. (Table 2).

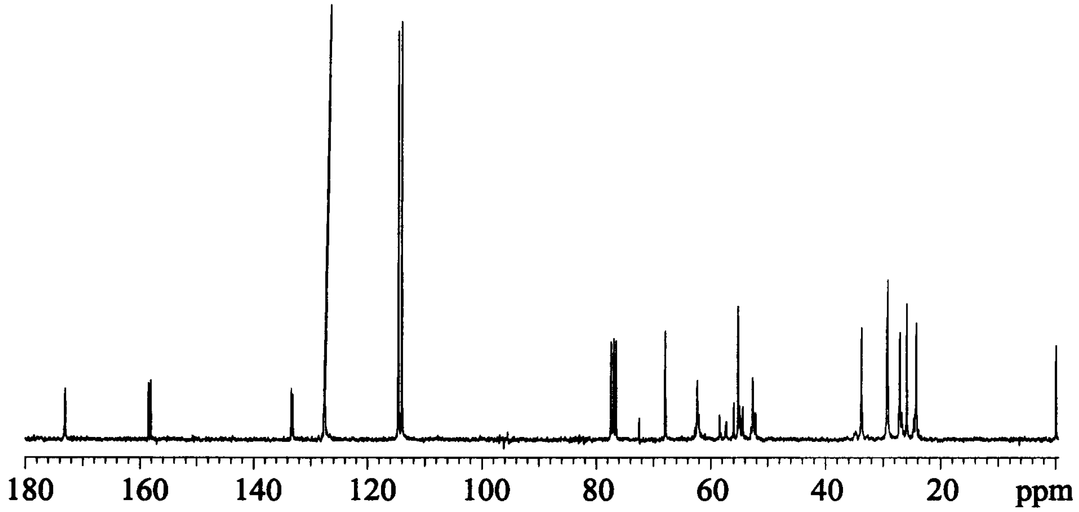


Figure 1: $^{13}$C NMR spectra of PES-8-90.

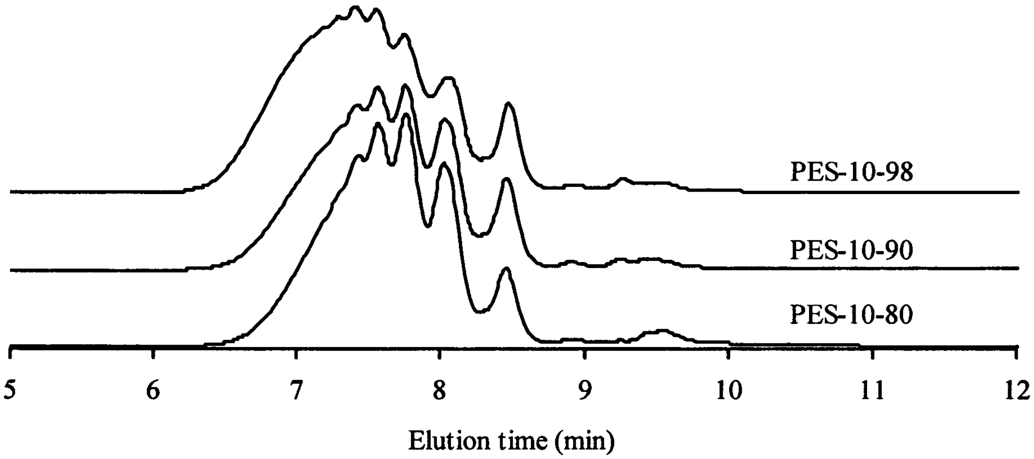


**Figure 2: SEC chromatograms of PES-10 synthesized at different molar ratios of reactants.**

Onset melting temperatures of C6, C8 and C10-diols are 108°C, 105.4°C and 102.5°C respectively, whereas polyesters melt at lower temperatures than diols. The melting points of polyesters decrease with increasing molar mass. It appears that incorporation of methylene groups between diols enhances the mobility of macromolecules, increases $\Delta S_m$ and therefore reduces $T_m$. The effect is more pronounced in oligomers, as can be observed by DSC. Unpurified polyesters melt in a broad temperature range from 50 to 95°C. After purification they melt at lower temperatures in a narrow temperature range between 7°C (PES-8, PES-10) and 11°C (PES-6) (Figure 3). The width of the melting peak depends on the reaction conditions, purification procedure, crystallization conditions, and spacer length. Isothermally crystallized PES-8-98 (16h at 53.5°C) melts (99.5%) in a temperature range of only 3.5°C which is comparable to the melting range of indium (99.5%, in a temperature range of 2°C). A study of the crystallization kinetics is in progress.

The melting temperature of polyesters depends not only on molar mass, but also on the length of the side chains. As expected, the melting temperature increases with the number of $CH_2$ units in the side chain. The differences are small, only 2-3°C, which is in agreement with those for polyurethanes [17]. The enthalpy of melting decreases with increasing molar mass of polyester and with the length of the side chain. The melting temperatures and enthalpies for all the synthesized polyesters are summarized in Table 2.

As it is known that liquid crystalline transitions are sometimes kinetically controlled [20,26], DSC experiments were also performed at a cooling rate of 2 and 0.5°C/min. Nevertheless, no liquid crystalline transitions were observed.

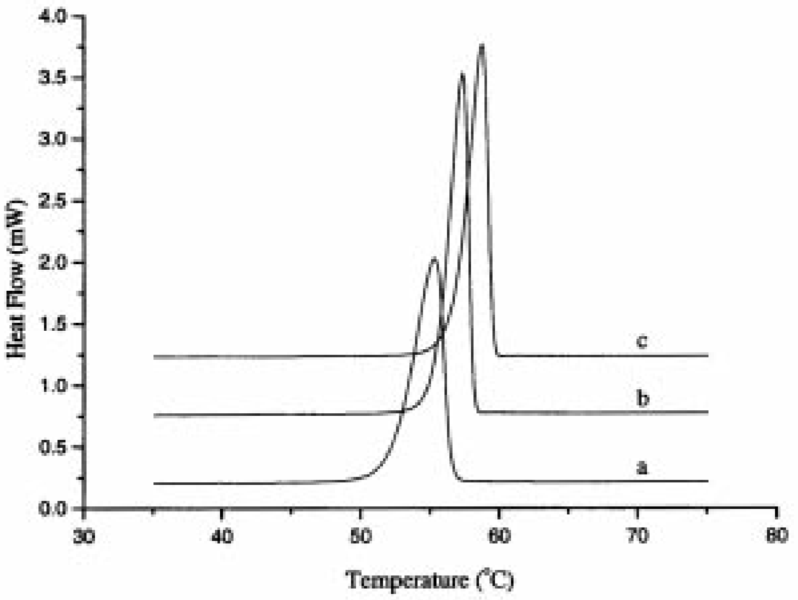


Figure 3: DSC melting curves of PES-6-98 (a), PES-8-98 (b) and PES-10-98 (c).

However, X-ray powder diffraction experiments at room temperature give some evidence of ordered structure in PES-n (Figure 4). In a middle-angle region there are Bragg reflections of the second, third, and higher orders, corresponding to the layer spacing (d) 3.02nm (PES-6), 3.28nm (PES-8) and 3.68nm (PES-10). These layer spacings are 1.6 times (PES-6) and 1.55 times (PES-8 and PES-10) the lengths of the fully extended mesogenic unit together with the spacer (trans-planar conformation), thus indicating the partially interdigitated bilayer structure. It appears that on cooling from the isotropic melt, side chains of polyesters organize in a layered smectic structure, which as a consequence of attraction forces between side chains, crystallize to form a crystal smectic phase. The signals in the wide-angle region have been ascribed to side chain crystallization, which supports above explanation. In polyurethanes which were synthesized from the same diols [17,19] and hexamethylene diisocyanate, the side chains are more separated and the attraction forces are weaker, so stable liquid crystals could be formed.

The comparison of the X-ray diffractograms of PES-8 and C8-diol (Figure 5) shows that in the wide-angle region the diffractograms are almost the same, except that the reflections of polyester are shifted for about 0.1-0.3° towards lower angles and, contrary to C8-diol, the sharp reflection at 23.2° is more intensive than the reflection at 19.4°. In the middle-angle region the diffractograms are also very similar. Closer examination reveals that some reflections are shifted towards lower angles, and some are shifted towards higher angles. The intensity of the reflections at 5.8°, 11.7° and 16.0° in the diffractogram of C8-diol is much higher than that of the PES-8 reflections in similar positions.

Low intensity of the peaks in middle-angle region has also been observed in the diffractograms of polyurethanes synthesized from diols of this kind [18].

**Table 2: Weight and number average molar masses, ($M_w$, $M_n$), polydispersity index ($M_w/M_n$) , melting temperatures ($T_m$) and melting enthalpies ($\Delta$ $H_m$) of polyesters.**

| Sample | $M_w$ (g/mol) | $M_n$ (g/mol) | $M_w/M_n$ | $T_m$ (°C) | $\Delta$ $H_m$ (J/g) |
|---|---|---|---|---|---|
| PES-6-80 | 3300 | 2550 | 1.30 | 57.5 | 30.7 |
| PES-6-90 | 4000 | 2950 | 1.36 | 55.5 | 30.1 |
| PES-6-98 | 4700 | 3300 | 1.42 | 55.3 | 29.4 |
| PES-8-80 | 3950 | 3100 | 1.26 | 59.5 | 29.7 |
| PES-8-90 | 4800 | 3200 | 1.49 | 58.8 | 29,4 |
| PES-8-98 | 5250 | 3750 | 1.40 | 57.3 | 28.6 |
| PES-10-80 | 3900 | 3000 | 1.30 | 61.8 | 28.5 |
| PES-10-90 | 4100 | 3000 | 1.37 | 61.0 | 28,2 |
| PES-10-98 | 4950 | 3400 | 1.47 | 58.8 | 27.6 |

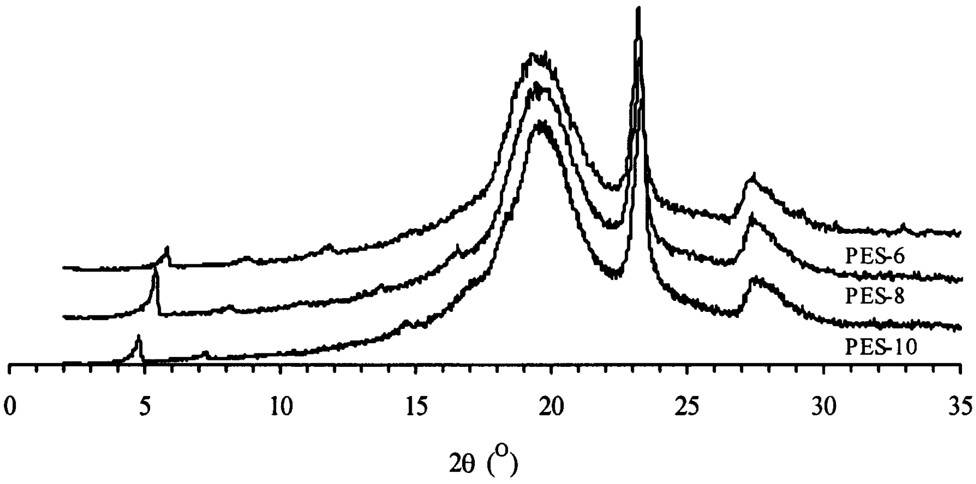


Figure 4: X-ray diffractograms of PES-n.

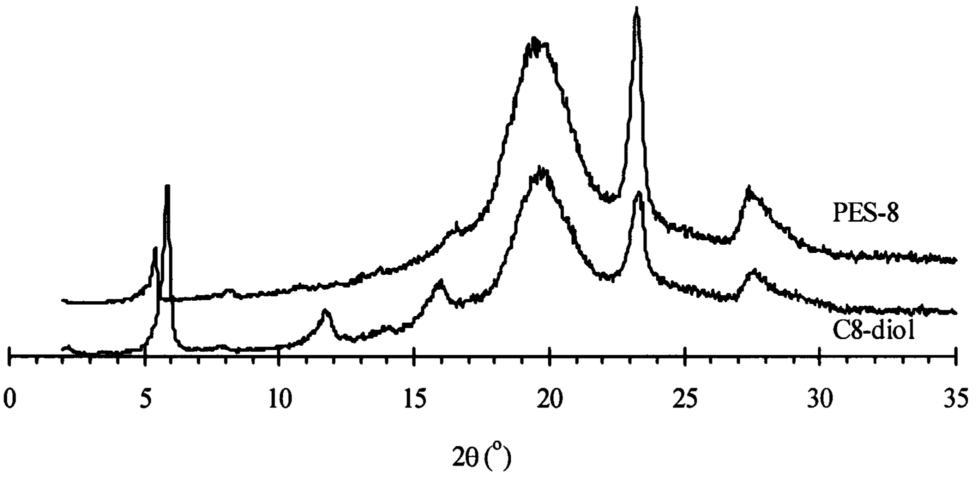


Figure 5: The comparison of X-ray diffractograms of C8-diol and PES-8.

## Conclusions

A series of low molar mass polyesters were synthesized from adipoyl chloride and α-(bis(2-hydroxy ethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy)alkanes with different spacer lengths in dichloroethane using pyridine as an acid acceptor. Polyesters of different molar masses (3300-5200g/mol) having low polydispersity index (1.26-1.49) were synthesized using molar ratios of Cn-diol : AC = 1 : 0.8, 0.9 and 0.98. All the polyesters melt between 55-62°C. The melting point and the melting enthalpy of the polyesters decrease with increasing molar mass, and increase with the increasing spacer length. No liquid crystalline phase transitions were found during cooling and heating by DSC, whereas an ordered structure was observed by XRD experiments and was ascribed to a crystal smectic phase.

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