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The influence of side-chain and main-chain spacer lengths on the thermal and structural properties of diethanolamine based side-chain polyesters

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Summary

A series of linear side-chain aliphatic polyesters have been synthesized from α-(bis(2-hydroxyethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy) alkanes and aliphatic acid chlorides. The side-chain and main-chain spacer lengths were varied and their influences on thermal and structural properties of polyesters, as determined by DSC and X-ray diffraction, are discussed.

Introduction

Side-chain (SC) or comb-shaped polyesters are attractive members of the polymer family because their properties, such as crystallinity, melting temperature etc., can be tailored by the choice of constituent units. Main-chain can be fully aromatic [1,2,3], aromatic-aliphatic [4,5] or fully aliphatic [6]. Side chains, which can be bound to diol or/and acid unit, may be aliphatic [1-6] or with a mesogenic group and an aliphatic spacer. [7-16] Polyesters with mesogenic groups in the side chain can be amorphous, crystalline or liquid crystalline (SCLC).

Diethanolamine is rarely used in the synthesis of polymers. However, it allows making versatile products as well as subsequent modification of polymers. So far, N-substituted diethanolamines were used to synthesize LC [17,18] or non-LC polyesters [19-22], LC polyurethanes [23-27] and hyperbranched polymers [28,29]. Nitrogen atoms in diethanolamine based polyesters are highly basic and therefore able to be quaternized by acids. The properties of polyester hydrochlorides greatly differ from parent polyesters [21].

The aim of our work was to investigate the effect of side-chain and main-chain spacer lengths on the thermal and structural properties of polyesters based on diethanolamines with a methoxybiphenyl mesogenic group and aliphatic acids. We varied the number of CH_2 units in the main chain (1, 2, 4, 6, 8) as well as in the side chain (6, 8, 10). The synthesis, the thermal and structural properties of the polyesters are discussed.

Experimental

Materials

The synthesis of α-(bis(2-hydroxyethyl)amino)-ω-(4'-methoxy biphenyl-4-oxy) alkanes with different spacer lengths (Cn-diol, n=6,8,10) has been described elsewhere [25]. Acid chlorides (malonyl chloride (MA), succinyl chloride (SUC), adipoyl chloride (AD), suberoyl chloride (SUB), sebacoyl chloride (SE), and 3-methyladipoyl chloride (MAD)) were obtained from Aldrich. They were used as received.

Synthesis of polymers

The Cn-diol (3.3 mmol) was dissolved in a mixture of 15 ml 1,2-dichloroethane and 1 ml triethylamine (TEA) under an inert (N_2) atmosphere. The reaction vessel was then sealed with a rubber septum and acid chloride (AC) was added by syringe. The Cn-diol : AC molar ratio was 1:1. 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 TEA hydrochloride and TEA. The water was changed five times (every 30 minutes), then the mixture of organic and aqueous phases 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 remained at the bottom of the flask as viscous liquids. Ethanol was removed and purification was repeated twice using 50 ml ethanol. Finally, the polyesters were dried *in vacuo* at 55°C. The reaction is depicted in Scheme 1. The following designation of polyesters is used throughout the text: for example P-nMA stands for polyester prepared with Cn-diol with n (6, 8 or 10) CH_2 groups and malonyl chloride.
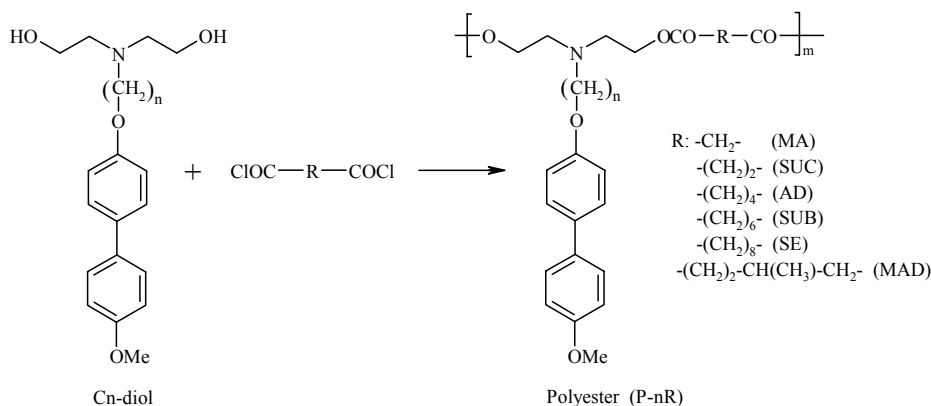
Scheme 1: The reaction of α-(bis(2-hydroxy ethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy) alkane with acid chlorides; n = 6, 8, 10.

Characterization

^{1}H 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 (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. X-ray diffraction patterns were taken on a Siemens D-5000 diffractometer using Cu K$_\alpha$ radiation (λ=1.54Å) in 0.04^o steps from 2-35° (in 2θ) with 2 s per step.

Results and discussion

The weight-average molar masses (M$_w$) of polyesters synthesized from MA (P-nMA), SUC (P-nSUC), AD (P-nAD), and MAC (P-nMAD) were 4500-5500 g/mol and the polydispersity indexes were 1.7-2.1. The M$_w$ of polyesters synthesized from SUB (P-nSUB) and SE (P-nSE) were 9000-16000 g/mol, with polydispersity indexes 2.0-3.9.

^{1}H NMR spectra confirmed the predicted structures of all the synthesized polyesters. The signals are assigned as follows: 6.9 and 7.4 ppm (biphenyl), 4.1 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 1.2-2.4 ppm (inner -CH_2- groups of the spacer and acids). There were no signals at 10.7-11.8 ppm indicating the presence of polyester hydrochloride [21].

Thermal properties

Onset melting temperatures of C6, C8 and C10-diols are 108°C, 105.4^{o}C and 102.5^{o}C respectively, whereas polyesters melt at lower temperatures than diols due to reduced number of OH groups and corresponding dipole interactions [23]. The DSC curves of aliphatic polyesters mostly exhibit one melting peak, meaning that all polyesters are crystalline and do not exhibit LC behavior. We tried to suppress the crystallization using branched 3-methyladipoyl chloride imposing steric hindrance to dense main-chain packing. Nevertheless, the P-nMAD also exhibits only melting. It can be concluded that for the synthesized polyesters, the crystallization could not be suppressed by changing the length or mobility of the main chain spacer.

The influence of the length of both spacers, i.e. of the acid residue and the side-chain, on the melting temperature can be seen in Figure 1. The peak melting temperatures were taken on the second heating scan to avoid the effect of thermal history on the sample. The melting temperatures (T$_m$) of side-chain polyesters with a given side-chain length decrease with increasing acid residue length, which is the opposite of what is seen in common aliphatic polyesters [30], but in agreement with observations on side-chain polyesters [13,15].

The influence of the side chain length on T$_m$ is not so straightforward (Figure 1). The T$_m$ values of P-nAD and P-nSE decrease with decreasing side-chain length. Results for other polyesters scatter and no correlation could be found. This can be explained by the presence of cyclic oligomers, which influence the T$_m$ value of linear polyesters. This phenomena has already been observed in side-chain polyesters synthesized from Cn-diols and terephthalic acid (P-nT) [21].
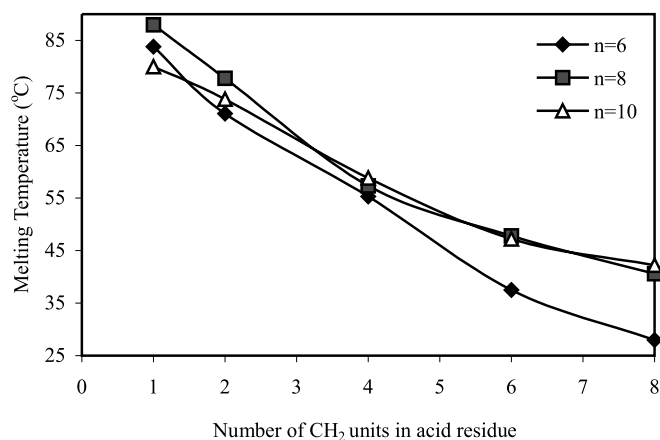
Figure 1: The influence of the acid residue and side chain length on the melting temperature of polyesters (n – number of CH$_2$ units in the side chain).

In the aliphatic polyesters described in this article cyclic oligomers were detected by DSC only in P-8MA and P-10MA. The small melting peaks of cyclic oligomers were about 10°C above the melting peaks of the related linear polyesters. In other polyesters the presence of cyclic oligomers could not be detected by DSC. It was deduced from polarizing optical microscopy (POM), except in the case of P-nAD. Melting of the polyesters was observed by POM at the same temperatures as determined by DSC. First, a sanded texture was formed which gradually turned into an isotropic melt at heating and then reformed again at cooling. Similar behavior was observed in cycle-containing P-nT. Conversely, P-nAD showed no characteristic sanded texture above the T$_m$ and turned directly into an isotropic melt, thus indicating no cyclic oligomers. On cooling from the isotropic melt a focal conic texture was formed.

Melting enthalpies are 24-30 J/g for all polyesters. In most cases the ΔH_m decreases with increasing side-chain length. The two exceptions are P-8SUC (too low value) and P-10SUB (too high value), which are most probably the consequence of anomalies in chain packing and crystalline structure as is explained below. The results are presented in Table 1.

Table 1: Melting temperatures and enthalpies of polyesters.

	n=6		n=8		n=10	
	T$_m$ (^{o}C)	ΔH_m (J/g)	Tm (^{o}C)	ΔH_m (J/g)	Tm (^{o}C)	ΔH_m (J/g)
P-nMA	83.8	28.3	88.0	26.3	80.0	23.8
P-nSUC	71.1	29.9	77.8	26.2	73.8	27.7
P-nAD	55.3	29.4	57.3	28.6	58.8	27.6
P-nSUB	37.5	24.7	47.8	24.0	47.2	26.6
P-nSE	28.0	27.4	40.6	25.3	42.2	24.9
P-nMAD	52.5	29.9	46.1	28.8	53.3	28.6

X-ray diffraction

In the small and middle-angle region there are small Bragg reflections of the first, second and third order indicating smectic structure (Figure 2). Not all reflections are present in all diffractograms. In the wide-angle region there are three Bragg reflections. Similar diffractograms were obtained for side-chain polyacrylates having the same mesogenic unit and were ascribed to the crystal smectic E phase [31]. The only exceptions are P-8SE and P-10SE where an additional diffraction between the second and the third order diffractions appears indicating hexagonal arrangement within the layer.
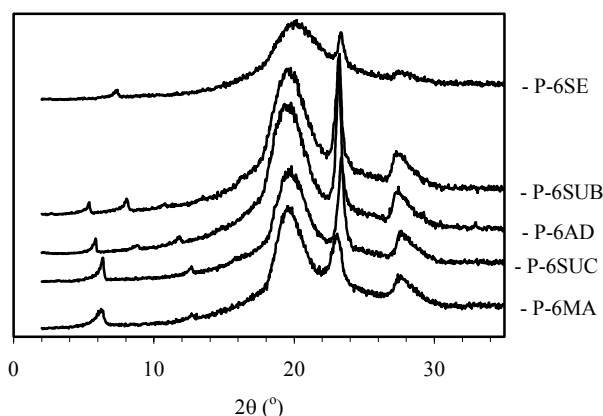

Figure 2: X-ray diffractograms of polyesters.

Table 2: Layer thickness of polyesters P-nR smectic crystals as calculated from X-ray diffractograms.

| | n=6 | n=8 | n=10 |
	d (nm)	d (nm)	d (nm)
P-nMA	2.83	3.13	3.53
P-nSUC	2.78	3.16	3.45
P-nAD	3.02	3.28	3.68
P-nSUB	3.27	3.53	3.78
P-nSE	3.65	3.88	4.22

The smectic layers in SC polymers are usually presented as stacks of side-chains, which might form monolayers or bilayers. In all schematic presentations the backbones are presented as a flat discs between layers [32-34]. These discs are supposed to be thin and therefore the layer spacing (d) of SC polymers is usually compared with the side-chain length (L); the d/L ratio is used to predict the type of smectic layer, phase and tilt angle [12,18,35]. When the polymer backbone is polyacrylate, polystyrene or a similar type, whose side-chains are close together, this approach is valid. In SCLC polyesters it was found that not only the side-chains but also the backbone might be part of a smectic layer [7]. In this case the layer thickness depends on the side-chain as well as on the main-chain spacer length. The layer thickness increases with increasing main-chain spacer length until its length becomes longer than the side-chain. Then the structure of the LC phase changes and layer thickness decreases. Recently, this prediction has been confirmed by NMR

spectroscopy [36]. Though the analyzed polyesters are not liquid crystals but are smectic crystals, our observations are similar. In Table 2 it can be seen that the values of layer spacing (d) increase in dependence on the number of CH_2 units in the side chain as well as in the main chain.

The influence of the main-chain spacer length on layer spacing of P-nR

Generally, the layer thickness increases by increasing main-chain spacer length, as shown in Table 3. This is possible only in cases where the main-chain spacer is part of a smectic crystal and not just a sublayer. The only exceptions are P-nMA and P-nSUC (1 and 2 CH_2 units), where the layer spacing is practically the same or even decreased. The layer spacing of P-nSUC could be the same as that of P-nMA only when the -CH_2-CH_2- group in P-nSUC is oriented perpendicular to the director, otherwise it should be increased. The deviations can be explained by steric effects, which might extend or shrink the layer spacing.

Table 3: The differences in layer spacing thickness by increasing the main-chain and side-chain spacer lengths.

	n=6	n=8	n=10
	Δd (nm)	Δd (nm)	Δd (nm)
P-nMA$\rightarrow$ P-nSUC	-0.05	0.03	-0.08
P-nSUC$\rightarrow$ P-nAD	0.25	0.11	0.23
P-nAD$\rightarrow$ P-nSUB	0.24	0.26	0.10
P-nSUB$\rightarrow$ P-nSE	0.38	0.35	0.44

Further increases in the main-chain (acid residue) spacer length (from P-nSUC to P-nSE) increase the layer spacing. The increase in layer spacing from P-6SUC to P-6AD and further to P-6SUB is 0.24 and 0.25 nm respectively, which corresponds to the increase in the calculated length (0.25 nm for two CH_2 groups). In polyesters with 8 and 10 methylene units in the side chain the situation is more complex. The increase in layer spacing is of the same order (0.23 and 0.26 nm) while for two polyesters it is much lower (0.11 nm for P-8SUC$\rightarrow$ P-8AD and 0.10 nm for P-10AD$\rightarrow$ P-10SUB). From the melting enthalpies presented in Table 1 and by comparison with the differences in layer thickness of other P-nR presented in Table 3 (an increase from P-8MA to P-8SUC is positive, other values are negative, increase from P-10SUB to P-10SE is 0.44 nm, comparing to 0.35 and 0.38 nm for m=6 or 8), we can assume that P-8SUC forms the thicker layers and P-10SUB forms the thinner layers as expected. The increase in layer spacing from P-nSUB to P-nSE (0.35-0.44 nm) is higher than expected from the calculated length for two CH_2 units and from the differences for other P-nR (Table 2). This is a consequence of a hexagonal packing of molecules within a layer as can be concluded from X-ray diffractograms.

The influence of the side-chain spacer length on the layer spacing of P-nR

The layer spacing increases by increasing the side-chain length for 0.23 to 0.41 nm (Table 4). When n is increased from 6 to 8 methylene units the layer spacing increases by $\approx$0.25 nm, except in the case of P-nMA (0.30 nm) and P-nSUC (0.38 nm). A much higher increase in P-nSUC is a consequence of the thicker P-8SUC layer as explained above. When n is increased from 8 to 10 methylene units the layer spacing increases

by 0.34-0.41 nm, again with two exceptions, which are also a consequence of the thicker P-8SUC and the thinner P-10SUB layer.

Table 4: The influence of the increase in side-chain spacer length on the layer spacing of polyesters P-nR

	n=6→8 Δd (nm)	n=8→10 Δd (nm)
P-nMA	0.30	0.40
P-nSUC	0.38	0.29
P-nAD	0.24	0.41
P-nSUB	0.26	0.25
P-nSE	0.23	0.34

The calculations of molecular lengths were performed on P-6AD using HyperChem 7 (Hypercube, Inc.). It appeared that the calculated length from the methoxy group on the biphenyl to the oxygen atom on the adipic acid bonded to another diol is 2.85 nm, which is very close to the layer spacing (3.03 nm). This leads to the conclusion that P-nR form monolayered smectic crystals. The increase in layer spacing by 0.25 nm by increasing chain length by 2 CH_2 units is usually related with monolayer structure, and the higher increase is related to bilayer structure. On the basis of these results we can therefore infer that the synthesized polyesters form monolayered crystals. The deviations in layers spacings are probably the consequence of steric hindrance, which induces differences in main-chain and/or side-chain conformations, and consequently in the layer spacings. More accurate results could probably be obtained from X-ray diffraction patterns of oriented samples.

The X-ray diffractograms of branched P-nMAD are similar to the diffractograms of other polyesters. The calculated layers spacings are 3.18, 3.40, and 3.81 nm for P-6MAD, P-8MAD, and P-10MAD respectively. The values are higher than for P-nAD and smaller than for P-nSUB, except for P-10SUB, whose layer thickness is smaller than expected as previously discussed. Apparently, the bulky methyl group precludes denser chain packing and leads to larger layer spacings than in P-nAD.

Conclusions

A series of polyesters with different main-chain and side-chain spacer length were synthesized from aliphatic acid dichlorides (with 1, 2, 4, 6 and 8 CH_2 units and branched 3-methyladipoyl chloride) and mesogenic α-(bis(2-hydroxyethyl)amino)-ω-(4'-methoxybiphenyl-4-oxy)alkanes with 6, 8, and 10 CH_2 units. The influence of the main-chain and side-chain spacer lengths on their thermal and structural properties was investigated by DSC and XRD.

The melting temperature of polyesters decreases with increasing main-chain spacer length, whereas the influence of side-chain length is not so straightforward. The melting temperature of polyesters synthesized from adipoyl and sebacoyl chloride increase with increasing side-chain length. The results for other polyesters scatter, most probably due to the presence of cyclic oligomers.

An ordered structure was observed by XRD experiments and was ascribed to a crystal smectic phase. The layer thickness depends on the main-chain as well as on the side-chain length. Besides, it is also influenced by the denser or looser packing of molecules in the smectic crystal imposed by steric effects.

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