LIQUID CRYSTALLINE POLYESTERS WITH AZOBENZENE SIDE CHAIN MESOGENIC UNITS†

Aneta Mirčeva, Miroslav Huskić, Majda Žigon
National Institute of Chemistry, 1000 Ljubljana, Slovenia

†This paper is dedicated to the late Professor Dr. Drago Kolar

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Abstract

A series of low molecular weight side-chain liquid crystal polyesters with azobenzene side chain mesogenic units were synthesised by transesterification of dimethyl terephthalate and α-[bis(2-hydroxyethyl)amino]-ω-(4-methoxyazobenzene-4'-oxy) alkanes (Cn-diol, n=8, 10, 12). Monotropic low molecular weight liquid crystalline polyesters were synthesized using a reactant molar ratio of 1:1.2; upon cooling from the isotropic phase they form a smectic phase. With reactant molar ratios of 1:1.4 and 1:1.6 only oligomers were formed, which melt over a broad temperature range, thus preventing the determination of possible mesophase transitions.
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Introduction

Side-chain liquid crystalline polymers (SCLCP) have been the subject of intensive research work during the last decade. Their unique properties and applications are due to their specific structure and the possibility of rearranging their structural units. SCLCPs consist of polymer backbones onto which the low molecular weight mesogenic units are attached by flexible spacers. Since SCLPs combine the mechanical and processing properties of polymers with the anisotropic properties of low molecular weight LCs, they can be applied in many different areas: in nonlinear optics,[1-3] optical information data storage devices,[4-6] as stationary phases in chromatography (GC, SFC, HPLC),[7-9] for the preparation of separation membranes,[10] and as solid polymer electrolytes,[11] to name a few areas.

SCLCPs have been systematically studied ever since Finkelmann first introduced polymers of this type in 1978. The liquid crystalline properties of SCLCPs depend on the polymer's chemical structure (the nature of the polymer backbone, the flexible spacer and its length, and the mesogenic unit), molecular weight, polydispersity and tacticity.

Several systematic investigations into the correlation between the above-mentioned variables and liquid crystalline behaviour have been reported. Most of the research work refers to SCLCPs with an acrylic, methacrylic or siloxane backbone,[12-15] while only a few studies have dealt with SCLC polyurethanes (SCLC-PU). SCLC-PUs are usually prepared by addition polymerization of diisocyanate and mesogenic diols using various spacer lengths,[16-19] or by attaching the mesogenic units to the COOH functionalized PU backbone via covalent bonds.[20] SCLC-PUs without flexible spacers in the mesogenic diol have also been synthesized[21] or prepared by self-assembly of the PU backbone (containing a pendant pyridyl unit) and 4-dodecyloxybenzoic acid via hydrogen bonding.[22]

The SCLC-PUs mentioned above consist of only hard segments. By introducing a non-liquid crystalline polyether into the PU backbone to obtain a segmented SCLC-PU the liquid crystallinity could be lost.[18] Therefore, we synthesized low molecular weight SCLC polyesters that could be further used to prepare novel segmented SCLC-PUs.

SCLC polyesters were synthesized via trans-esterification of dimethyl terephthalate using α-[bis(2-hydroxyethyl)amino]-ω-(4-methoxyazobenzene-4'-oxy) alkanes with different spacer lengths (Cn-diol, n=8, 10, 12).

Experimental

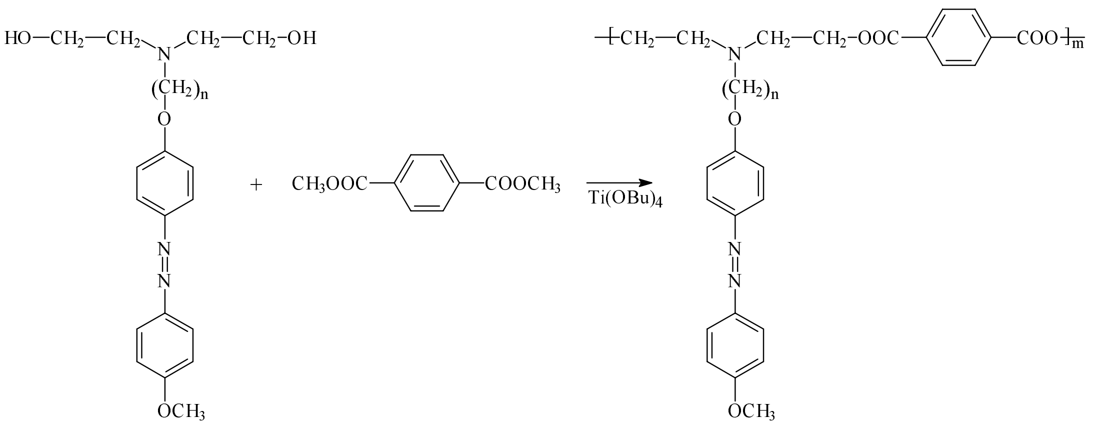
Synthesis of Cn-diols

α-[bis(2-hydroxyethyl)amino]-ω-(4-methoxyazobenzene-4'-oxy) alkanes (Cn-diol, n=8, 10, 12) were synthesised according to the procedure described in our previous papers.[16,17]

Synthesis of SCLC polyesters

Polyesters were synthesized according to the method described by Reck.[23] Dimethyl terephthalate (DMT), Cn-diol and titanium (IV) butoxide as a catalyst were mixed under a nitrogen atmosphere and heated to 120 °C for one hour to obtain a homogenous melt of diol and DMT. The temperature was then raised to 140 °C and maintained there for 12 hours. Molar ratios of DMT and diol were 1:1.2, 1:1.4 and 1:1.6.

After cooling to room temperature polyesters were dissolved in chloroform and purified by precipitation in ethanol. The purification procedure was repeated three times. The reaction is shown in Scheme 1. Polyesters were designated as PES-n, n being the number of methylene groups in the diols.



Scheme 1: Trans-esterification of dimethyl terephthalate with α-[bis(2-hydroxyethyl) amino]-ω-(4-methoxyazobenzene-4'-oxy) alkanes.

Methods

Average molecular weights and molecular weight distributions were determined by size exclusion chromatography (SEC) on a modular Perkin Elmer liquid chromatograph equipped with a DAD detector working at a wavelegth of 254 nm; a PLgel Mixed D column with a precolumn using THF as an eluent with a flow rate of 1 ml/min was used. The calibration was performed using narrow distribution polystyrene standards.

Fourrier transform infrared (FTIR) measurements were made on a Perkin Elmer spectrometer FTIR 1725X by casting films from sample solutions in $CHCl_3$ onto NaCl plates.

Thermal characterization was performed using differential scanning calorimetry (DSC) on a Perkin Elmer DSC-7. Each sample was placed into a DSC heating cell at 25 °C, cooled to –50 °C, maintained at -50 °C for 3 min, heated to 150 °C, maintained at

150 ^{o}C for 3 min, cooled to –50 ^{o}C, maintained at -50 ^{o}C for 3 min, and then reheated once again - all at a scan rate of 10 ^{o}C/min.

Optical textures were obtained using a Carl Zeiss Stemi SV polarising optical microscope (POM) equipped with a Mettler Toledo FP82 hot stage and MC 80 microscope camera.

X-ray diffraction patterns were taken on a Siemens D-5000 diffractometer using Cu K_{α}radiation (λ=1.54Å) in 0.02^{o} steps from 2-37^{o} (in 2θ) with 2 s per step.

Results and discussion

The transesterification reaction was followed by FTIR spectroscopy. FTIR spectra of C8-diol and the corresponding polyester (PES-8) are shown in Figure 1. The characteristic COO band for polyester can be observed at 1728 cm^{-1} and is clearly distinguished from the same band in dimethyl terephthalate at 1719 cm^{-1}. The intensity of the OH band at 3400 cm^{-1} is much smaller in the polyester than in the C8-diol indicating the disappearance of OH groups.

During the transesterification mostly low molecular weight polyesters and oligomers were formed, as confirmed by SEC. The molecular weights of the products were in the range from 1,500 to 10,000. The SEC chromatograms of the polyesters synthesized using different molar ratios of C8-diol to DMT are shown in Figure 2. The highest molecular weights were achieved using the molar ratio 1: 1.2.

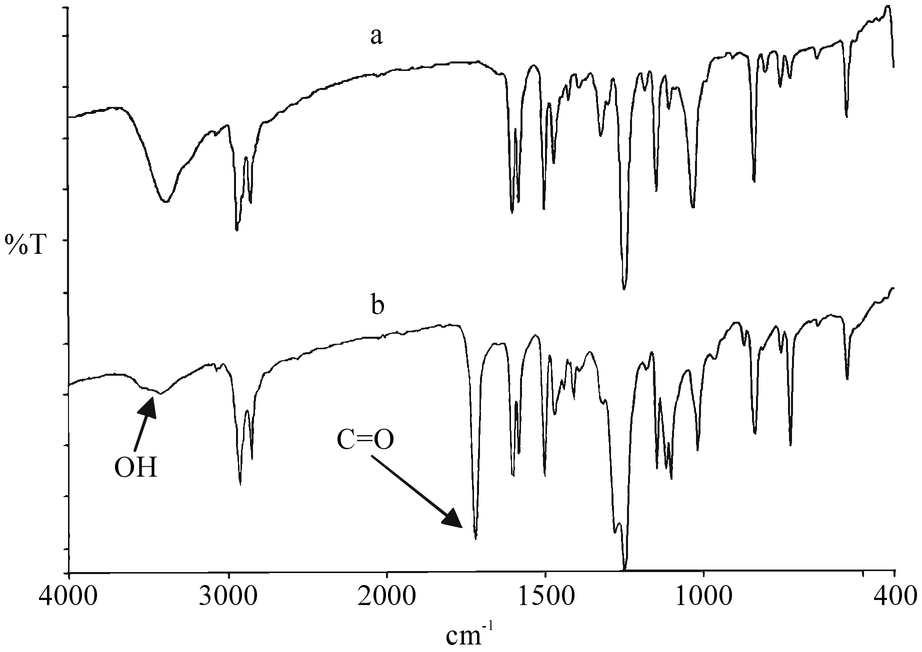


Figure 1: FTIR spectra of C8-diol (a) and polyester PES-8 (b).

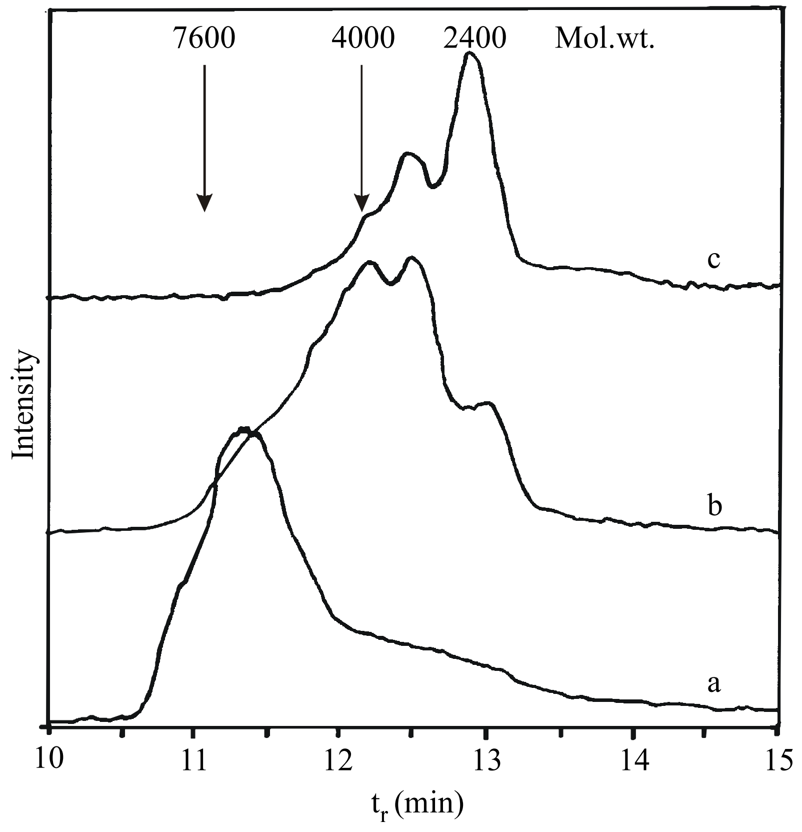


Figure 2: SEC chromatograms of PES-8 synthesized with molar ratios of DMT and C8-diol: 1:1.2 (a), 1:1.4 (b) and 1:1.6 (c).

The thermal properties of the polyesters were determined by DSC. The DSC curves of low molecular weight oligomers, which were mostly formed at high reactant ratios (1:1.4, 1:1.6), exhibit multiple peaks that are not well resolved. Multiple peaks have been ascribed to the melting points of oligomers with different molecular weights. It is known that the melting points of polymers are dependent on the molecular weight up to a certain value. In addition, oligomers might form liquid crystalline phases, which could not be detected due to complex melting patterns.

The molecular weights of the polyesters synthesized at a low reactant ratio (1:1.2) seem to be high enough not to influence the transition temperatures to such an extent. However, melting proceeds over a relatively broad temperature range (≈30 ^{o}C) and there was no other peak observed which would indicate an LC/isotropic transition.

DSC curves, obtained on cooling, exhibit two peaks as shown in Figure 3. Exothermic transitions from the isotropic to liquid crystalline phase are at 61 ^{o}C (PES-8), 71 ^{o}C (PES-10) and 72^{o}C (PES-12). The peak at the lower temperature (57 ^{o}C (PES-8), 56 ^{o}C (PES-10) and 54 ^{o}C (PES-12)is ascribed to the transition from the liquid crystalline to crystalline state. Both peaks are well resolved in PES-10 and PES-12 while in PES-8 the transition peak from the isotropic to liquid crystalline state is a shoulder on a crystallization peak. From the data obtained by DSC measurements we can conclude that polyesters synthesised using a 1:1.2 molar ratio of reactants are monotropic liquid crystals.

The nature of the mesophases was also investigated by polarized light microscopy. When the isotropic melt of PES-8 was cooled to 65 ^{o}C a sanded smectic structure was formed (Figure 4). The smectic structures of PES-10 and PES-12 (Figure 5) differ from the structure of PES-8.

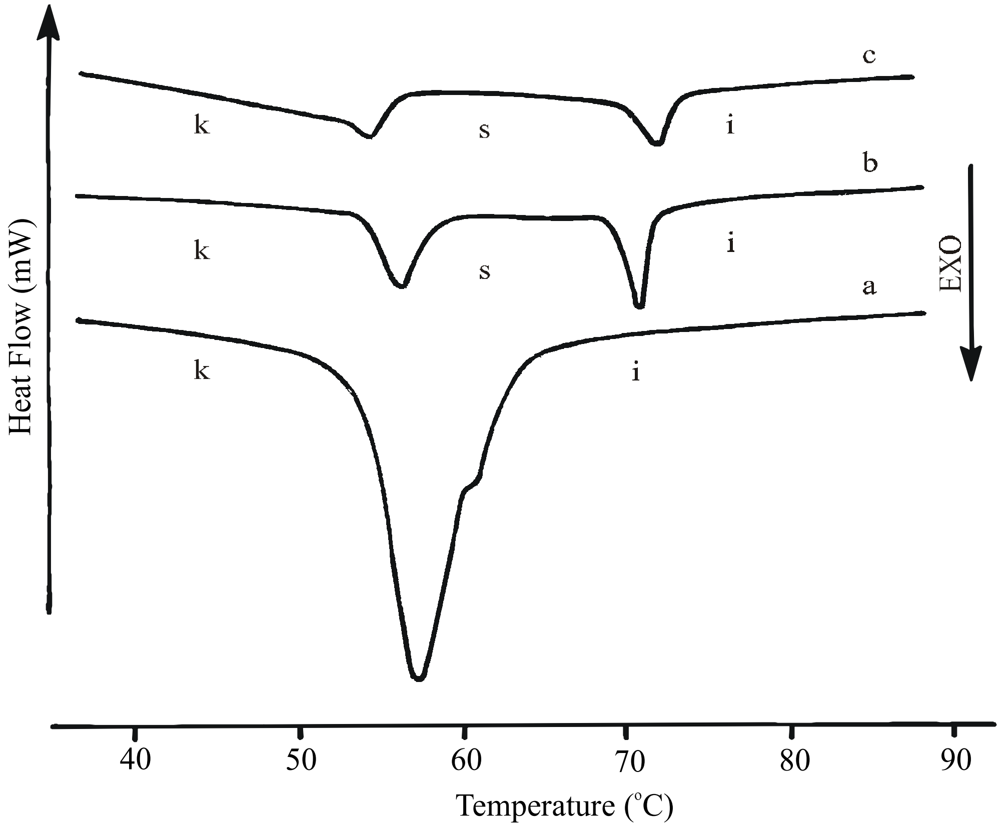


Figure 3: DSC cooling curves of PES-8 (a), PES-10 (b) and PES-12 (c); k-crystalline phase, s-smectic phase, i-isotropic phase.

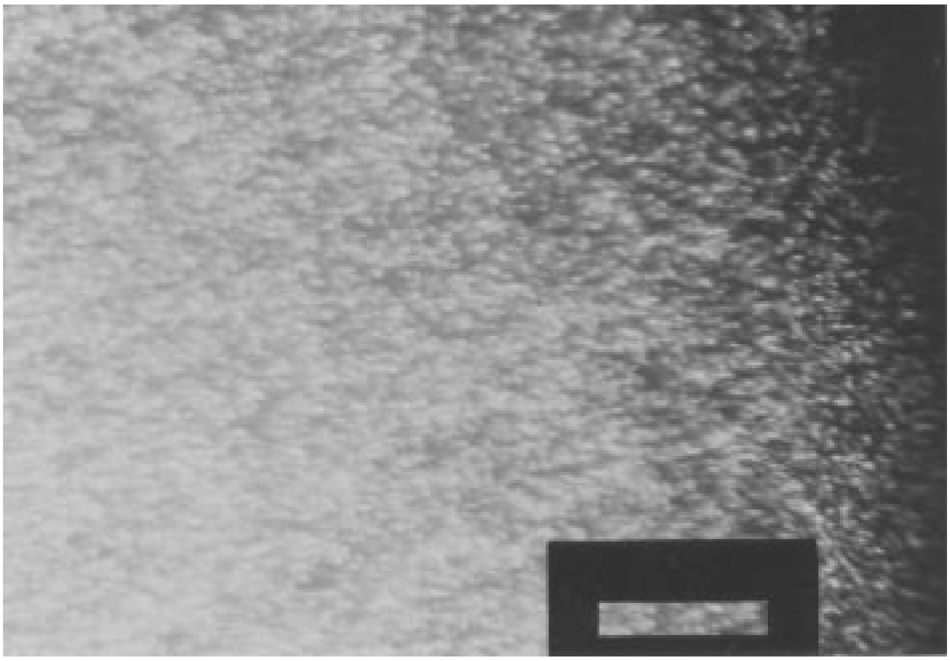


Figure 4: Smectic phase of PES-8 at 65 °C.

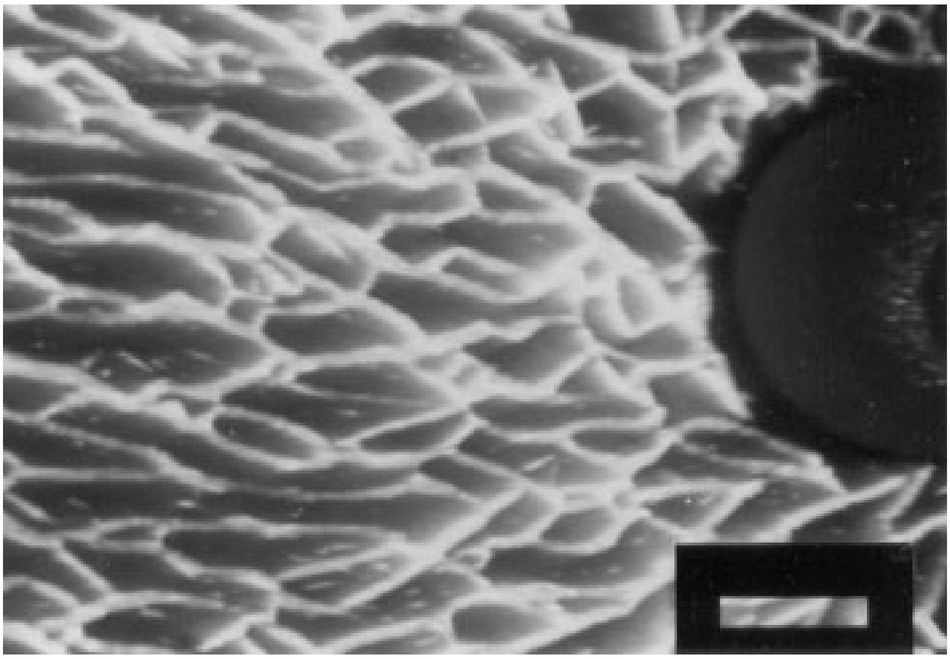


Figure 5: Smectic phase of PES-10 and PES 12 at 65 ^{o}C.

All polyesters exhibit similar X-ray diffractograms; a diffractogram of PES-10 is presented as a representative example in Figure 6. In a small-angle region there are two Bragg reflections of the first and second order corresponding to the smectic layer spacing (d), which is 3.2 nm for PES-8, 3.8 nm for PES-10 and 4.1 nm for PES-12. These layer spacings are 1.4 times (PES-8) and 1.6 times (PES-10, PES-12) the lengths of the fully extended mesogenic units (FEMU) together with the spacer (trans-planar conformation) thus indicating the partially interdigitated bilayer structure of the smectic phase.

The differences in layer spacing/FEMU indicate that PES-8 forms a different smectic phase than the other two polyesters as already observed by POM. In the wide-angle region, the diffractograms show two strong sharp signals, which are related to the high degree of order within smectic layers. The maxima of the two Bragg reflections correspond to a periodicity of 0.5 nm and 0.38 nm, respectively.

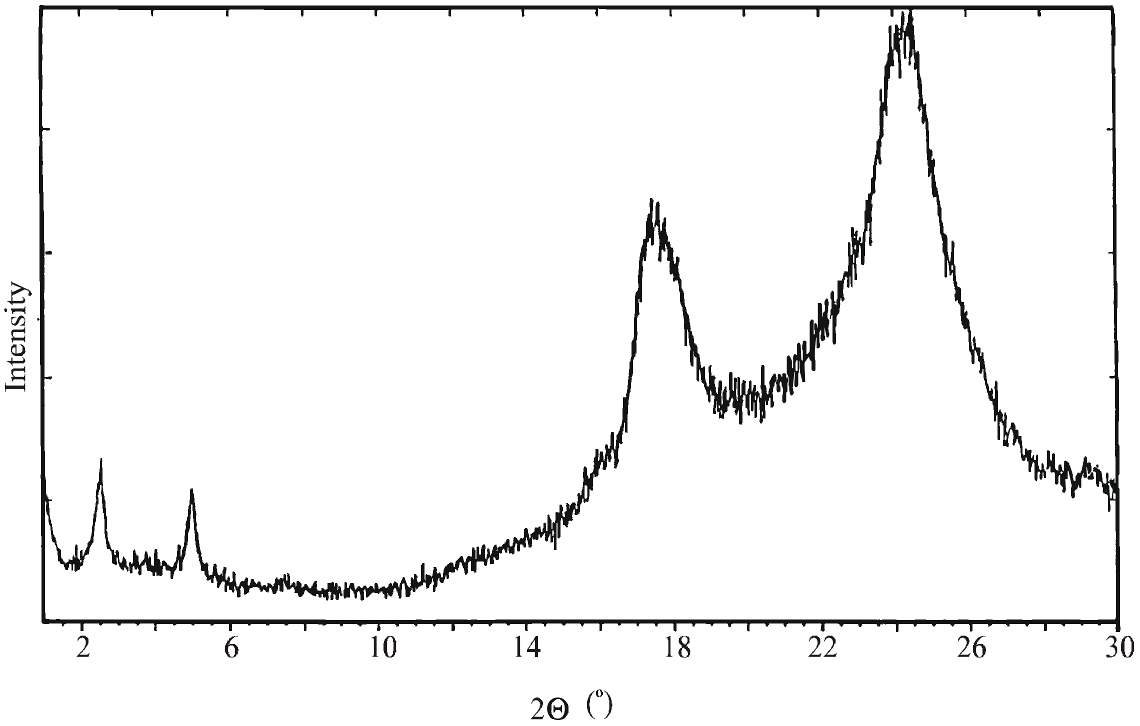


Figure 6: X-ray diffractogram of PES-10.

Conclusions

A series of low molecular weight side-chain liquid crystal polyesters were synthesised via trans-esterification of dimethyl terephthalate (DMT) with α-[bis(2-hydroxyethyl)amino]-ω-(4-methoxyazobenzene-4'-oxy) alkanes. All polyesters melt below 100 °C. The liquid crystalline properties were confirmed for polyesters with a DMT/ diol ratio of 1:1.2. These polyesters could be further used to synthesize side-chain liquid crystal polyurethanes. Higher molar reactant ratios (1:1.4, 1:1.6) yield a mixture of oligomers.

Acknowledgement

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Povzetek

S preestrenjem dimetiltereftalata (DMT) z α-[bis(2-hidroksietil)amino]-ω-(4-metoksiazobenzen-4'-oksi) alkani (Cn-diol, n=8, 10, 12) smo sintetizirali serijo nizkomolekularnih stranskoverižnih tekoče kristaliničnih poliestrov. Pri poliestrih z molskim razmerjem DMT: Cn-diol = 1:1,2 pri ohlajanju iz izotropne taline nastane smektična faza. Pri molskem razmerju reaktantov 1:1,4 in 1:1,6 so nastali oligomeri, ki se talijo v širokem temperaturnem območju, kar onemogoča določevanje tekočekristaliničnih lastnosti.