Side-chain liquid crystalline polyurethanes on the basis of biphenyl mesogenic units

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Summary

Liquid crystalline diols containing a biphenyl mesogenic core, methoxy or cyano terminal groups and spacers of various lengths were synthesized and used for the preparation of side-chain thermotropic polyurethanes. The structure of the synthesized diols and polymers was confirmed by elemental analysis, FTIR and NMR spectroscopy. Phase transition temperatures were studied by DSC, while optical textures were characterized by polarizing microscopy. A smectic type arrangement was found for the mesophases of all products.

Introduction

Side-chain liquid crystalline (SCLC) polymers are of theoretical and practical interest due to the duality of their properties; their unique behaviour is caused by the specific structure which consists of a polymer chain, a flexible spacer and a mesogenic unit. They combine the anisotropic, particularly electrooptic properties of monomeric liquid crystals with the mechanical and processing properties of polymers. Therefore, SCLC polymers are of special interest for the application in data storage systems, in piezo-, pyro- and ferroelectric devices, and in other systems that require nonlinear optical characteristics.

There are numerous reports in the literature concerning the synthesis, characterization and structure-property correlation of SCLC polyacrylates, polymethacrylates, polysiloxanes, polyvinyl ethers, etc. However, only a few papers refer to SCLC polyurethanes (PU) (1–5). The results of studies done on a series of azobenzene mesogenic unit containing SCLC PUs have been presented recently (6).

The aim of this work was to synthesize SCLC PU from low molecular weight liquid crystalline diols and hexamethylene diisocyanate (HDI) and to find the effect of the spacer length and of the terminal mesogenic unit groups on the liquid crystalline behaviour of the products. We prepared diols consisting of a mesogenic core with methoxy terminal groups, spacers containing 6, 8 or 10 methylene groups, and a diol with a cyano terminal group and a 10 methylene group spacer. The diols and PUs were characterized by elemental analysis, Fourier-transform infra-red (FTIR) and nuclear magnetic resonance (NMR) spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and polarizing optical microscopy (POM).

Experimental

Synthesis of monomers

The synthetic route to obtain methoxybiphenyl diols (denoted Dn-A, n = 6, 8 or 10 methylene groups in the spacer) is presented in Scheme 1. The mesogenic core of 4-hydroxy-4'-methoxybiphenyl has been synthesized according to literature data (7). The units with spacers of different length, α-bromo-ω-(4'-methoxybiphenyl-4-oxy)alkanes (Sn-A), have been prepared by the method described by Crivello et al. (8). Dn-A diols were obtained similarly as described for other mesogenic diols (6,9). In this case, α-bromo-ω-(4'-methoxybiphenyl-4-oxy)alkane (0.01 mol) and diethanolamine (0.05 mol) were mixed in 2-propanol (70 ml) under reflux for 20 hours. After the reaction was completed, the precipitate of the warm reaction mixture was filtered off. The filtrate was evaporated to dryness in vacuo. Thus obtained diols were dissolved in chloroform and purified by extracting the impurities with water. The chloroform phase was dried over anhydrous Na_2SO_4 and filtrated. The filtrate was evaporated to dryness and the product was recrystallized from a mixture of ethylacetate and hexane. Additionally, the product was purified by column chromatography on silica-gel with a mixture of $CHCl_3$ and CH_3OH (9:1) as eluent.
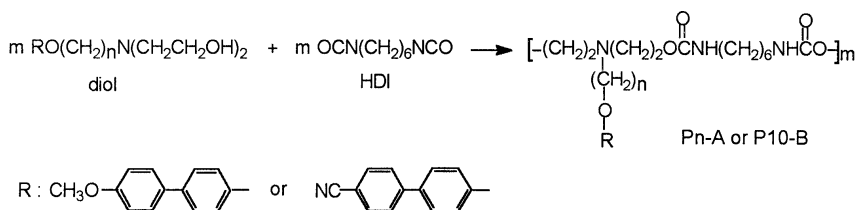
To obtain cyanobiphenyl diol with 10 methylene groups (D10-B) we started with 4-hydroxy-4'-cyanobiphenyl and used the same procedure as described for the synthesis of Sn-A and Dn-A.
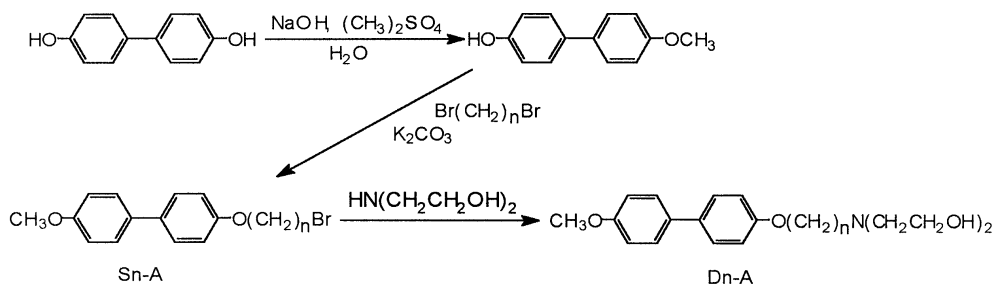
Scheme 1: Synthesis of Dn-A diols

Synthesis of polymers

A series of polyurethanes (Pn-A) and P10-B were synthesized from equivalent amounts of HDI and Dn-A or D10-B diols (Scheme 2). The syntheses were carried out in 15% solutions of anhydrous dimethylformamide at 70°C, in an inert atmosphere. The reaction was catalysed by dibutyltin dilaurate (0.2 wt% with respect to the diol). The course of polymerization was followed by IR spectroscopy (disappearance of NCO group absorbance at 2270 cm^{-1}). Oligomers were removed by precipitation of the products in water or in ethanol. Polymers were dried in vacuo at 40°C.

$$m\ RO(CH_2)_nN(CH_2CH_2OH)_2\ +\ m\ OCN(CH_2)_6NCO\ \longrightarrow\ [-(CH_2)_2N(CH_2)_2OCNH(CH_2)_6NHCO-]_m$$

diol   HDI

Pn-A or P10-B

R : CH₃O— or NC—

Scheme 2: Synthesis of polyurethanes

Methods

IR spectra were recorded on a Perkin-Elmer spectrometer FTIR 1725X. ^{1}H and ^{13}C NMR spectra were recorded at 25 °C on a Varian VXR 300 spectrometer using $CDCl_3$ as solvent and TMS as internal standard. The molar mass averages were determined relative to polystyrene standards by SEC on a modular Perkin-Elmer liquid chromatograph equipped with an UV detector. A Plgel Mixed D column with a precolumn and THF with a flow rate of 1 mL/min were used. The elemental analyses were performed on a Perkin-Elmer Analyser 2400 CHN. Thermal characterization was done on a Perkin-Elmer DSC-7. The samples were heated twice and subsequently cooled in the range between -50 and 150 °C. Heating and cooling rates were 10 °C/mill., After the first heating cycle, the samples were held at 150 °C for 5 min to obtain identical thermal histories for all compounds before the second heating/cooling cycle. Optical textures were obtained by using a Carl Zeiss polarizing optical microscope Stemi SV equipped with a Mettler Toledo FP82 hot stage and microscope camera MC 80.

Results and discussion

A high purity of mesogenic diols is a prerequisite for obtaining polyurethanes with liquid crystalline properties. Therefore, the synthesized diols were purified by repeated recrystallization and by column chromatography. The results of elemental analysis are shown in Table 1.

Table1. Elemental analysis of mesogenic diols (Dn-A and D10-B)

Sample	Formula	%C		%H		%N	
		calc.	found	calc.	found	calc.	found
D6-A	$C_{23}H_{33}NO_4$	71.29	70.82	8.58	9.08	3.61	3.70
D8-A	$C_{25}H_{37}NO_4$	72.26	71.87	8.97	9.10	3.37	3.38
D10-A	$C_{27}H_{41}NO_4$	73.10	72.59	9.31	9.77	3.16	3.28
D10-B	$C_{27}H_{25}N_2O_3$	73.94	73.56	8.73	9.04	6.39	6.51

The first qualitative information about the synthesized products was obtained by IR spectroscopy. As an example, the spectra of the methoxybiphenyl mesogenic unit with a 10 CH$_2$ group spacer (S10-A), of the corresponding diol (D10-A) and polymer (P10-A) are presented in Figure 1. The characteristic C-Br band of Sn-A and S10-B bromoalkanes was observed at 640–650 cm^{-1}. After the reaction with diethanolamine, the C-Br band disappeared and the new broad OH stretching band of the obtained diol appeared at 3300–3400 cm^{-1}. The polyurethane was characterized by the bands of urethane group vibrations (NH stretching band at 3332 cm^{-1}, C=O band at 1703 cm^{-1}, δNH + νCN combination band at 1540–1530 cm^{-1}).
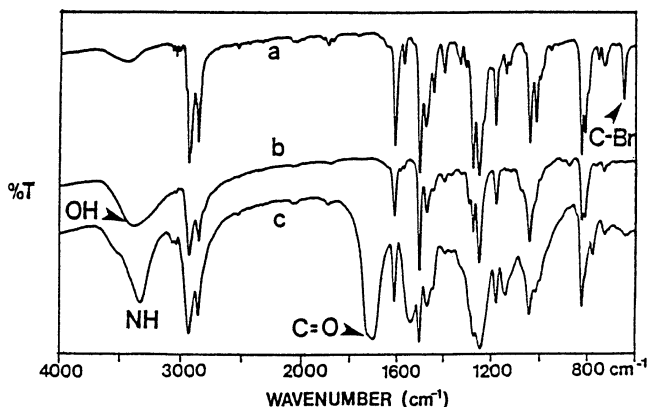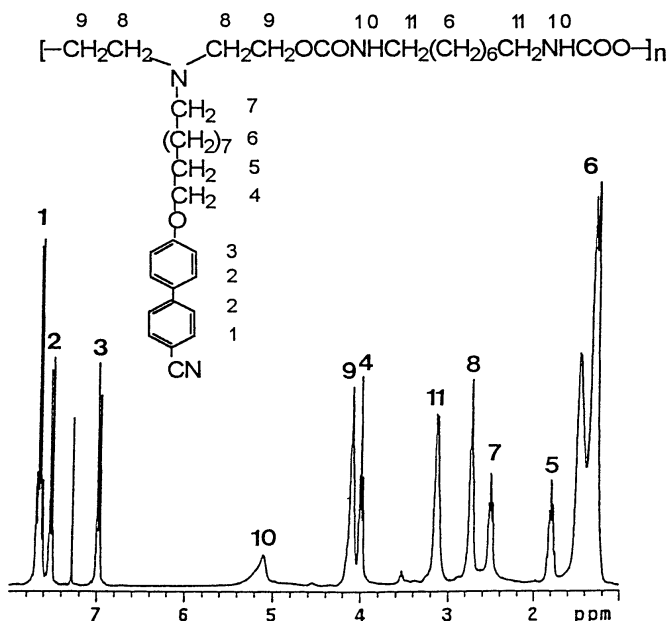

Figure 1. FTIR spectra of S10-A (a), D10-A (b), P10-A (c)

^{1}H and ^{13}C NMR spectra confirmed the supposed structures of all the synthesized diols and polymers. ^{1}H spectrum and the assignation of P10-B polymer is presented as a representative example in Figure 2.

Figure 2.
^{1}H NMR spectrum of P10-B

Phase transitions of diols

The thermal transition temperatures and the corresponding enthalpy changes obtained by DSC during the first heating and second cooling scans of the diols are listed in Table 2. The cooling curves are presented in Figure 3.

Table 2. DSC data of the first heating and second cooling of mesogenic diols

Sample	T_c (°C)	ΔH_c (J/g)	T_1 (°C)	ΔH_1 (J/g)	T_2 (°C)	ΔH_2 (J/g)	T_i (°C)	ΔH_i (J/g)
				Heating				
D6-A	63	17.5	100.7	1.5	-	-	108.1	39,6
D8-A	73	25.3	96[a]	-	-	-	104.6	34.3
D10-A	70.5	27.4	100.8	38.9	-	-	107.5	24.2
D10-B	80.7[b]	137.2[b]	-	-	-	-	-	-
				Cooling				
D6-A	-	-	98.3	-1.3	-	-	102.3	-38.1
D8-A	69.3	-15.5	83.3	-2.1	-	-	96.3	-32.5
D10-A	51.5	-1.9	81.1	-24.5	87.3	-2.5	103.3	-24.5
D10-B	7	-28.7	2.1	-	-	-	67.3	-9.4

[a] shoulder, [b] melting

The first heating curves of all methoxybiphenyl diols show a broad peak at about 70 °C which is ascribed to the crystal to liquid crystal phase transition (T_c). At a higher temperature, we observed an endothermic transition between two mesophases (a peak in D6-A and D10-A and a shoulder in D8-A) followed by a sharp peak indicating the liquid crystalline to isotropic phase transition (T_i). In the second cooling sequences, after the isotropic to liquid crystal phase transition, there is one exothermic peak in D6-A and D8-A and two peaks in 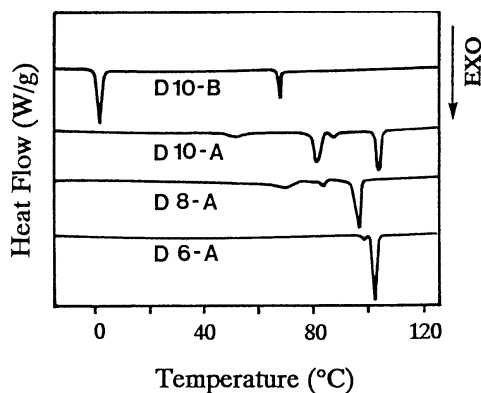D10-A, which are ascribed to the transitions between different mesophases. The broad peak at the lowest temperature in D8-A and D10-A is ascribed to the crystallization. This transition is slow, with a small enthalpy change. That may be the reason why the crystallization was not detected in D6-A.

The POM investigations of D6-A and D8-A revealed well developed mosaic textures in the liquid crystalline phases which suggested the formation of mesophases of a smectic type (7).

Figure 3: DSC cooling curves of diols

As a representative example, the texture of D8-A is shown in Figure 4. In the case of D10-A, a well developed focal-conic type texture, as it was presented in the literature data for many other biphenyl monomers (10,11), resulted at 85 °C (Figure 5).

The DSC first heating curve of cyano-biphenyl diol D10-B exhibits a broad endothermic peak due to the crystal to isotropic transition, whereas the cooling curve shows two exothermic peaks indicating the isotropic to liquid crystalline transition and crystallization. A fan-like smectic mesogenic texture was observed in the temperature range of the liquid crystal mesophase by POM.
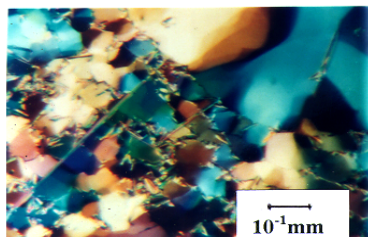

Figure 4.
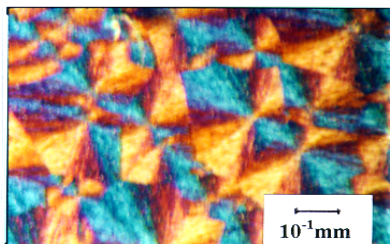Mosaic smectic texture of D8-A diol
(88 °C)

Figure 5.
Focal conic smectic texture of D10-A
(85 °C)

Phase transitions of polyurethanes

The weight- and number-average molar masses (M_w and M_n), polydispersities, thermal transitions and the corresponding enthalpy changes of polyurethanes Pn-A and P10-B are summarized in Table 3. The influence of molar mass on the phase transition temperatures of SCLC polymers has been investigated by many researchers and it was found that in most cases the phase transition temperatures became independent of the molar masses when M_n exceeded 10^4 g/mol (13). According to this, the phase transitions of the PUs with methoxybiphenyl mesogenic units may be influenced by molar masses. This should be considered when they are compared with other SCLC PUs of the same type.

Table 3. Molar mass averages, polydispersity and DSC data (second cooling) for the polyurethanes

Sample	$10^{-3} \times M_w$ (g/mol)	$10^{-3} \times M_n$ (g/mol)	M_w/M_n	T_g (°C)	T_i (°C)	ΔH_i (J/g)
P6-A	16.7	8.8	1.9	21	45	-10.8
P8-A	15.2	8.4	1.8	19	53	-14.6
P10-A	15.9	10.6	1.5	-	64	-15.8
P10-B	48.3	19.3	2.5	8	42	-5.5

DSC curves of the second heating and cooling cycles of all methoxybiphenyl polyurethanes are similar (P10-A curves are shown as a representative example for this type of polymers in Figure 6). They exhibit only one peak, which is ascribed to the liquid crystalline to isotropic transition, and barely or not visible glass transition (T_g). According to the literature data, the same behaviour was observed for several liquid crystalline polymers containing methoxybiphenyl mesogenic units (7,14,15). Generally, such behaviour is characteristic for highly ordered smectic polymers (16,17). It was found, namely, that T_g of some poly(byphenylylmethacrylate)s could only be observed when the polymers exhibited a nematic phase, whereas for the smectic polymers the change in the specific heat capacity at the glass transition was too low to be detected by DSC. A possible reason for this could be the restricted motions of the polymeric backbone due to the lamellar smectic structure of the mesogenic side chains. On cooling from the isotropic state, all Pn-A products exhibit well developed focal conic smectic textures (Figure 7). The same type of texture, obtained for the methoxybiphenyl mesogenic units containing SCLC methacrylates, was shown in the work of Rodriges-Parada and Percec (14).

The heating and cooling DSC traces of cyanobiphenyl polyurethane P10-B exhibit a glass transition and one weak peak due to the isotropic to liquid crystalline transition (Figure 6). The polarized optical microscopic observations confirmed the liquid crystalline behaviour of P10-B. The fine grain texture obtained for the mesophase was ascribed to a smectic structure (11).

The increase of isotropisation temperatures with the spacer length within the Pn-A series is in agreement with the expected decoupling effect. The higher T_i value of methoxybiphenyl P10-A in comparison with cyanobiphenyl P10-B was explained by a different packing density of the mesogenic units i.e. by the more compact packing within the mesophase of methoxy-substituted biphenyl mesogenic units (12).
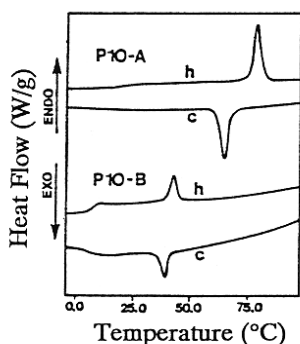

Figure 6.
DSC heating (h) and cooling (c)
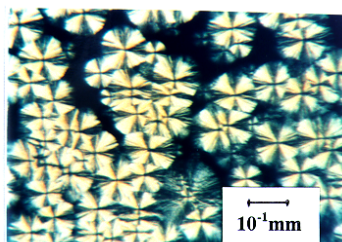traces of P10-A and P10-B

Figure 7.
Focal conic texture of P10-A (62 °C)

It was interesting to notice that the T_i values of SCLC polyurethanes were lower than the T_i values of the corresponding diols. The same behaviour was observed in the series of 11 homologues of liquid crystalline diols based on nitroazobenzene mesogenes

and the corresponding polyurethanes (3) and was explained by the strong stabilization effect due to the dipole interactions of hydroxyl groups in diols which resulted in higher isotropization temperatures. After the reaction of diols with HDI, the stabilization effect of the OH interactions is lost and consequently the Ti values of PUs are lowered.

Conclusions

Liquid crystalline behaviour was studied for diols and side chain polyurethanes containing a biphenyl mesogenic core, cyano or methoxy terminal groups and spacers of different lengths. The diols displayed different smectic mesophases (mosaic, focal conic and fan-like type textures were seen by polarizing optical microscope). In polyurethanes based on hexamethylene diisocyanate, focal-conic and fine grain smectic mesophases were observed.

Polymers with longer spacers exhibited higher isotropisation and lower glass transition temperatures. The isotropisation temperature was influenced by the therminal groups of mesogenic units as well: higher T_i was observed for the methoxy biphenyl mesogenic unit containing polymer due to its more compact packing.

Acknowledgement

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