Aromatic side-chain liquid-crystalline polyurethanes with azobenzene mesogenic units

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Summary

We have synthesized SC-LCPUs from 1,1'-methylenebis(4-isocyanatobenzene) (MDI) and azobenzene mesogenic diols (α-[bis(2-hydroxyethyl)amino]-ω-(4-R-azobenzene-4'-oxy)alkanes, R = -OCH$_3$, -CN and -NO$_2$) with 4, 8 or 12 methylene spacer units. All the C4RMDIP are amorphous polymers showing no mesomorphic properties, whereas for C8RMDIP polyurethanes only C8OMeMDIP is liquid-crystalline. The smectic structures of C12RMDIP polymers are defined by the terminal group; the layer spacing values give the order CN>NO$_2$>OMe.

Introduction

Most of the research work on side-chain liquid-crystalline polymers (SC-LCP) concerning the synthesis, characterisation and the structure-to-properties correlation refers to SC-LCP with an acrylic, methacrylic, siloxane or styrene backbone [1]. It has been established that structure of the polymer backbone has a considerable influence on mesomorphic properties of SC-LCPs. The introduction of rigid aromatic moieties reduces the flexibility of the polymer main chain and, consequently, influences the ordering of mesogenic units.

Only a few investigations deal with the side-chain liquid-crystalline polyurethanes (SC-LCPU)[2-5]. Over the past few years, our research group synthesised several series of SC-LCPU by an addition polymerisation of hexamethylene diisocyanate and liquid crystalline azobenzene or biphenyl diols with different spacer lengths (2-12 methylene groups) and various terminal groups (methoxy, cyano, nitro). The influence of structural units on the phase transitions, i.e. on the liquid-crystalline behaviour of the products, has been systematically studied [6-10].

In this contribution, we present the results on the synthesis and characterisation of SC-LCPU based on 1,1'-methylenebis(4-isocyanatobenzene) (MDI) and azobenzene mesogenic diols (α-[bis(2-hydroxyethyl)amino]-ω-(4-R-azobenzene-4'-oxy)alkanes) with various spacer lengths (*n* = 4, 8, and 12 methylene groups) and terminal groups (R = -OCH$_3$, -CN and -NO$_2$). The thermal and structural properties of CnRMDIP were determined by means of differential scanning calorimetry (DSC), polarising optical microscopy (POM) and X-ray diffraction (XRD).

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Experimental

Synthesis of Mesogenic diols (CnR-diols) was performed as described in our previous papers [6,7,10]. Scheme 1 shows the sequence of reactions leading to CnR-diols and corresponding polyurethanes (CnRMDIP).

Synthesis of Polyurethanes (CnRMDIP):

CnR-diols were polymerised by addition polymerisation with 1,1'-methylenebis(4-isocyanatobenzene) (MDI) to the corresponding CnRMDIP polyurethanes. CnR-diol (0.002 mol), MDI (0.002 mol), DMF (10 mL) as a solvent, and dibutyltin dilaurate (0.2% with respect to the diol) as catalyst were placed into a 50 mL round-bottomed flask. All the reagents as well as the solvent were weighed in a dry box to avoid water contamination. The reaction mixture was stirred by a magnetic stirrer at 70°C for 3 hours. Polyurethanes were precipitated in ethanol, purified by dissolution in DMF and reprecipitation in ethanol, subsequently they were dried in vacuo. Their compositions were examined by elemental analysis and molar mass averages by SEC (Table 1).
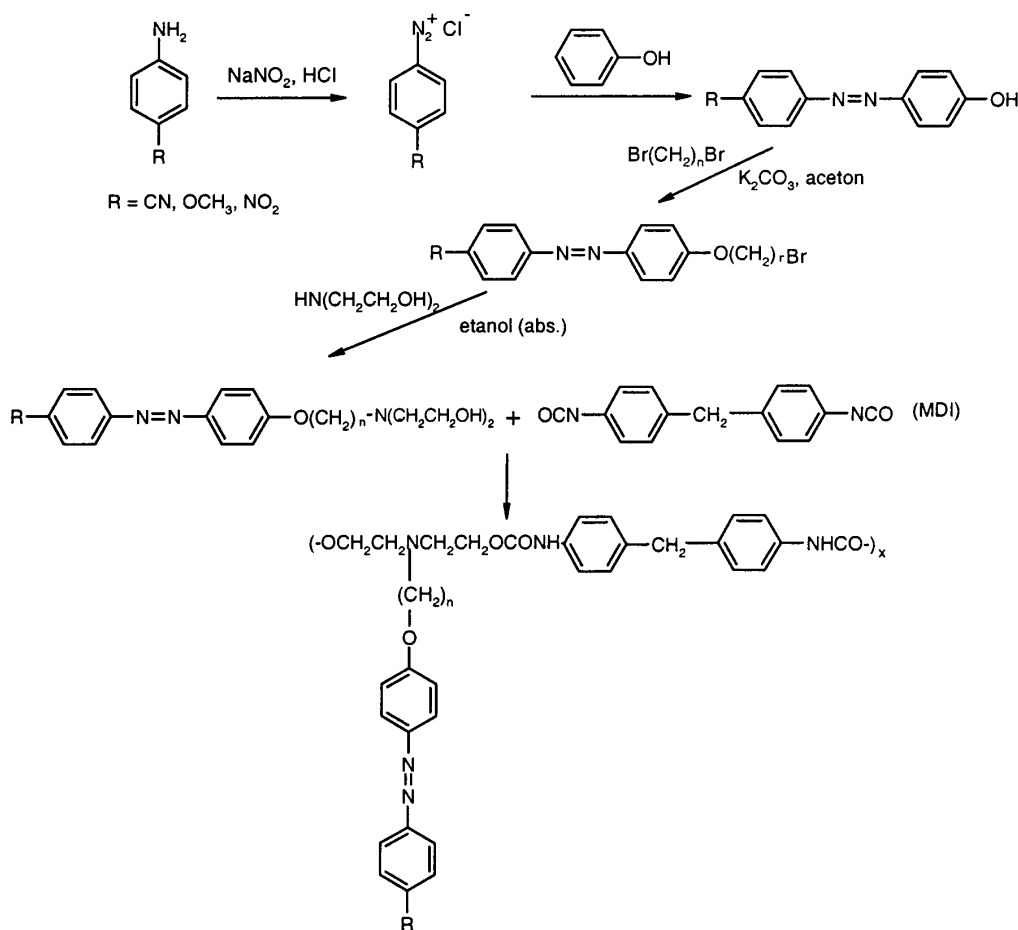
Scheme 1.

Table 1: Elemental analysis, weight-average molar masses ($\overline{M}_w$) and polydispersities ($\overline{M}_w / \overline{M}_n$) of CnRMDIP

Formula	Mol.wt.	% C Calc.	Found	% H Calc.	Found	% N Calc.	Found.	$\overline{M}_w$ 10^3 (g/mol)	$\overline{M}_w / \overline{M}_n$
CnOMeMDIP									
n = 4	$(637.73)_x$	67.80	66.42	6.16	6.56	10.98	11.32	33	2.4
8	$(693.84)_x$	69.24	68.88	6.83	7.05	10.09	10.15	74	3.1
10	$(749.95)_x$	70.47	70.11	7.39	7.70	9.34	9.36	86	3.5
CnCNMDIP									
n = 4	$(632.72)_x$	68.34	67.06	5.73	6.19	13.26	13.57	87	3.6
8	$(688.82)_x$	69.75	68.75	6.44	6.82	12.20	12.41	72	3.9
10	$(744.93)_x$	70.94	70.58	7.04	7.20	11.28	11.30	67	3.1
CnNO$_2$MDIP									
n = 4	$(652.71)_x$	64.41	63.09	5.56	5.93	12.88	13.21	55	2.8
8	$(708.81)_x$	66.09	65.08	6.26	6.67	11.86	12.19	76	3.7
10	$(764.92)_x$	67.52	67.34	86.85	7.05	10.29	11.03	69	2.8

Characterisation

Elemental Analyses were done on a Perkin-Elmer analyser, model 240 C (Table 1).
Size-Exclusion Chromatography (SEC) analyses were performed on a Perkin-Elmer liquid chromatograph equipped with a UV detector. A precolumn, PLgel column 5 µm Mixed C (30 cm x 7 mm, Polymer Laboratories) and THF as an eluent (1 mL/min) were used. Calibration was conducted with polystyrene standards (Toyo Soda manufacturing) in the molar mass region of 500-3.7 10^6 g/mol.
Differential Scanning Calorimetry (DSC) analyses were carried out by a Perkin-Elmer DSC 7 calorimeter. The values of T_g, transition temperatures and corresponding enthalpies are given for the second heating and cooling cycle. Each sample was placed into a DSC heating cell at 50°C, cooled to -50°C and after 3 minutes heated to 150°C, maintained at 150°C for 3 minutes, cooled to -50°C and after 3 minutes reheated once again. The scanning rate was 10 K/min. The calorimetry and temperature precisions of the instrument are better than ± 0,1 % and ± 0.01 °C, respectively.
Polarising Optical Microscopy (POM): optical textures were obtained by using a Carl Zeiss polarising optical microscope Stemi SV6 equipped with a microscope camera MC 80 and a Mettler Toledo FP82 hot stage. The sample was pressed between a glass slide and cover slip at 150°C, cooled to room temperature and heated again to the LC-temperature range.
X-Ray Diffraction patterns were taken on a Siemens D-5000 diffractometer using CuK$_\alpha$ radiation (λ = 1.54 Å) in 0.02° steps from 1-30° (in 2θ) with 20s (Figures 5, 6) or 2s (Figure 4) per step. X-ray measurements were carried out on free-standing unoriented films approximately 0.5 mm thick prepared by moulding the polymers at 150°C followed by the rapid cooling to room temperature.

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Results and Discussion

All the C4RMDIP are amorphous polymers with no mesomorphic properties.
The POM investigations (Figures 1 and 2) show a schlieren texture for C12CNMDIP
and C12NO$_2$MDIP. We were not able to obtain clear optical textures for
C12OMeMDIP.
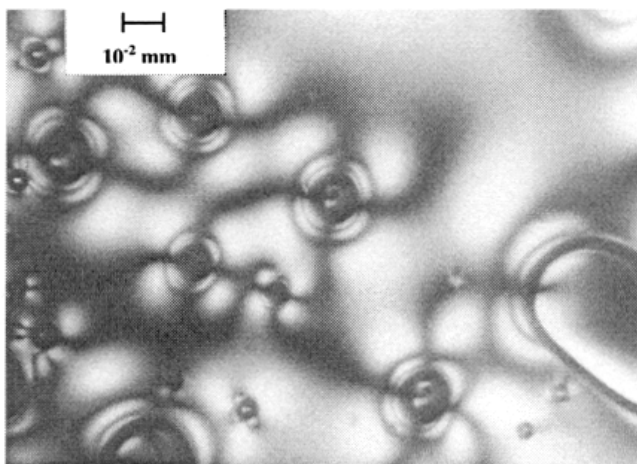
Figure 1. The schlieren texture of C12CNMDIP polyurethane obtained upon heating
(10 °C/min) at 90 °C. The sample was previously molded between a glass slide and a
cover slip at 150°C and then rapidly cooled to room temperature.
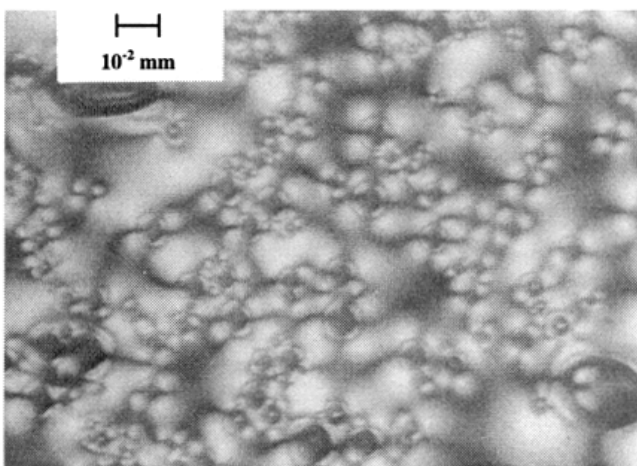
Figure 2. The schlieren texture of C12NO$_2$MDIP polyurethane obtained upon heating
(10 °C/min) at 90 °C. The sample was previously molded between a glass slide and a
cover slip at 150°C and then rapidly cooled to room temperature.

The second heating DSC scans of CnRMDIP polyurethanes are shown in Figures 3
and 4, whereas Table 2 summarizes their phase transition temperatures and enthalpies.

The second heating scan of C4OMeMDIP shows only a glass transition and that of C12OMeMDIP an endothermic transition at 112°C attributed to the isotropisation of mesogenic units and main chain melting. C8OMeMDIP exhibits a glass transition at 41°C, a faint exothermic peak at 55 °C and an endotherm at 94°C representing a mesophase to isotropic transition. The nature of the peak at 55 °C is not clear; it can be due to the local crystallization of the polymer segments.
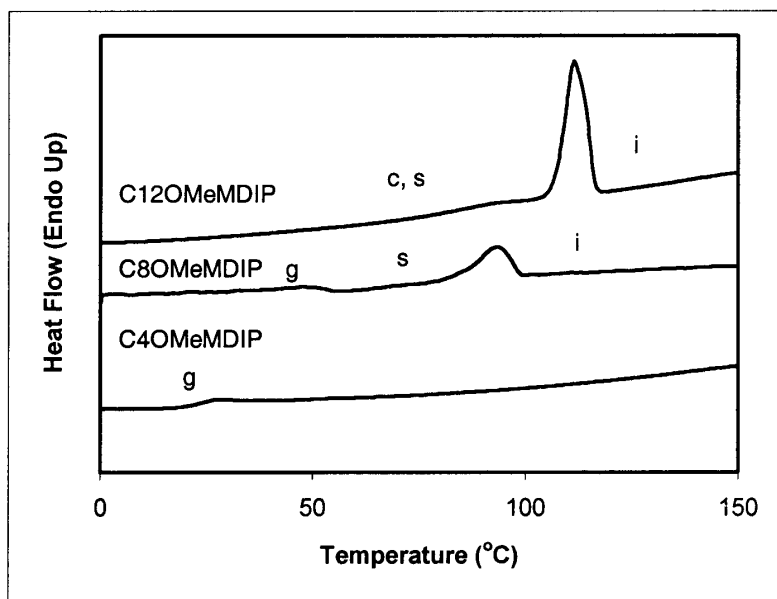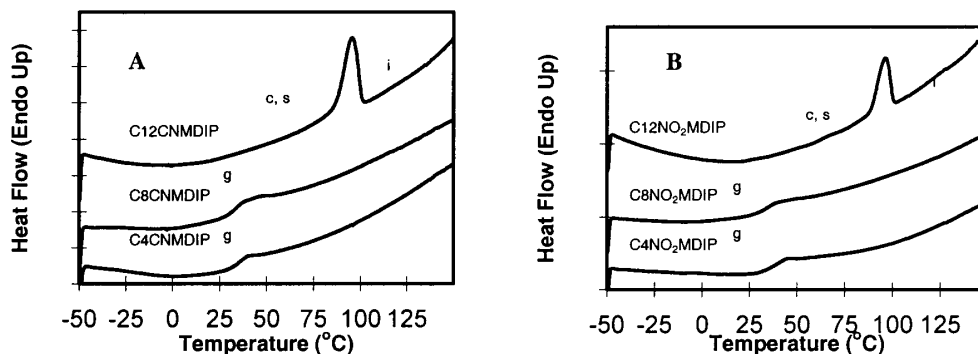

Figure 3. The normalised second heating DSC scans of CnOMeMDIP polyurethanes (g – glassy phase, c – crystal phase, s - smectic phase, i – isotropic phase)

The second heating DSC scans of CnCNMDIP polyurethanes are given in Figure 4A C4CNMDIP and C8CNMDIP are amorphous, whether C12CNMDIP exhibits an endothermic transition at 96°C attributed to the isotropisation of mesogenic units and main chain melting.

Figure 4B shows the second heating DSC scans of $CnNO_2MDIP$ polyurethanes. As for CnCNMDIP polyurethanes, C4- and $C8NO_2MDIP$ are amorphous while $C12NO_2MDIP$ shows an endothermic transition at 96°C due to simultaneous mesophase-isotropic and melting transitions.

X-ray diffractograms of C4RMDIP polyurethanes are consistent with their amorphous nature. In contrast to amorphous C8CNMDIP and $C8NO_2MDIP$ polyurethanes, the x-ray diffractogram of C8OMeMDIP in the small-angle region shows Bragg reflections of the first and third orders corresponding to the smectic layer spacing (d) of 38.0 Å (Figure 5). In the wide-angle region, a diffuse signal at the periodicity of 4.3 Å due to the lateral intermolecular spacings of the mesogenic units was observed. X-ray scattering curves of C12RMDIP polyurethanes also consist of a few signals as a consequence of the lamellar structure (Figure 6A). As can be seen in Figure 6B, for the C12RMDIP Bragg reflections of the first, second, third and fourth order were observed. The main periodicities (d) are 40.3 Å for C12OMeMDIP, 43.8 Å for C12CNMDIP and 42.8 Å for $C12NO_2MDIP$.

Figure 4. The normalised second heating DSC scans of CnCNMDIP (A) and CnNO₂MDIP polyurethanes (B) (g – glassy phase, c-crystal phase, s – smectic phase, i – isotropic phase)

Table 2: Temperatures (T) and enthalpies (ΔH) of the phase transitions of CnRMDIP polyurethanes at the second heating with a rate of 10°C/min

SC-LCPU	T_g (°C)	ΔCp (J/gK)	T_i (°C)	ΔH_i (J/g)
C4OMeMDIP	23	0.46		
C8OMeMDIP	41	0.55	94	28.3
C12OMeMDIP			112	44.0
C4CNMDIP	32	0.66		
C8CNMDIP	35	0.96		
C12CNMDIP			96	21.9
C4NO2MDIP	40	0.79		
C8NO2MDIP	34	0.45		
C12NO2MDIP			96	15.8

The measured values of the layer spacings (d) are higher than those calculated from standard bond lengths and angles (L) for fully extended trans planar conformation of side chains (Table 3) indicating the bilayer structure of the smectic phase. The layer spacing of C8OMeMDIP (d ≈ 1.7 L) is higher than the layer spacings of C12RMDIP (d ≈ 1.6 L, partially interdigitated bilayer structure) indicating the less intense overlapping of smectic layers. The order of smectic structures of C12RMDIP is influenced by the terminal groups. Overlapping of the aromatic mesogens for the methoxy-containg polymers is larger than is observed for the nitro- and cyano-containing polymers, respectively [11].
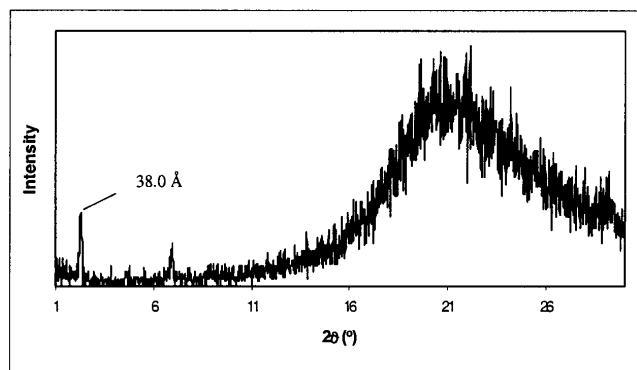
Figure 5. X-ray diffractogram of C8OMeMDIP polyurethane
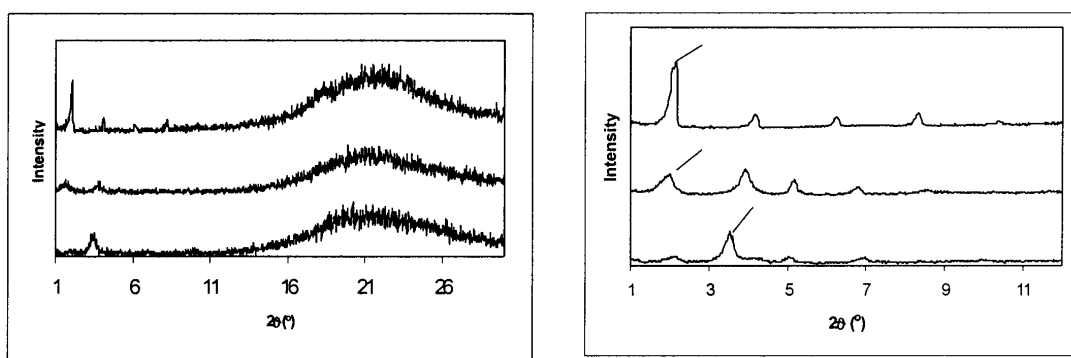
Figure 6. X-ray diffractograms of C12RMDIP polyurethanes (6A). The corresponding small angle regions are shown in Figure 6B.

Table 3: Layer spacings (d) obtained by XRD and the theoretically calculated length (L) of fully extended mesogenic unit with spacer

SC-LCPU	d (Å)	L (Å)	d /L
C8OMeMDIP	38.0	22.2	1.7
C12OMeMDIP	40.3	26.3	1.5
C12CNMDIP	43.8	27.3	1.6
C12NO₂MDIP	42.8	26.5	1.6

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Conclusions

Liquid-crystalline behaviour was studied for side chain aromatic polyurethanes (SC-LCPU) containing an azobenzene mesogenic core, methoxy, cyano or nitro terminal groups and spacers of different lengths (n = 4, 8, or 12).

Contrary to the hexamethylene diisocyanate based SC-LC polyurethanes, all the MDI-based C4RMDIP with various terminal groups show a completely amorphous nature. According to DSC traces, the glass transition of C8NO$_2$MDIP is at 34°C and of C8CNMDIP at 32°C. C8OMeMDIP exhibits the glass transition at 41°C and the endothermic transition at 96°C ascribed to the isotropisation of mesogenic units. All three C12RMDIP exhibit one endothermic peak at around 100°C due to simultaneous mesophase-isotropic and melting transitions. They show a schlieren optical texture. X-ray diffraction patterns of C8OMeMDIP and C12RMDIP consist of several small-angle region signals representing the lamellar smectic structure.

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