Synthesis of side-chain liquid crystalline polyurethanes via ester type attachment

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Summary

A series of side-chain liquid crystalline polyurethanes was prepared by reacting a COOH functionalized polyurethane with monomers based on a biphenyl core with a methoxy terminal group and spacers of different lengths (α-bromo-ω-(4'-methoxybiphenyl-4-oxy)alkanes) in the presence of triethylamine. FTIR and NMR spectroscopic analysis of the products revealed that the monomers were attached to the polymer backbone as side chains by covalent, ester bonds. Thermotropic liquid crystalline behaviour of the ester type derivatives was analysed by differential scanning calorimetry and polarizing optical microscopy. All products exhibited smectic mesophases of highly ordered focal-conic structures.

Introduction

Side-chain liquid crystalline (SCLC) polymers are of both theoretical and practical interest, since they combine the anisotropic properties of monomeric liquid crystals with polymeric properties and have the potential of being used for some new applications, particularly in the field of optics and optoelectronics.

SCLC polymers are prepared by two general methods. The most often used method involves mesogenic molecules with reactive groups capable of undergoing addition polymerization. The second route starts with the functionalized polymer which can be modified to a SCLC polymer by attaching suitable reactive mesogenic monomers. A new concept in designing liquid crystalline materials is based on strong noncovalent interactions (hydrogen bonds, electrostatic interactions). The advantage of the last two methods lies in the use of well-characterized reactive polymers which subsequently interact with a variety of substrates.

So far, there are few literature reports concerning investigations of SCLC polyurethanes (PU) compared with numerous reports of other SCLC polymers (polyacrylates, polysiloxanes). Usually, SCLC PUs are obtained by an addition polymerization of low molecular weight liquid crystalline diols and a diisocyanate (1-6). We have already reported the results obtained by this synthetic method (7-9).

In this paper, we present the preliminary results of the attempts to obtain SCLC polyurethanes by attaching the α-bromo-ω-(4'-methoxybiphenyl-4-oxy)alkane mesogenic units to the COOH functionalized polymer backbone.

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The intention was to obtain the connections of ester type. For this purpose, we first employed the phase-transfer method which was found to be convenient for the preparation of ester type SCLC polymers from polyacrylic acid (10, 11). However, in the case of polyurethanes this method gave only poor results. It appears that the main reason for the inefficiency of the attachment reaction are the steric hinderances among large molecules of the phase-transfer catalyst (tetrabutylammonium bromide) and hydrogen bonded urethane groups of the PU backbone. Better results were obtained by esterification in the presence of triethylamine (TEA). So far, SCLC PU have not been synthesized by this way. For this synthesis we prepared a series of biphenyl monomeric compounds with various spacer lengths and PU, containing carboxyl functional groups, which reacted then in DMF solution in the presence of TEA. Besides the expected esterification reaction, an amination of a part of the brominated monomer had taken place, particularly in the presence of an excess of TEA. According to the work of Basuin et al. (12), SCLC polyacrylates can be obtained by ionic attachment of the aminated biphenyl compounds to the COO⁻ groups of the polyacrylic acid backbone. This kind of interaction could also be expected between the aminated by-products and the COOH groups of PU. However, since the aim of our work was to prepare an ester type SCLC PU, the small amount of the aminated by-product was removed during the purification procedure. The results of the investigations concerning the preparation of SCLC PU with ionically attached mesogens will be the subject of our next report.

Experimental

Methods

Fourrier transform infrared (FTIR) measurements were made on a Perkin Elmer spectrometer FTIR 1725X. The samples were prepared as KBr pellets or by casting films from the sample solutions onto NaCl plates. Nuclear magnetic resonance (NMR) spectra were recorded at 60 °C on a Varian VXR 300 spectrometer using TMS as an internal standard and DMSO-D$_6$ as the solvent. Average molar masses and molar mass distributions were determined by size exclusion chromatography (SEC) on a modular Perkin Elmer liquid chromatograph equipped with a DA detector (wavelength 254 nm). A PLgel Mixed D column with a precolumn and THF eluent with a flow rate of 1 mL/min were used. The calibration was performed with polystyrene standards. Thermal characterization was made by differential scanning calorimetry (DSC) 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/min. 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. Polarizing optical microscopy (POM) was used to observe the structure of the mesophases. The optical textures were obtained by a Carl Zeiss polarizing optical microscope Stemi SV equipped with a Mettler Toledo FP82 hot stage and microscope camera MC 80.
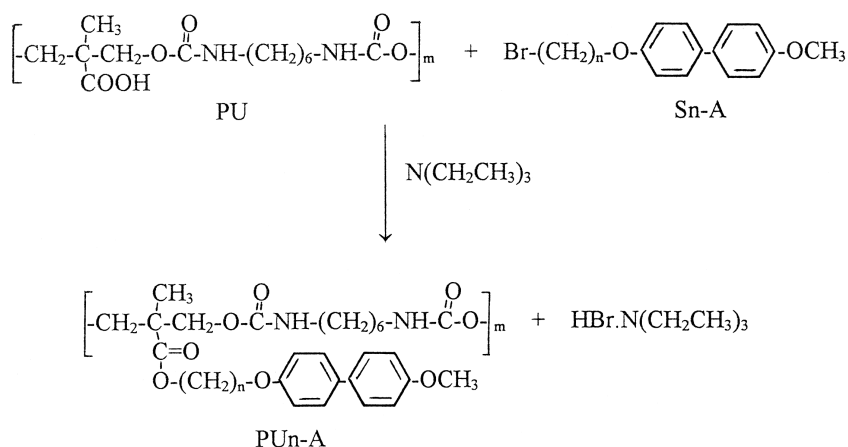
Synthesis

The reactive, COOH functionalized PU was prepared by a step polyme-rization of hexamethylene diisocyanate (HDI) and dimethylol-propionic acid (DMPA) in a 1:1 mole ratio. In order to obtain a linear backbone with free COOH groups and to avoid branching of the backbone, i.e. to prevent the side-reaction of COOH and NCO groups, the diisocyanate was added dropwise to the DMF solution of DMPA. The synthesis was performed in an inert atmosphere, at maximum 60 °C, without a catalyst.

A series of α-bromo-ω-(4'-methoxybiphenyl-4-oxy)alkanes, denoted Sn-A (n = 6, 8 or 10 methylene groups) has been synthesized according to the literature data (13).

The SCLC PUs (denoted PUn-A) were obtained by a reaction of PU with Sn-A monomers and TEA in mole ratios of 1 : 1.1 : 1.5 and 1 : 1.5 : 5. TEA was added to PU first to neutralize COOH groups and afterwards the corresponding Sn-A compound was added. The syntheses were performed in DMF at 60-80 °C.

Results and discussion

FTIR spectra gave first indications for the esterification reaction between PU and the examined monomer according to the reaction shown on Scheme 1. The disappearance of the characteristic C-Br absorption band at 648 cm^{-1} indicated a reaction of the bromide. The appearance of bands in the 2750 - 2400 cm^{-1} region was ascribed to vibrations of HBr.TEA salt (NH$^+$ and N$^+$-H...Br$^-$ hydrogen bonds) (14). Changes due to new ester group vibrations were not observed because they overlap with -COO- vibrations of the urethane group. Figure 1 presents the spectra of reactants, reaction products mixture and of the purified PU8-A.

$$\left[-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O- \right]_m \quad + \quad Br-(CH_2)_n-O-\langle\bigcirc\rangle-\langle\bigcirc\rangle-OCH_3$$

PU   Sn-A

N(CH$_2$CH$_3$)$_3$

$$\left[-CH_2-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\underset{\displaystyle O-(CH_2)_n-O-\langle\bigcirc\rangle-\langle\bigcirc\rangle-OCH_3}{|}}{\underset{\displaystyle C=O}{|}}}{C}}-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-NH-(CH_2)_6-NH-\overset{\overset{\displaystyle O}{\|}}{C}-O- \right]_m \quad + \quad HBr.N(CH_2CH_3)_3$$

PUn-A

Scheme 1

To remove the HBr.TEA salt, DMF solutions of the synthesized products were precipitated twice in water. The spectra of the purified Pn-A products do not contain bands in the 2750 -2400 cm^{-1} region. As it was expected, the bands in that region appeared in the FTIR spectra of the dried water solution residue. In cases when TEA was added in greater excess the bands due to the biphenyl monomer bands were also observed in the FTIR spectra of the water residue. This indicated the formation of a water soluble aminated biphenyl by-product due to the reaction between the brominated mesogenic compounds and TEA. This assumption was confirmed by the preparation and analysis of aminated biphenyl model compounds.
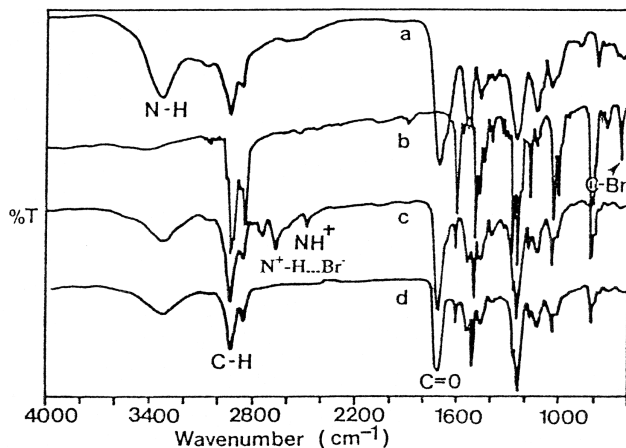

Figure 1.
FTIR spectra of PU (a), mesogenic monomer S8-A (b), mixture of the reaction products (c) and purified PU8-A (d)

The different behaviour of PU and PUn-A products in some solvents confirmed the attachment of the mesogenic moiety on the PU backbone as well. For example, unlike PU, PUn-A products are soluble in chloroform, which is a good solvent for mesogenic Sn-A monomers. The purification of PUn-A compounds from the unreacted Sn-A monomers was done by repeated dissolution in chloroform and precipitation of PUn-A from boiling diethyl ether. Purity of the obtained polymer products was verified by using thin layer chromatography and NMR analysis.

As expected, the molar masses of PUn-A compounds, measured by SEC, were higher than the molar mass of starting PU. The chromatograms displayed unimodal distribution of the products and confirmed their purity. The weight average molar masses and polydispersities are given in Table 1.

NMR analysis of the starting PU and Sn-A compounds, and of the PUn-A products confirmed the attachment of the brominated mesogenic compound onto the PU backbone through an ester linkage in agreement with

reaction Scheme 1. In the ^{1}H spectrum of PU8-A (Figure 2) two new signals appeared at 4.01 ppm and 1.55 ppm that were ascribed to proton resonances of -CH$_2$OCO- and -CH$_2$CH$_2$OCO- groups. At the same time the signals at 3.49 ppm and 1.79 ppm of -CH$_2$Br and -CH$_2$CH$_2$Br groups disappeared. In the ^{13}C spectrum of PU8-A (Figure 3) a new signal due to the carbon resonance of the - CH$_2$OCO-, methylene bonded to the ester group, appeared at 63.79 ppm. The carbon signal at 174.12 ppm of the PU carboxylic group shifted, after the reaction, to 172.12 ppm due to the formed ester -COO- group.

Figure 2.
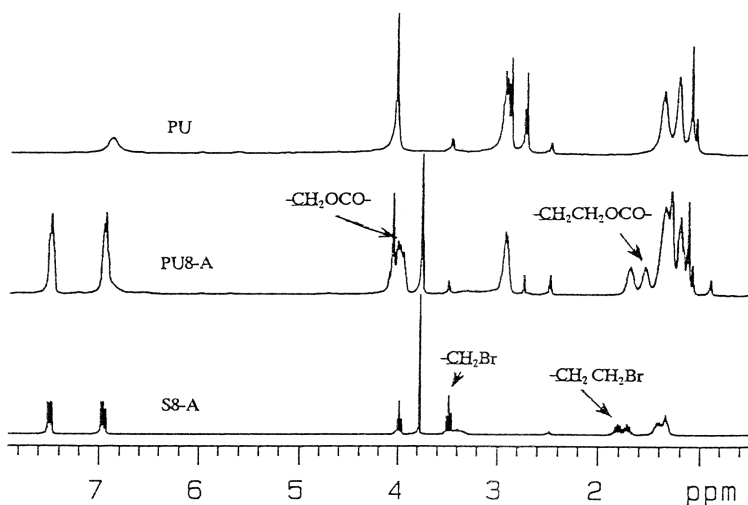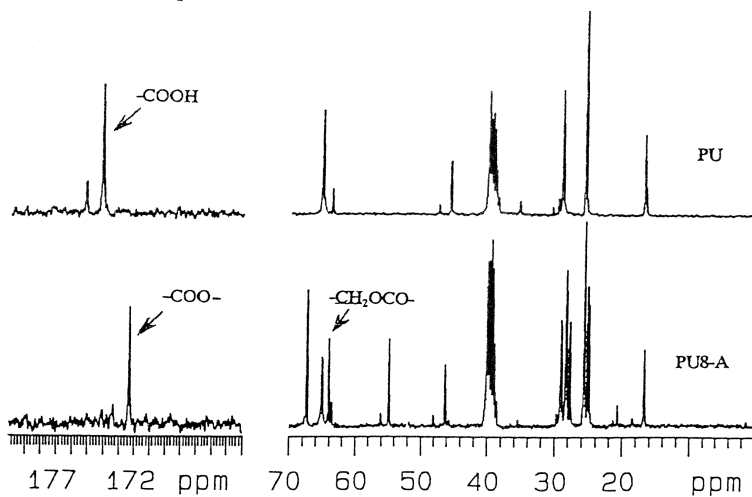^{1}H NMR spectra of PU, PU8-A and S8-A

Figure 3.
^{13}C NMR spectra of PU and PU8-A

Liquid crystalline properties

Thermal transitions of the second cooling sequence and the corresponding enthalpy changes of PU and PUn-A are summarised in Table 1. DSC curves of the second heating and cooling cycles of PUn-A compounds were similar. They exhibited only one exothermic peak which was ascribed to an isotropic to liquid crystalline transition during the cooling sequence (clearing temperature T_{cl}), and glass transition (T_g) of a very low specific heat (ΔC_p from 0.031 to 0.012). These results are very similar to those obtained for SCLC PU synthesized previously by addition polymerization (8). The same behaviour was also observed in numerous liquid crystalline polymers containing methoxy-biphenyl mesogenic units (15,16) and was found to be characteristic for highly ordered smectic polymers (17,18). The increase of PUn-A series isotropisation temperatures with increasing space length is in agreement with the expected decoupling effect. Regarding the dependence of phase transition temperatures on the number average molar mass being lower than 10^4g/mol (19), the obtained phase transitions may be influenced by the molar masses of the samples.

Table 1: Molar mass averages, polydispersity and DSC data (the second cooling)

Sample	10^{-3} x M_w (g/mol)	10^{-3} x M_n (g/mol)	M_w/M_n	T_g (°C)	T_{cl} (°C)	ΔH_{cl} (J/g)
PU	8.6	5.1	1.7	3.2	-	-
PU6-A	16.8	8.4	2.0	39.3	54.1	-7.1
PU8-A	17.8	9.9	1.8	37.1	59.3	-8.0
PU10-A	18.3	9.6	1.9	34.2	62.4	-8.7

Thermal behaviour of the samples was examined by polarizing microscopy. During slow cooling (0.5 °C/min) from an isotropic melt, focal conic smectic textures were observed; the well developed texture of PU8-A is presented as an
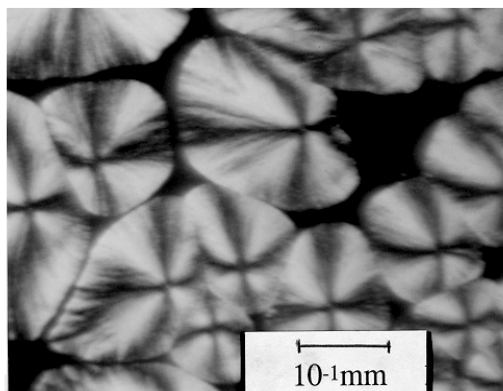

10⁻¹mm

Figure 4.
Focal conic smectic texture of PU8-A (89 °C)

example in Figure 4. This texture was obtained at a higher temperature (89 °C) than expected from DSC phase transition measurements. The difference is most likely due to the slower cooling rate used with POM.

Conclusion

A new synthetic route was examined to obtain SCLC PU by attaching mesogenic monomers on the PU backbone. In the presence of TEA an esterification reaction took place between α-bromo-ω-(4'-methoxybiphenyl-4-oxy)alkanes and the COOH functionalized linear PU. Polymers with longer spacers showed higher isotropisation temperatures. Optical micrographs of the products exhibited focal-conic textures due to a smectic-type arrangement of the mesophases.

Acknowledgement

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