

A novel side chain liquid crystalline polyurethane

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Summary

Side chain liquid crystalline polyurethanes (SCLP) without flexible spacer were synthesized by a two step block copolymerization reaction. The polyurethanes were based on azobenzene-type mesogenic diol chain extender (DR-19), a poly(tetramethylene oxide) (PTMO) soft segment, and different diisocyanates, including 4,4-diphenylmethane diisocyanate (MDI) and hexamethylene diisocyanate (HDI). The polyurethane samples obtained from DR-19 or DR-19 and PTMO with HDI had mesomorphic phases as determined by DSC and polarizing microscopy.

Introduction

Side chain liquid crystalline polymers (SCLP) contain rigid or mesomorphic units in the side chains. In 1978, Finkelmann and Rinsdorf (1) conclude a key role: By introduction of flexible spacer groups between the polymer main chain and the mesogenic side chain, it was possible to synthesize liquid crystalline (LC) polymers. They exhibit enantropic nematic or smectic phases depending on the substituent. The model consideration of decoupling of the polymer main chain and mesogenic side chain is thereby confirmed (2).

In the liquid state above T_g , the polymer tends to adopt a statistical chain conformation that hinders anisotropic orientation of the mesogenic side chains. The systematic realization of liquid crystalline side-chain polymers is to get rid of the influence. It is possible to decouple motions of the polymer segments and mesogenic groups in different ways and thus to construct different types of liquid crystal polymers. Most recently, Hessel (3) and Zhou Qifeng (4) reported the synthesis of a new class of liquid crystal side-chain polymers where the mesogenic groups are laterally attached to the polymer backbones.

Tanaka (5) had described the synthesis of LC polyurethanes containing an azobenzene group in the side chain attached via a flexible alkyl spacer. In our previous work (6), the synthesis of SLCP by N-substitution of PU with a bromoalkyl azobenzene derives, however, showed no LC phases. In this paper, polyurethanes were synthesized by DR-19, an azobenzene dye diol as chain extender. We predicted that for our new type of side-chain polymers the introduction of flexible spacers to decouple the motions of the main chain and the mesogens may be in the main chain, because in this case two flexible methylene units act as a buffer zone to weaken the interaction. Consequently, the motion of the main-chain segments should have only minor coupling effects on the motion of the segments. However, the polyurethanes of MDI series showed no LC phase any way. This may be contributed to the rigidity of MDI, which hinders anisotropic orientation of

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the mesogenic side chains. Instead, HDI with six methylene units was used to synthesize polyurethanes. The obtained samples exhibit typical nematic phases.

Experimental

Materials

4,4'-Diphenylmethane diisocyanate (MDI) was purified by vacuum distillation (0.3 mm Hg) until the boiling point was reached at 170 °C. Hexamethylene diisocyanate (HDI) was purchased from Aldrich Chemical Co.. DMF was dried over molecular sieves (5 angstrom). PTMO ($M_n = 981$) was a product of the Aldrich Co..

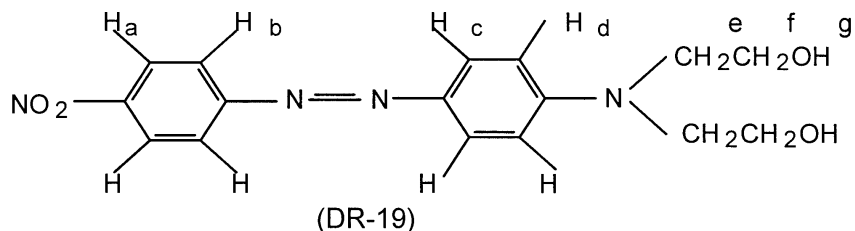
Measurements

The intrinsic viscosities of the polymers were determined at 30 °C in DMF by using a Cannon Ubbelohde viscometer. Thermal analysis was carried out on a Perkin-Elmer DSC-2C interfaced with a Model 3600 data station using TADS software. Temperature and enthalpy calibration were carried out using indium and mercury as standards. A heating rate of 20 K/min under a 20 ml/min flow of dry air as the purge gas was used in samples of 10-3 mg. The data processing unit allowed automatic substraction of the base line and normalization of the thermogram for the sample weight. $^1\text{H-NMR}$ spectra were recorded on a Bruker AM-500 spectrometer in a solution of deuterated acetone. Chemical shift (δ) is given in ppm with tetramethylsilane as a standard. Infrared survey spectra were recorded with a Nicolet 170SX Fourier transform infrared spectrophotometer. One hundred scans at a resolution of 2 cm^{-1} were signal averaged before Fourier transformation. All IR spectra covered the range 400-4000 cm^{-1} . Optical texture was studied with a Leitz-350 polarizing optical microscope equipped with a Linkam hot stage and a polaroid camera. The sample was molten in thin layers between slide glasses and heated to the isotropic melt, and the slides were then sheared to produce a thin layer of melted polymer. The sample was then cooled at 10 °C/min to room temperature and observed or photographed at that temperature.

Synthesis

γ -nitrobenzene-azo-di-hydroxyethyl-aniline (DR-19)

0.167 mol (23g) of p-nitrophenylamine was dissolved in 47 ml of conc. sulfuric acid and 47 ml of water. For the diazotization 0.167 mol of sodium nitrite dissolved in 67 ml of water was slowly added at temperature below 5 °C. To the cooled solution, 0.333 mol of 1M sulfuric acid solution with 0.167 mol N,N'-dihydroxyethyl-aniline were added and the reaction mixture was stirred for 1 h at room temperature. The final solution was adjusted to $\text{PH} < 7$ by sodium hydroxide solution. The precipitated azo dye was isolated by filtration and washed with water. The residue was recrystallized from ethanol/toluene (vol. ratio 1:1) to give 33 g (60% yield) of DR-19. $^1\text{H-NMR}$ and element analysis of DR-19 revealed that the following data:



$^1\text{H-NMR}$ Acetone- d_6)

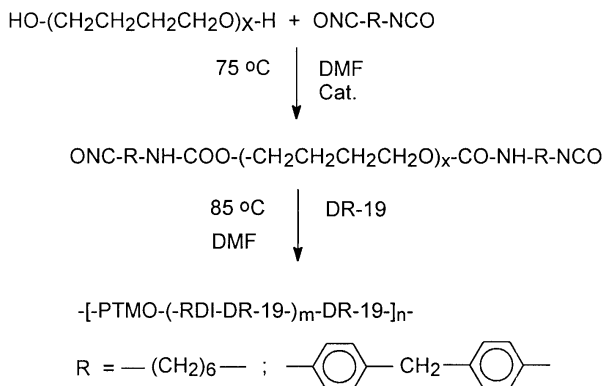
δ (ppm): 8.38 (2H, H_a); 7.98 (4H, H_b, H_c); 6.69 (2H, H_d);
3.82 (4H, H_f); 3.74 (4H, H_e); 3.35 (2H, H_g).

Anal: Calcd: C, 58.18%; H, 5.45%; N, 16.97%

Found: C, 58.30%; H, 5.56%; N, 17.02%.

Liquid Crystalline Polyurethanes

The LC polyurethanes were synthesized by the two-step condensation reaction (shown in Scheme 1). HDI, 1.30 g, and 2 drops of stannous octoate were dissolved in 15 ml of DMF in a heat-dried four-neck round-bottom flask fitted with a reflux condenser, mechanical stirrer, thermometer, and addition funnels charged 10 ml of DMF and 2.54 g of PTMO. Nitrogen was kept flowing through the system. The PTMO solution was added dropwise at 60 °C, and the temperature was raised to 75 °C. After 1.5 h, a solution of 1.71 g DR-19 in 20 ml DMF was added dropwise to the above solution, and the temperature was raised to 80 °C and kept there for 10 h. By the end of the reaction period, the solution was poured into cold water to precipitate the polymer in the form of a red elastomeric material. The polymer was extracted in a Soxhlet with ethanol to remove DMF and unreacted starting materials, and the product was dried under vacuum at 60 °C for 72 h.



Scheme I Synthesis of liquid crystalline polyurethane

All materials studied are described in Table I. A polymer made from 1 mol of 981 M_w PTMO, 3 mol of HDI, and 2 mol of DR-19 is designated as PHD-54. The code indicates that this polymer contains 54 wt.% hard segment.

Table I Properties of LC Polyurethanes

No.	Sample Code	Composition	Mole Ratio	Yield (%)	$[\eta]$	T_m (°C)	T_i (°C)
1	PMD-46 ^a	PTMO:MDI:DR-19	1:2:1	80	0.53	105.6 ^c	/
2	PMD-59	PTMO:MDI:DR-19	1:3:2	85	0.57	110.5	/
3	PHD-54	PTMO:HDI:DR-19	1:3:2	70	0.43	131	169
4	HD-100	HDI:DR-19	1:1	68	0.37	105	145

a: 46 refer to hard-segment content (%); T_g from E'' of DMA;
c: high temperature transition from DSC.

Results and discussion

IR Spectroscopy

A typical IR spectrum of PMD-59 is illustrated in Fig. 1. The wide single peak appears in the region of 3300-3200 cm^{-1} , which is contributed to the hydrogen-bonded N-H stretchings. In the carbonyl region between 1650-1750 cm^{-1} , the peak due to bonded C=O stretching centered at 1700 cm^{-1} predominates, and that due to free C=O appears as a shoulder at 1730 cm^{-1} . The benzene C=C stretchings appear at 1600 and 1500 cm^{-1} ; >C-O stretchings at 1250 cm^{-1} ; C-O-C stretchings at 1110 cm^{-1} ; -NO₂ stretchings at 1335 cm^{-1} ; the benzene ring bendings of p-substitution at 820 cm^{-1} ; and -(CH₂)_n- stretchings of n>4 at 730 cm^{-1} .

These results indicate that the chemical structure of the polymers is in according with our design. The IR spectra of other samples, which are not presented here, are very similar.

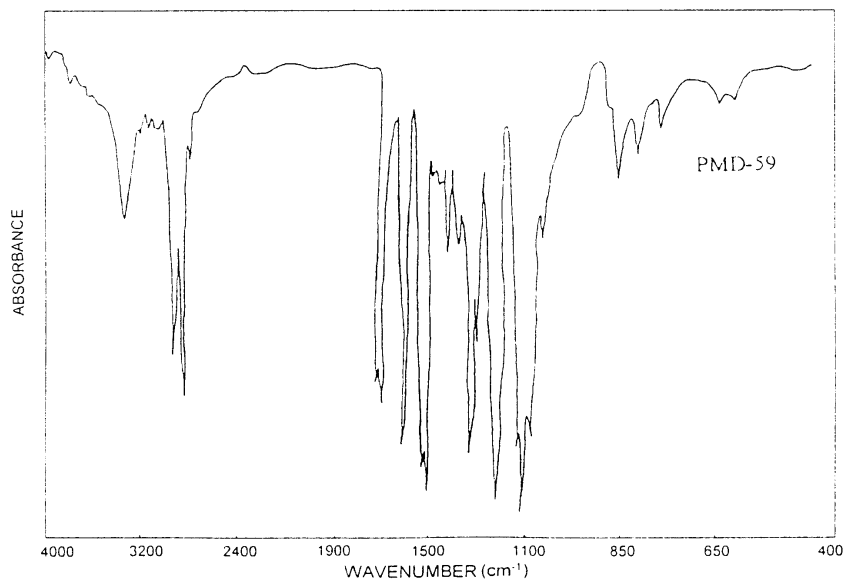


Fig.1 FT-IR spectrum of PMD-59

Optical Texture Analysis

We used DR-19 as a chain extender to synthesize a series of side chain polyurethanes. Some of them exhibited liquid crystal properties, though the mesogenic unit was directly connected to main chains without spacer. The formation of LC was strongly related to main chains of polyurethanes.

The polyurethanes of MDI series showed no LC phase any way. This may be contributed to the two reasons: one is the rigidity of MDI, and the other is that the formation of allophanate and biuret is hard to be avoided in the process of polyurethane preparation, which hinders anisotropic orientation of the mesogenic side chains. Instead, the polyurethanes of HDI series showed typical nematic phases. In this case, the two flexible methylene units of HDI can act as a buffer zone to weaken the interaction as shown in Figure 2.

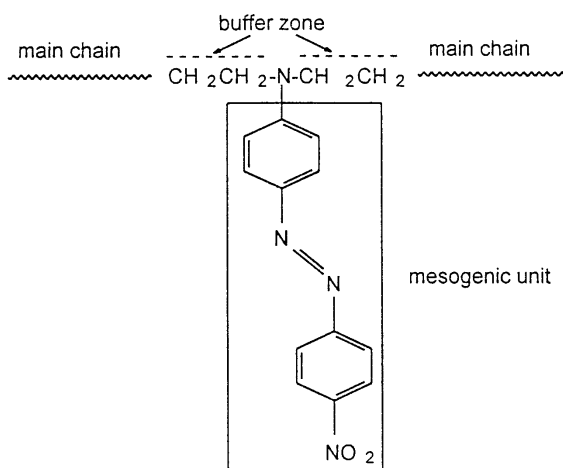


Fig. 2 The flexible spacers in the main chain act as a buffer zone

Figure 3 shows polarizing optical microphotographs of the polymers, in which HD-100 and PHD-54 show droplet texture at 130 °C and 158 °C, respectively.

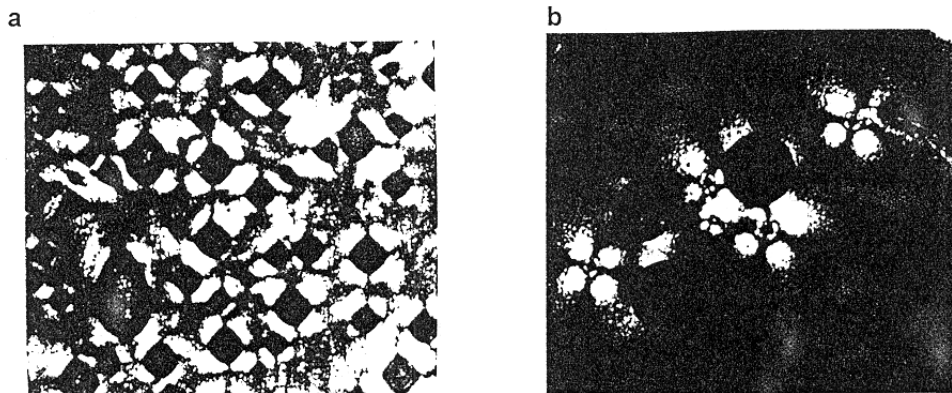


Fig. 3 Textures of the nematic phase (a: HD-100 at 130 °C, b: PHD-54 at 158 °C)

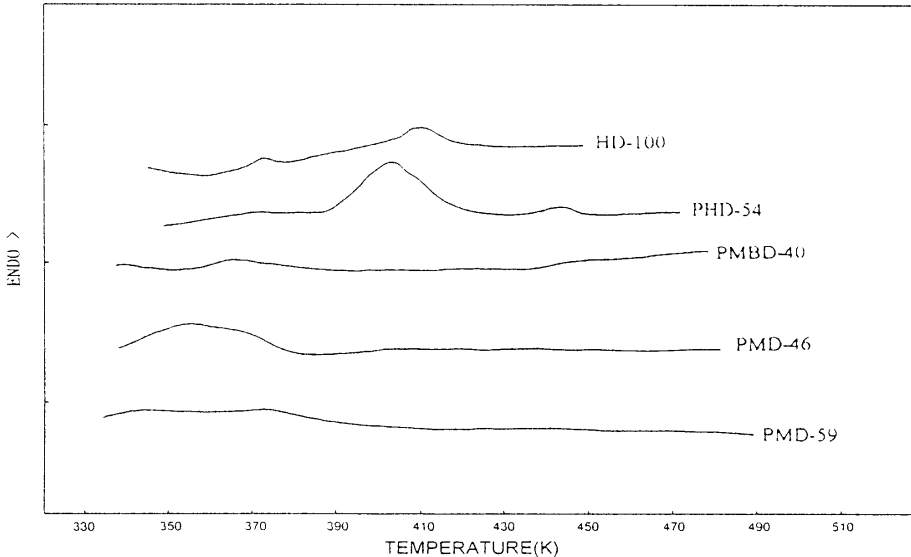


Fig 4. DSC traces of polyurethanes at heating of 20 K/min

Thermal Analysis

The DSC scans (Figure 4) show that HD-100 with no flexible segment has a nematic phase between 105 °C and 145 °C. When the PTMO was imparted for PHD-54, it can be observed that T_i and T_m decrease to 131 °C and 169 °C. This is contributed to the phase separation between the hard and soft segments. Compared to the polyurethanes of HDI series, all polyurethanes of MDI series gave only a high temperature transition respectively. These were confirmed by microscopy.

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