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Liquid-Crystalline Polyurethanes. 5. Polyurethanes Containing the Cholesterol Moiety in the Side Chain

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NOTE

LIQUID-CRYSTALLINE POLYURETHANES. 5. POLYURETHANES CONTAINING THE CHOLESTEROL MOIETY IN THE SIDE CHAIN †

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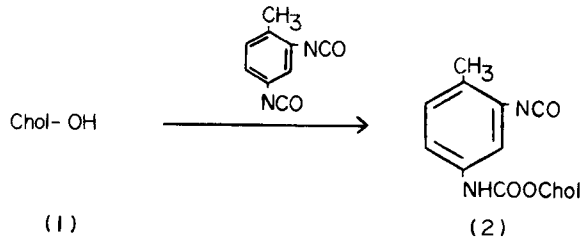
INTRODUCTION

In the preceding papers of this series, we reported the synthesis of liquid-crystalline polyurethanes containing mesomorphic moieties in the main chain and in side chains [1-4]. Liquid crystalline polymers with side groups containing the cholesterol moiety have also been studied [5, 6]. The main focus of attention has centered around the study of phase transitions of acrylic and methacrylic derivatives of cholesterol. This paper describes the synthesis of a new type of liquid-crystalline polyurethane containing the cholesterol moiety in side chains.

† Part 4, see Reference 4.



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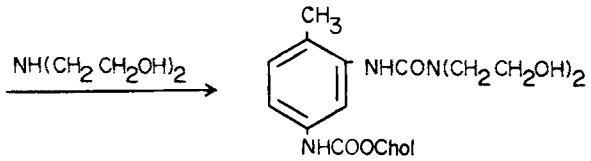

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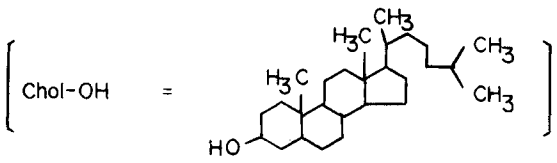

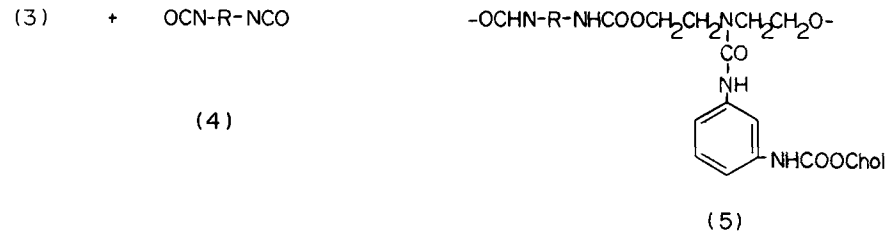

(4) (5)

	4a, 5a	4b, 5b	4c, 5c	4d, 5d	4e, 5e
R	$(CH_2)_6$	CH_2	CH_2 CH_2	CH_3	CH_2

SCHEME 1.

EXPERIMENTAL

Materials

Isocyanates **4a**, **4d**, **4e**, and the solvent were commercial products, and purified by vacuum distillation. Cholesterol was purified by the bromination method. Diethanolamine was a commercial product, used without further purification. Diisocyanates **4b** and **4c** were supplied by Takeda Seiyaku Co., and purified by vacuum distillation.

Compound **2**: Into a 500-mL four-necked round-bottomed flask, equipped with a mechanical stirrer, thermometer, reflux condenser with drying tube, and dropping funnel, were placed 19.3 g (0.05 mol) cholesterol in 400 mL benzene. After 8.7 g (0.05 mol) 2,4-tolylene diisocyanate in 100 mL benzene was added with shaking at 60°C, the solution was kept at this temperature for 2 h. The reaction mixture was poured into dry, cold ether, and the precipitate was recrystallized from dry benzene. T_m 103°C, T_i 148°C, yield 19.8 g (51%). IR (KBr): 3300 cm^{-1} (>NH), 2300 cm^{-1} (–N=C=O), 1710 cm^{-1} (C=O).

Compound **3**: Into a 500-mL three-necked round-bottomed flask, equipped with a mechanical stirrer, thermometer, and reflux condenser, were placed 14.0 g (0.025 mol) **2** and 2.6 g diethanolamine in 300 mL DMF. They were stirred at 60°C for 2 h. After the solution was cooled, the precipitate formed was filtered and recrystallized from ethanol. T_m 175°C, T_i 202°C, yield 10.8 g (65.1%). IR (KBr): 3350 cm^{-1} (>NH), 1710 cm^{-1} (=CO), 1640 cm^{-1} (=CO).

Analysis. Calculated for $C_{40}H_{63}N_3O_5$ (665.9): C, 72.14; H, 9.53; N, 6.31% Found: C, 71.93; H, 9.81; N, 6.11%.

Polymerization Procedure

Into a 100-mL round-bottomed flask, equipped with a reflux condenser with a drying tube and a thermometer, were placed a 1:1 mole ratio of **3** and the corresponding diisocyanate (see Table 1) in 10 mL DMF. The mixture was stirred at 100-120°C for 3 h. At the end of the reaction, the mixture was poured into 200 mL ether, filtered, and washed with methanol.

Viscosity Measurement

The measurement were carried out at 25°C with an Ubbelohde-type viscometer.

Polarization Microscopy

This was carried out with a polarizing optical microscope with a Yanaco Model MP heating stage.

DSC-T_g Measurement

Thermal analysis was performed in the differential scanning calorimetry mode of the Rigaku Thermoflex instrument. The samples, weighing 0.01 g, were heated at 5°C/min from room temperature to 400°C.

Wide-Angle X-Ray Diffraction Measurement

The wide angle x-ray diffraction patterns of powders were recorded with the Rigaku Geigerflex RAD-2B.

Spectroscopic Measurement

The ^{1}H-NMR and IR measurement were carried out on JNM-PMX60 and Jasco Model IR-G spectrometers.

RESULT AND DISCUSSION

The synthetic route leading to polyurethanes based on cholesterol is outlined in Scheme 1.

Compound **2** was prepared by the equimolar reaction of cholesterol (**1**) with 2,4-tolylene diisocyanate (TDI) in benzene. Next, diol was introduced by the equimolar reaction of **2** with diethanolamine. Products **2** and **3** were characterized by IR and NMR spectroscopy.

The polymers obtained from **3** and diisocyanates in DMF at 100-130°C are listed in Table 1. The thermal properties of the polymers were determined by polarized light microscopy and DSC. As shown in Table 1, polymers **5a**, **5c**, and **5d** exhibit a liquid crystalline state at 130-203, 145-177, and 165-198°C, respectively. Polymers **5b** and **5e** show only one transition. These result are nearly consistent with the DSC-T_g measurement (Fig. 1). Figure 2 shows x-ray diffraction patterns at a wide angle at RT for Polymer **5a**. A very sharp and intense peak at $2\theta = 1.55°$, corresponding to a periodicity of 57.0 Å, and another weak peak at $2\theta = 3.10$, are shown. From these results it is estimated that the polymer has a smectic structure. The distance from the center of the main chain to the end of the side group is estimated to be 28.5 Å, i.e., approximately the sum of the lengths of the phenyl and cholesterol groups.

TABLE 1. Polyurethanes Obtained from **3** and Diisocyanates **4a-e**[a]

Polymers	Weight of isocyanate, g	T_m, °C	T_i, °C	Yield, %	$[\eta]$, dL/g
5a	0.253	130	203	73	0.37
5b	0.394	—	172	89	0.21
5c	0.292	145	177	78	0.15
5d	0.262	160	198	80	0.14
5e	0.376	—	225	90	0.19

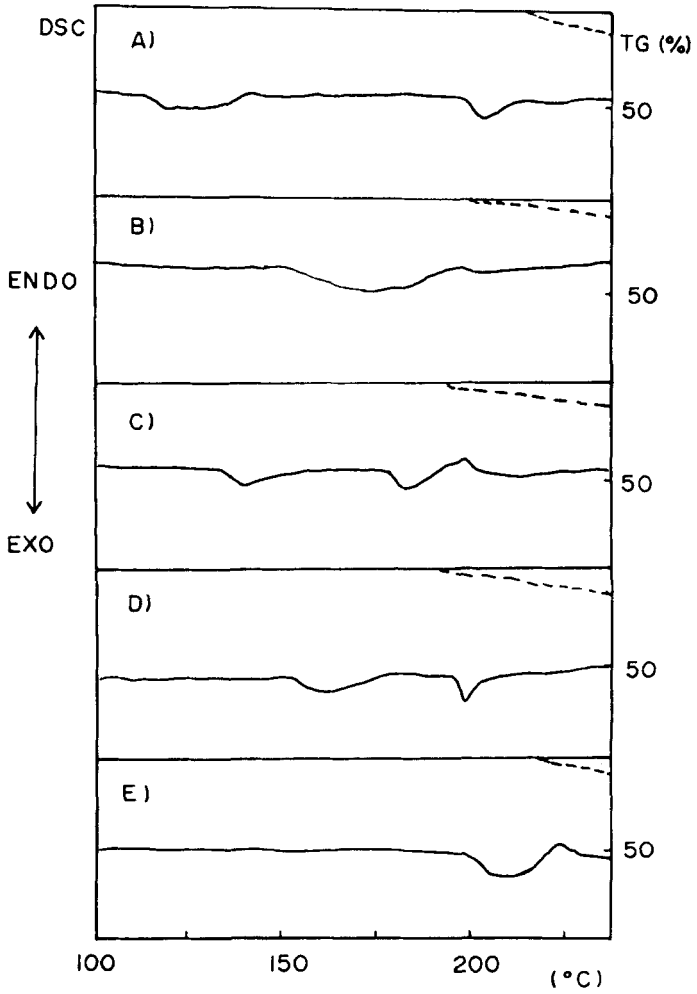

FIG. 1. DSC-T_g curves for polyurethanes. (—) DSC, (- -) TG. A) **5a**, B) **5b**, C) **5c**, D) **5d**, E) **5e**.

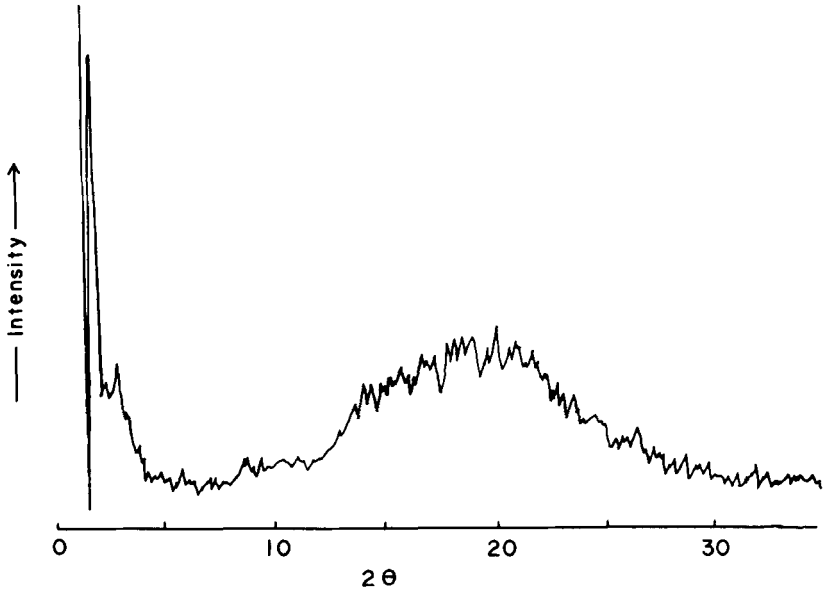

FIG. 2. Wide-angle x-ray diffraction scans for polyurethane **5a** at room temperature.

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