

Synthesis and Liquid Crystalline Properties of New Thermotropic Polyurethanes

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ABSTRACT: Mesogenic diol monomer, terephthaloyl dioxydibenzoic acid diol ester ($n=2, 3, 4, 5, 6$), were prepared from ω -hydroxyalkyl-4-hydroxybenzoate and terephthaloyl chloride, using Schotten–Baumann Reaction. New liquid crystalline polyurethanes (LCPUs) were obtained by solution polymerization mesogenic diol monomers with 4,4'-diphenylmethane diisocyanate (MDI) and 2,4-tolylene diisocyanate (2,4-TDI). The monomer and polyurethanes were investigated by DSC, polarizing microscopy, wide-angle X-ray diffraction (WAXD), small-angle X-ray diffraction (SAXD) and high temperature X-ray diffraction. All LCPUs synthesized showed a nematic LC nature with wide temperature range.

KEY WORDS Polyurethane / Thermotropic Liquid Crystalline Polymer /

The synthesis of liquid crystalline (LC) main-chain polymers has been intensely investigated because of their theoretical properties and technological applications.^{1–3} In particular, a large variety of works has focused on thermotropic polyesters and polyamides. For polyurethanes, the polymer backbone becomes very rigid due to the formation of hydrogen bonds so that considerable investigation in this field were not made until last decade.

In 1981, Iimura and co-workers first reported thermotropic polyurethanes prepared by polyaddition of 3,3'-dimethyl-4,4'-biphenyldiyl diisocyanate with α,ω -alkanediols.⁴ Later, main-chain liquid crystalline polyurethanes (MLCPUs) with various molecular structures were synthesized. These polyurethanes can be subdivided into five groups by synthetic routes^{5,6}:

(1) MLCPU, prepared by reactions of diisocyanates with diols having mesomorphic groups as core units,^{7,8–27}

(2) those prepared by reactions of diols with diisocyanates having mesomorphic groups as core units,^{4,28–35}

(3) those prepared by condensation reactions of dichloroformates with diamines,³⁶

(4) those prepared by melt condensation reactions of diisocyanates blocked with phenol with diols having biphenyl groups as core units,^{37–39}

(5) those prepared by reaction of an aromatic carbamoyl dichloride with a mesogen-containing diol.^{40,41}

This research investigates the synthesis and thermotropic properties of a new series of MLCPUs by reactions of diisocyanate monomers, *i.e.*, 2,4-tolylene diisocyanate (2,4-TDI), 4,4-diphenylmethane diisocyanate (MDI), with mesogenic diol monomers, terephthaloyl dioxydibenzoic acid diol esters (**3a–e**) (Scheme 1). The polymers are prepared by solution polyaddition in *N,N*-dimethylformamide (DMF). The effects of the length of the alkylene spacers on thermal properties are discussed for both polyurethanes.

EXPERIMENTAL

Materials

Commercially available 2-chloroethanol, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, and 4-hydroxybenzoic acid were used without further purification. Commercially available MDI, 2,4-TDI, and terephthaloyl chloride were distilled before use.

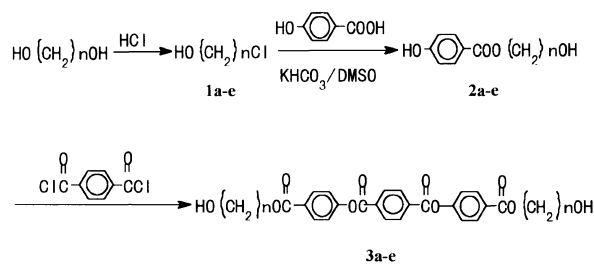
Monomer Synthesis

Mesogenic diol monomer, terephthaloyl dioxydibenzoic acid diol ester **3a–e**, were synthesized according to the same general procedure outlined in Scheme 1. As a typical example, the synthesis of terephthaloyl dioxydibenzoic acid hexanediol ester (**1e**) is reported.

6-Chlorohexanol (1e). A solution of 45 mL (0.38 mol) 1,6-hexanediol in 200 mL (2.03 mol) hydrochloric acid was reacted under 90°C for 15 h, using toluene to consecutively extract the product. The crude product was distilled under normal pressure to remove toluene and then distilled under vacuum pressure (100–104°C/9.3 × 10⁻⁴ MPa) to give **1e** (yield 27.5%).

1a was commercially available and **1b**, **1c**, and **1d** were synthesized according to the similar procedure with yields ranging from 24% to 34%.

6-Hydroxyhexyl-4-hydroxybenzoate (2e). **2e** was prepared by a similar procedure given by Angeloniet *al.*²⁶ A solution of 4-hydroxybenzoic acid (0.258 mol, 35.6 g), anhydrous potassium bicarbonate (0.258 mol, 25.8 g) and



1a-3a: $n=2$; **1b-3b:** $n=3$; **1c-3c:** $n=4$; **1d-3d:** $n=5$; **1e-3e:** $n=6$

Scheme 1.

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1e (0.215 mol, 29.4 g) in 120 mL of dry dimethylsulfoxide was stirred at 80°C. After 5 h, the mixture was poured into 700 mL cold water saturated with sodium chloride and kept at 5°C overnight. The crude product was filtered, washed with cold water and dried. The residue was recrystallized from chloroform to give 37.4 g (yield 73%) of **1e**: mp 100°C.

¹H NMR (dimethyl sulfoxide (DMSO)-*d*₆): δ = 10.35 (s, -Ar-OH, 1H), δ = 7.80, 6.85 (q, -Ar-H, 4H), δ = 4.40 (s, -OH, 1H), δ = 4.20 (t, -COOCH₂-, 2H), δ = 3.40 (t, -CH₂OH, 2H), δ = 1.90–1.20 (m, -(CH₂)₄-, 8H).

C₁₃H₁₈O₄ (238) Calcd C 65.55 H 7.56
Found C 65.51 H 7.65

Crude products **2a–d** were recrystallized from water (mp_a: 142°C), chloroform (mp_b: 99°C), chloroform (mp_c: 92°C), and benzene (mp_d: 110°C) respectively with yields ranging from 52% to 65%.

Terephthaloyl Dioxidybenzoic Acid Hexanediol Ester (**3e**). **3e** was prepared by condensation reaction of 2 mol of **2e** with 1 mol of terephthaloyl chloride according to the Schotten–Baumann reaction. Into a 100 mL three-necked flask, equipped with a mechanical stirrer, thermometer and dropping funnel, were placed 9.52 g (0.04 mol) **2e** and a solution of 1.76 g (0.044 mol) sodium hydroxide in 20 mL distilled water. After cooling the solution to 10°C, 4.06 g (0.02 mol) terephthaloyl chloride dissolved in 36 mL acetone were added slowly to the stirred solution, which caused the product to precipitate from the solution. The reaction mixture was maintained at 10–15°C during the addition and allowed to rise to room-temperature. After being kept at this temperature for 2 h, the precipitate was filtered and washed well with 1 wt% aqueous sodium hydroxide to remove the unreacted species and by-products. The residue was recrystallized two or three times from 2-butanone to give **3e** (yield 65%): *T*_m: 143°C, *T*_i: 174°C.

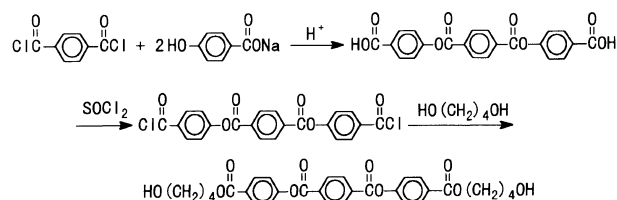
¹H NMR (DMSO-*d*₆): δ = 8.37 (s, -Ar-H, 4H), δ = 8.12 (d, -Ar-H, 4H), δ = 7.52 (d, -Ar-H, 4H), δ = 4.30 (t, -COOCH₂-, 2H), δ = 3.40 (t, -CH₂OH, 2H), δ = 1.90–1.30 (m, -(CH₂)₄-, 8H).

C₃₄H₃₈O₁₀ (606) Calcd C 67.33 H 6.27
Found C 67.30 H 6.29

2-Butanone was also used as recrystalline solvent to **3a** (*T*_m: 213°C, *T*_i: 265°C), **3b** (*T*_m: 177°C, *T*_i: 208°C), **3c** (*T*_m: 167°C, *T*_i: 211°C), and **3d** (*T*_m: 156°C, *T*_i: 188°C) with yields ranging from 45% to 65%.

Polymer Synthesis

All polymerizations were carried out under dry nitrogen and highly purified and dried *N,N*-dimethylacetamide (DMAc) was used as solvent. Into a 100 mL three-necked flask equipped with a reflux condenser with a drying tube, equimolar quantity of diisocyanate was added dropwise a solution of **3a–e** and catalyst dibutyl tin dilaurate in DMAc. The reaction mixture was maintained at 60°C for 2 h after the addition and allowed to rise to 70°C for 4 h. At the end of the reaction, the solution was poured into methanol to precipitate the polymer in the form of a white material. This polymer was washed with methanol, and subsequently dried under vacuum at 60°C.



Scheme 2.

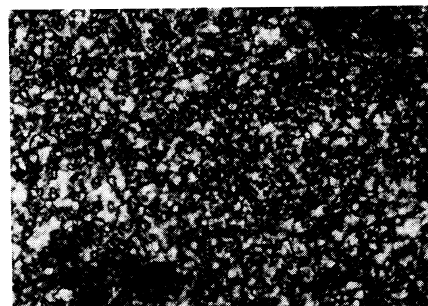


Figure 1. Optical microphotography (200×) of **3d** at 170°C.

Table I. LC phase transition temperature of mesogenic diol **3a–e** by DSC

Formula	Transition temperature/°C		Δ <i>T</i> /°C
	<i>T</i> _m	<i>T</i> _i	
3a	213	265	52
3b	177	208	31
3c	167	211	44
3d	156	188	32
3e	143	174	31

Measurements

¹H NMR spectra were measured in DMSO-*d*₆ by a UNITY-200 spectrometer. DSC and TGA data were obtained on a General 4.1 Dupont 2100 system at a heating rate of 10°C min⁻¹. Thermal properties in connection with the morphological observation were investigated by Olympus BH-2 microscope equipped with a Leitz heated stage. X-Ray diffraction patterns (SAXD or WAXD) were obtained with a diffractometer, type Ricon D/Max-RB with Cu-*K*_α. High temperature X-ray diffraction measurements were performed using the Rigaku D ϵ Max 200 diffractometer.

RESULTS AND DISCUSSION

Synthesis

General reaction routes for the series of mesogenic diol monomer, terephthaloyl dioxidybenzoic acid diol ester **3a–e** are shown in Scheme 1. Compared with another equivocal synthetic method (Scheme 2),⁴² ω-hydroxyalkyl 4-hydroxybenzoate **2a–e** are more likely to inhibit the polymerization because of the different natures of the aromatic hydroxyl and aliphatic hydroxyl.

According to the Schotten–Baumann reaction, mesogenic diol monomer **3a–e** can be obtained with typical nematic features. Figure 1 shows a polarizing optical microphotograph of diol **3d**. Similar textures were observed in other samples.

From the data in Table I increase in spacer length

results in lower phase transition temperature T_m and T_i .

General reaction routes of polymerization in this study are shown in Scheme 3. In the presence of dibutyl tin dilaurate as catalyst, all novel thermotropic liquid crystalline polyurethane was synthesized by polyaddition of mesogenic diol **3a–e** with MDI or 2,4-TDI. The LCPUs showed good solubilities in aprotic organic solvents, such as DMAc, *N*-methyl-2-pyrrolidone (NMP), and DMF.

Properties of Liquid Crystalline Polyurethanes

Inherent viscosities in DMF and phase transition of all LCPUs synthesized are shown in Table II and Figures 2–4. The results were in accordance with the polarizing optical microscope observation. DSC traces of LCPU1 and LCPU2 exhibited two or more endothermic peaks. TGA of **3d**-MDI showed the isotropization temperature (T_i) close to the degradation temperature (T_d).

Figure 5 shows typical polarizing optical microphoto-



Scheme 3.

Table II. η_{inh} and LC phase transitions by DSC of polyurethanes

Formula	$\eta_{inh}/\text{dl g}^{-1}$	Transition temperature/ $^{\circ}\text{C}$		$\Delta T/^{\circ}\text{C}$
		T_m	T_i	
3a -2,4-TDI	0.29	132	274	142
3d -2,4-TDI	0.10	92	269	177
3a -MDI	0.11	196	314 ^a	118
3b -MDI	0.13	191	333 ^a	142
3c -MDI	0.11	171	333 ^a	162
3d -MDI	0.13	156	332 ^a	176
3e -MDI	0.10	147	331 ^a	184

^a $T_i \approx T_d$.

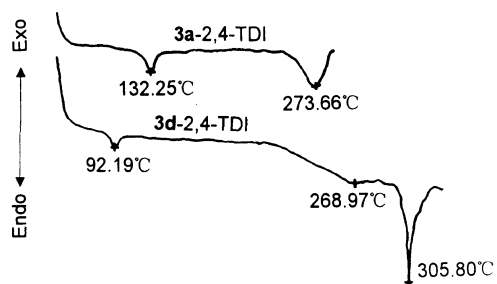


Figure 2. DSC curves of LCPU1.

graph of LCPU1 and LCPU2. Similar textures were observed for other samples.

Results of wide-angle X-ray diffraction (WAXD)

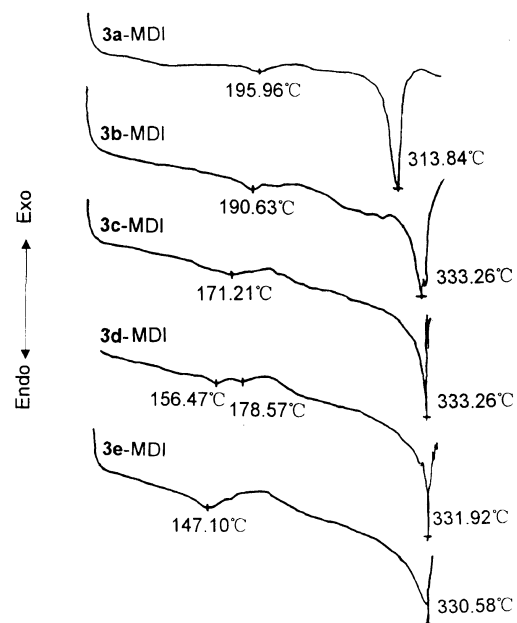


Figure 3. DSC curves of LCPU2.

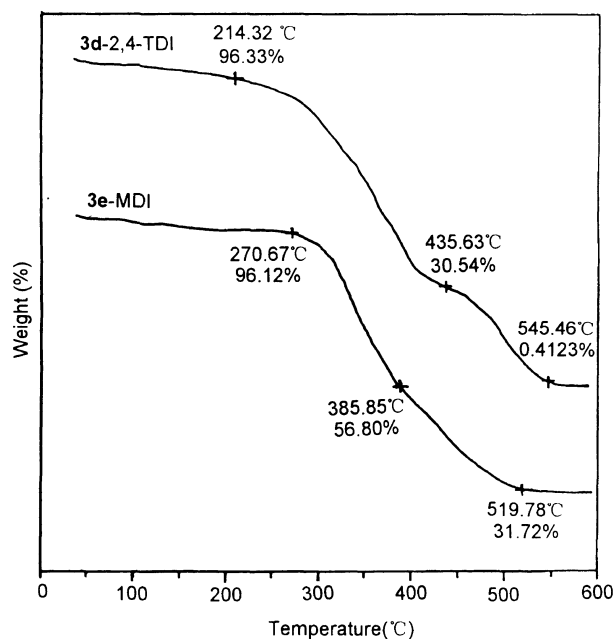
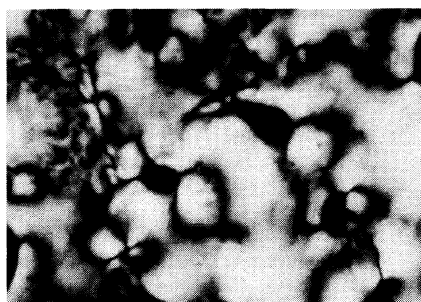
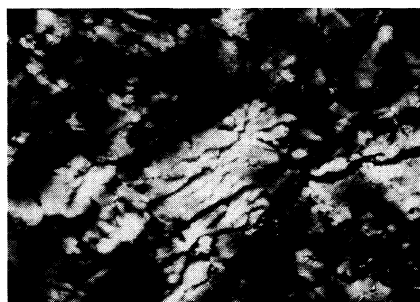


Figure 4. TGA curves of polyurethanes.



(a)



(b)

Figure 5. Optical microphotography (400 \times) of LCPU1 and LCPU2. (a), **3a**-2,4-TDI at 180 $^{\circ}\text{C}$; (b), **3e**-MDI at 180 $^{\circ}\text{C}$.

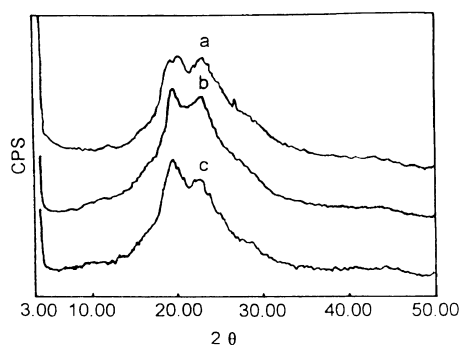


Figure 6. WAXD patterns for LCPU1 at room temperature. a, **3d**-2,4-TDI quenching in liquid-N₂ from 200°C; b, **3a**-2,4-TDI; c, **3d**-2,4-TDI.

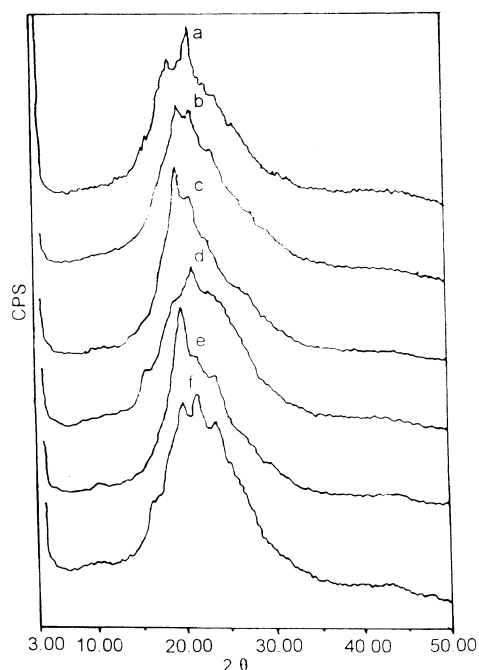


Figure 7. WAXD patterns for LCPU2 at room temperature. a, **3e**-MDI quenching in liquid-N₂ from 200°C; b, **3a**-MDI; c, **3b**-MDI; d, **3c**-MDI; e, **3d**-MDI; f, **3e**-MDI.

analysis of both PUs conducted at room temperature are shown in Figures 6 and 7. WAXD measurements showed dispersing peaks at $2\theta \approx 20^\circ$ as well as some crystalline peaks due to the strong tendency of the urethane groups to form H-bonds. Quenching from the mesomorphic temperature in liquid N₂ did not cause significant effects on WAXD profiles. There was a wide peak at $2\theta \approx 20^\circ$, but few sharp peaks in the X-ray diffraction pattern of **3d**-2,4-TDI at melting state (160°C), which had longer soft spaces (Figure 8). Figure 9 represents the SAXD patterns at room temperature for LCPUs of **3d**-2,4-TDI and **3e**-MDI quenching in liquid N₂ from mesomorphic temperature. The blank small-angle region indicated no long-distance order sequence for both LCPUs. With shorter flexible space, similar results were obtained for other LCPUs. It is obvious that all the samples are not smectic. They are nematic.

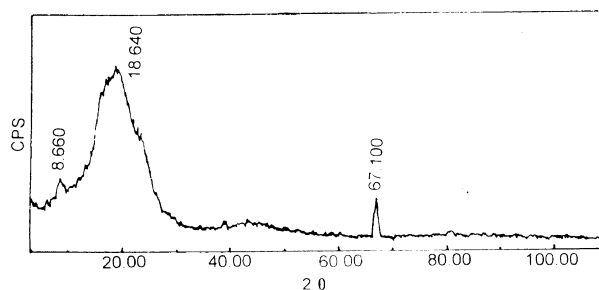


Figure 8. X-ray diffraction pattern of **3d**-2,4-TDI at 160°C.

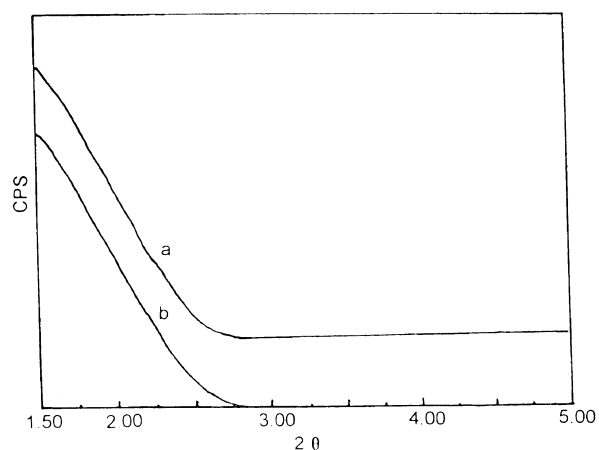


Figure 9. SAXD patterns for polyurethanes at room temperature. a, **3d**-2,4-TDI quenching in liquid-N₂ from 200°C; b, **3e**-MDI quenching in liquid-N₂ from 200°C.

CONCLUSIONS

A series of nematic liquid crystalline diol monomers (**3a–e**) were synthesized by a new method. Increase in spacer length results in lower phase transition temperature T_m and T_i .

Novel liquid crystalline LCPU1 and LCPU2 were prepared through solution polymerization of (**3a–e**) with MDI or 2,4-TDI respectively. They exhibit nematic LC textures. The T_i of polyurethanes based on MDI are close to the T_d . The phase transition temperatures of polyurethanes based on MDI are higher than those based on 2,4-TDI.

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