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## Liquid Crystals

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### Synthesis and thermal properties of side chain-type liquid crystalline polyurethanes

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## Synthesis and thermal properties of side chain-type liquid crystalline polyurethanes

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The synthesis of side chain-type polyurethanes is described. Their thermal properties were investigated by differential scanning calorimetry and polarizing microscopy and are discussed in terms of the dependence of the polymer backbone on temperature as shown by FT-infrared spectroscopy. The hydrogen bonding which arises from the rather flexible polymer backbone plays a more important role in determining the thermal stability than does the rigid polymer backbone.

### 1. Introduction

Recently, a large variety of side chain-type liquid crystalline polymers (LCPs) has been investigated by many research groups, because of their theoretical properties and technological applications [1]. In general, the factors which affect the thermal properties of side chain-type LCPs depend upon the structure of the polymer backbone, mesogenic unit and flexible spacer connecting the mesogenic group to the polymer backbone. In these polymers, the polymer backbone chains mostly consist of polyacrylate [2], polymethacrylate [3] or polysiloxane [4] as the rather flexible chain. On the other hand, relatively rigid backbones have also been used such as polystyrene [5], polymaleimide [6], polyester [7] and polyurethane [8]. In the case of LCPs having active hydrogen atoms as in the urethane bond, the polymer backbone becomes very rigid due to the formation of hydrogen bonds between the active hydrogen atoms in the urethane bond with adjacent polar atoms such as the carbonyl group.

In this paper, the synthesis and thermal properties of side chain-type LCPs with urethane bonds as the polymer backbone component were studied. Two new kinds of side chain-type liquid crystalline polyurethanes (PU-a, PU-b) were prepared by the polyaddition of the mesogenic diol monomer with hexamethylene (a) or *p*-phenylenediisocyanate (b), in order to show the effect of the chemical structure of the polymer backbone component on the polymer thermal properties. A 1,3-propanediol derivative containing a methoxybiphenyl moiety connected to a flexible alkyl spacer was synthesized as the mesogenic diol monomer. The thermal properties of the obtained polyurethanes were investigated by using polarizing microscopy, differential scanning calorimetry (DSC) and X-ray diffraction. Furthermore, the interactions between the polymer backbones due to hydrogen bonding were studied with a thermally-controlled Fourier transform infrared spectrometer (FT-IR).

### 2. Experimental

#### 2.1. Diethyl 2-[6-(4'-methoxy-4-biphenyloxy)hexyl]malonate 3

1,6-Dibromohexane (14 ml; 90 mmol) was added to a solution of THF (50 ml) containing 4-hydroxy-4'-methoxybiphenyl 1 (3.5 g; 18 mmol), 50 ml of an alkaline

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aqueous solution of sodium hydroxide (2.3 g; 58 mmol) and tetrabutylammonium hydrogensulphate (0.5 g; 1.5 mmol). Then, the mixture was refluxed for one day. After the solvent was distilled off, the mixture was extracted with chloroform. An excess amount of hexane was added to the concentrated mixture, the residue was filtered off to afford a pure product of **2** (2.8 g), which was confirmed by thin layer chromatography. The yield was about 70 per cent (temp. 122.4°C).

1.9 mol of sodium methylate solution (28 per cent in methanol) was added to a mixture of diethylmalonate (1.6 ml; 11 mmol) in 50 ml of THF at room temperature, and the mixture was refluxed for 30 min. Then, **2** was added to the mixture, and it was refluxed overnight. The mixture was evaporated, washed with diethyl ether, and the sodium bromide formed was removed by filtration. The filtrate was purified by column chromatography on silical gel with chloroform/hexane (1.5) to afford 2.8 g of a malonate derivative **3**. The yield was 62 per cent (temp. 67°C).

IR (nujol):  $\nu$  1734 (C=O), 1606 (Ar.), 1500, 1460, 1375, 1038, 820, 515  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.29 (t; 6 H,  $\text{CH}_3\text{CH}_2\text{O}$ -,  $J = 7.1$  Hz), 1.4–2.1 (m; 10 H,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 3.32 (t, 1 H,  $(-\text{C}=\text{O})_2\text{CH}-\text{CH}_2-$ ), 3.86 (s; 3 H,  $-\text{OCH}_3$ ), 4.00 (t; 2 H,  $-\text{CH}_2\text{CH}_2\text{O}$ -), 4.22 (q; 4 H,  $\text{CH}_3\text{CH}_2\text{O}$ -,  $J = 7.1$  Hz), 6.96 (dd; 4 H, ArH,  $J = 8.9, 1.2$  Hz), 7.49 p.p.m. (dd; 4 H, ArH,  $J = 8.9, 1.4$  Hz).

### 2.2. 2-[6-(4'-Methoxy-4-biphenyloxy)hexyl]propane-1,3-diol **4**

Lithium aluminium hydride (1.0 g; 26 mmol) was suspended in 40 ml of dry THF in a 300 ml flask, equipped with a reflux condenser and a dropping funnel at 0°C. A solution of **3** (1.5 g; 3 mmol) in 20 ml of dry THF was added dropwise to the mixture. The mixture was stirred with slowly increasing temperature, and refluxed for 4 h. After the mixture was cooled to 0°C, 30 ml of cool water was added dropwise to the mixture, and an aqueous solution of hydrochloric acid was added to the mixture until the salt was dissolved. Further, 50 ml of a saturated solution of sodium chloride was poured into the mixture, followed by the extraction of **4** with diethyl ether to afford 1.0 g of **4**. The yield was 77 per cent.

IR (nujol):  $\nu$  3313 (OH), 1606 (Ar.), 1500, 1466, 1275, 1248, 1182, 1039, 825, 808, 517  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  1.3–2.0 (m; 10 H,  $-\text{CH}_2\text{CH}_2\text{CH}_2-$ ), 2.2–2.4 (m; 1 H,  $-\text{CH}(\text{CH}_2-)_3$ ), 3.7–3.9 (m; 4 H,  $\text{HOCH}_2-$ ), 3.86 (s; 3 H,  $-\text{OCH}_3$ ), 4.00 (t; 2 H,  $-\text{CH}_2\text{CH}_2\text{O}$ -,  $J = 6.2$  Hz), 6.96 (dd; 4 H, ArH,  $J = 8.8, 0.9$  Hz), 7.49 p.p.m. (dd; 4 H, ArH,  $J = 8.8, 0.8$  Hz).

### 2.3. Polymerization

A solution containing 1.017 g of diol monomer **4** in 15 ml of dry DMF was heated at 90°C under a nitrogen atmosphere. Then, 0.477 g of 1,6-hexamethylenediisocyanate was added to the solution, and stirred for 13 h. The solution was poured into 400 ml of methanol to precipitate the polymer. The yield of the obtained polyurethane (PU-a) was 0.177 g (11.8 per cent).

PU-b was also prepared by polyaddition of **4** with p-phenylenediisocyanate instead of 1,6-hexamethylenediisocyanate in the same manner as above.

IR (nujol): PU-a;  $\nu$  3327 (NH), 1693 (C=O), 1608 (Ar.), 1539 (NH), 1500, 1466, 1273, 1244, 1146, 1041  $\text{cm}^{-1}$ . PU-b;  $\nu$  3321 (NH), 1705 (C=O), 1608 (Ar.), 1520 (NH), 1500, 1466, 1410, 1309, 1242, 1217  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$  and DMSO): PU-a;  $\delta$  1.2–2.0 (m), 3.82 (s), 3.98 (t), 4.04 (m), 4.47 (s), 5.94 (bs), 6.93 (d), 7.45 p.p.m. (d). PU-b;  $\delta$  1.2–2.0 (m), 3.82 (s), 3.97 (t), 4.20 (m), 6.93 (d), 7.36 (s), 7.45 (d), 8.68 p.p.m. (bs).

### 2.4. Characterization

$^1\text{H}$  NMR was carried out with a Hitachi R-90H FT-NMR (90 MHz) spectrometer using  $\text{CDCl}_3$  of a mixture of  $\text{CDCl}_3$  with  $\text{DMSO}-d_6$  as solvent. IR spectra were recorded on a JEOL JIR-100 FT-IR spectrometer. Gel-permeation chromatography (GPC) was carried out with a Tosoh HLC-802A instrument using THF as eluent, equipped with four columns of TSK gels G5000H<sub>6</sub>, G4000H<sub>6</sub>, G3000H<sub>6</sub> and G2000H<sub>6</sub>. Standard polystyrenes were used for calibration. Differential scanning calorimetry (DSC) was conducted by using a Seiko Electronic DSC-20 with SSC-580 thermal controller at heating and cooling rates of  $10^\circ\text{C min}^{-1}$ . X-ray diffraction patterns were recorded on a MAC Science MXP<sup>3</sup> X-ray diffractometer, equipped with a thermal controller Model 5310.

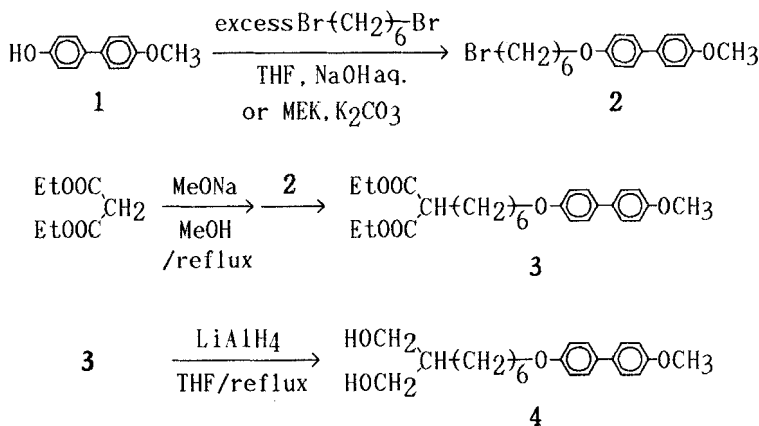
### 2.5. Measurement of thermally-controlled FT-IR spectra

Silicon bases were prepared by washing with an aqueous solution of hydrogen fluoride. Polyimide was applied to the side in contact with the sample of the base in one direction. Then, the bases were treated *in vacuo* at  $200^\circ\text{C}$  for 2 h. Polyurethane powder was interposed between the two silicon bases, and the silicon base pressed together at a temperature above the clearing temperature. The edge of the cell was sealed with an epoxy compound to prevent effusion of the sample. A stage having a window of 1 cm diameter at the midpoint was prepared and equipped with a thermoregulator. Then, the sample stage was placed in the light path of the FT-IR spectrometer to obtain the spectra. The raw spectra were corrected by the spectrum of the cell without the sample.

## 3. Results and discussion

The synthetic route of the diol monomer (**4**) is outlined in scheme 1. At first, the bromoalkyl ether derivative (**2**) was synthesized by etherification of 4-methoxy 4'-hydroxybiphenyl (**1**) with 1,6-dibromohexane. The malonate derivative (**3**) was prepared from a reaction of **2** with the carboanion derived from diethylmalonate. Then, the reduction of **3** with lithium aluminium hydride afforded **4**.

The mesogenic diol monomer thus obtained showed an enantiotropic mesophase. The thermal transitions for the mesogenic diol monomers are listed in table 1. Each pair of endothermic or exothermic peaks was observed from both heating and cooling DSC measurements. A liquid crystalline phase was detected for the temperature range



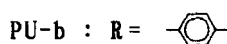
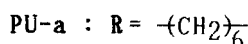
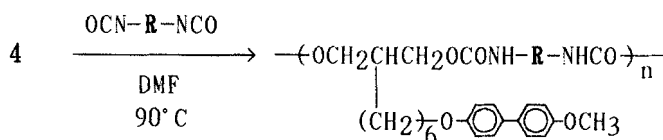
Scheme 1. Synthesis of the diol monomer.

Table 1. Phase transition temperatures of the diol monomer.

Phase transition temperature °C†	
Diol monomer 4	$C \xrightleftharpoons[65]{87.8} M \xrightleftharpoons[133.3]{138.7} I$

C, crystal; M, mesophase; I, isotropic phase.

† Phase transition temperatures were determined by DSC.



Scheme 2. Synthesis of the polyurethanes.

Table 2. Results from polyurethane synthesis.

Code	Yield %	$\bar{M}_w \times 10^{-3}\dagger$	$D\dagger$
PU-a	11.8	4.74	1.38
PU-b	76.3	7.30	1.42

† Determined by GPC (Polystyrene standard).

‡  $D = \bar{M}_w / \bar{M}_n$ .

between the two peaks. Fluidity and birefringence of the optical texture were observed by polarizing microscopy, but the texture of the liquid crystalline phase for these mesogenic diol monomers was not a well-known kind.

Side chain-type polyurethanes were prepared by the polyaddition of the corresponding mesogenic diol monomer with 1,6-hexamethylenediisocyanate of p-phenylenediisocyanate, as shown in scheme 2. Thus, an equivalent amount of diisocyanate was reacted with 4 to afford the desired polyurethane. The obtained polyurethanes were soluble in polar solvents such as tetrahydrofuran (THF), dimethylformamide (DMF) and other polar solvents. Results of the polyaddition for the polyurethanes are summarized in table 2.

DSC curves of PU-a and PU-b are shown in figure 1. Three transition points were observed for PU-a, whereas for PU-b, a glass transition and one peak were detected. The phase transitions and phase characterization of these polyurethanes were conducted by X-ray measurements and from the optical textures, as shown in table 3. The liquid crystalline phases were assigned on the basis of powder X-ray diffraction measurements at various temperatures (see figure 2). X-ray diffraction patterns of PU-a in figure 2(a) indicated that the smectic phase similar to a quasi-crystal phase was exhibited, as some sharp peak reflections were observed in the small angle region characteristic of a layer structure and also in the wide angle region characteristic of high order in the layers. X-ray diffraction patterns of PU-a in figures 2(b) and (c) showed

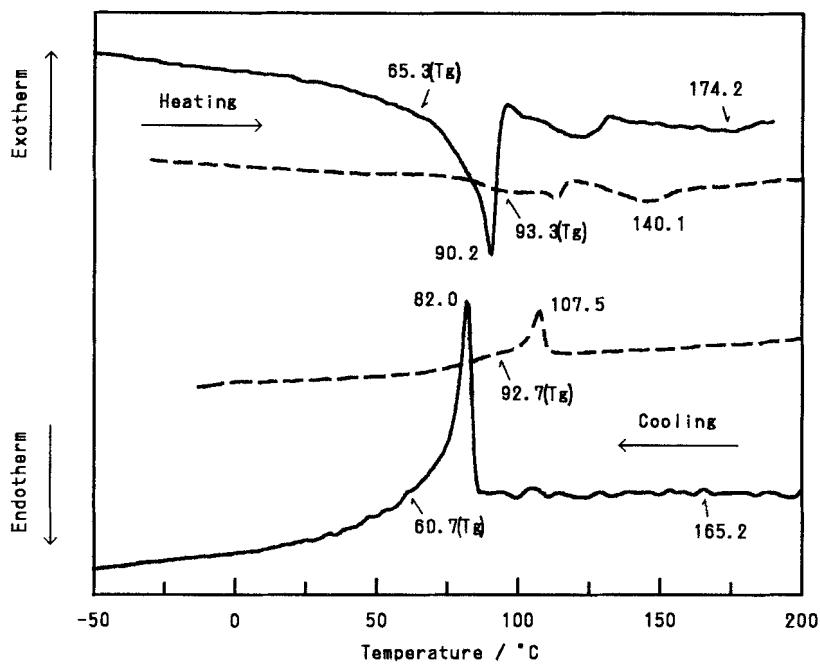


Figure 1. DSC curves of the polyurethanes. (—); PU-a, (---); PU-b.

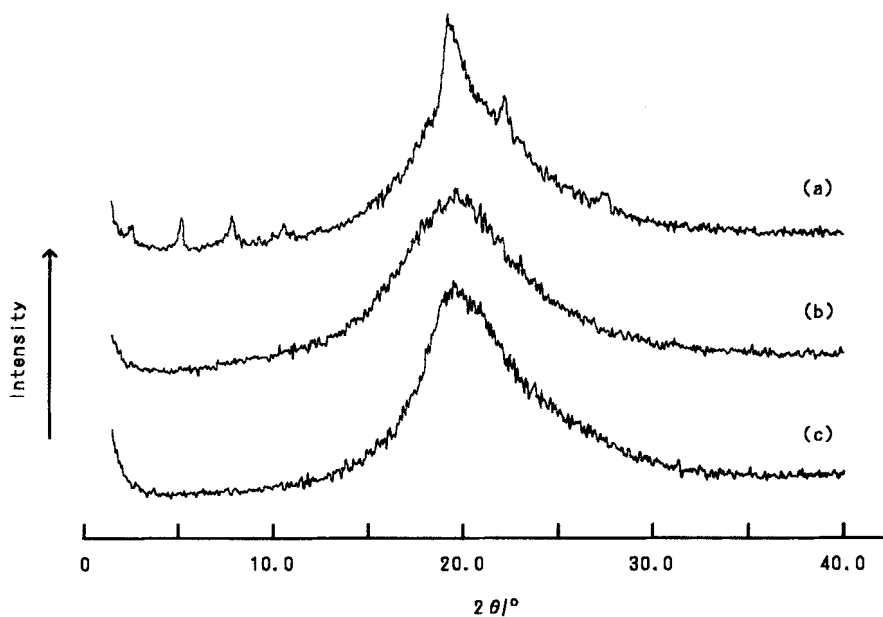


Figure 2. X-ray diffraction patterns of the polyurethanes. (a) PU-a at 70°C; (b) PU-a at 120°C; (c) PU-b at 120°C.

only broad peak reflections typical of a nematic phase in the wide angle region. A typical optical texture of the liquid crystalline mesophase was not observed for both PU-a and PU-b.

As shown in table 3, the thermal stability of the mesophase of PU-a containing flexible alkyl chains in the polymer backbone was superior to that of PU-b having rigid phenylene rings, whereas the isotropic temperature ( $T_i$ ) of PU-a was higher than that of PU-b. This result shows that differences in the rigidity of bulkiness of the polymer backbones affects the thermal properties of these two kinds of polymers. In order to polymers. In addition, the difference in the interactions between the polymer backbones effects the thermal properties of these two kinds of polymers. In order to establish these differences, FT-IR spectra were measured at various temperatures using thermally-controlled FT-IR spectroscopy. FT-IR measurements were conducted for both increasing and decreasing temperature.

FT-IR measurements are a convenient method of investigating the hydrogen bonding between N-H and C=O groups responsible for the interactions between polymer backbones. It is known that the absorption band of a hydrogen-bonded N-H (or C=O) stretching vibration differs from a free N-H (or C=O) stretching vibration [9, 10] in a polymer system. The change in the FT-IR spectra of PU-a, in the range  $3200\text{--}3600\text{ cm}^{-1}$ , for various temperatures is shown in figure 3(a). The absorption band for a free N-H stretching vibration was not observed below  $90^\circ\text{C}$ , the temperature which corresponds to the transition from a smectic phase to a nematic phase. In the region of the nematic phase, a new absorption band at nearly  $3420\text{ cm}^{-1}$  appeared. The maximum amplitude of the absorbance was observed at  $T_i$ . On the other hand, the hydrogen-bonded N-H stretching vibration at nearly  $3340\text{ cm}^{-1}$  was weakest at  $T_i$ , and the absorbance increased with decrease in temperature. Furthermore, it was recognized that the band peak of the hydrogen-bonded N-H stretching vibration was shifted to higher frequency with increasing temperature, and it returned to the initial frequency with decreasing temperature. A similar tendency was also observed for the absorption band arising from hydrogen-bonded C=O stretching vibration, at nearly  $1700\text{ cm}^{-1}$ , in figure 3(b). In addition, the absorption band for N-H deformation vibration, at nearly  $1530\text{ cm}^{-1}$ , was shifted to lower frequency with increasing temperature. These results indicate that the interaction between the polymer backbones varies with temperature.

The FT-IR measurements for PU-b are shown in figures 4(a) and (b) and are analogous to PU-a. The absorption bands arising from hydrogen-bonded N-H stretching vibration ( $3330\text{ cm}^{-1}$ ), hydrogen-bonded C=O stretching vibration ( $1710\text{ cm}^{-1}$ ) and N-H deformation vibration ( $1540\text{ cm}^{-1}$ ) were observed. However, the

Table 3. The polyurethane phase transition temperatures.

		Transition temperature $^\circ\text{C}^\dagger$					
PU-a	g	$\xrightarrow{65.3}$	S	$\xrightarrow{90.2}$	N	$\xrightarrow{174.2}$	I
		$\xleftarrow{60.7}$		$\xleftarrow{82.0}$		$\xleftarrow{165.2}$	
PU-b	g	$\xrightarrow{93.3}$	N	$\xrightarrow{140.1}$	I		
		$\xleftarrow{92.7}$		$\xleftarrow{107.5}$			

g, glassy state; S, smectic phase; N, nematic phase; I, isotropic state.

$^\dagger$  Determined by DSC.

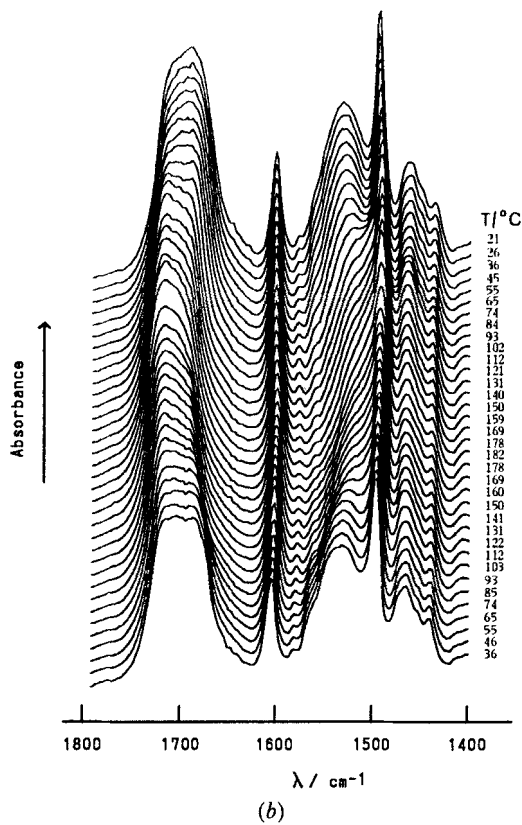
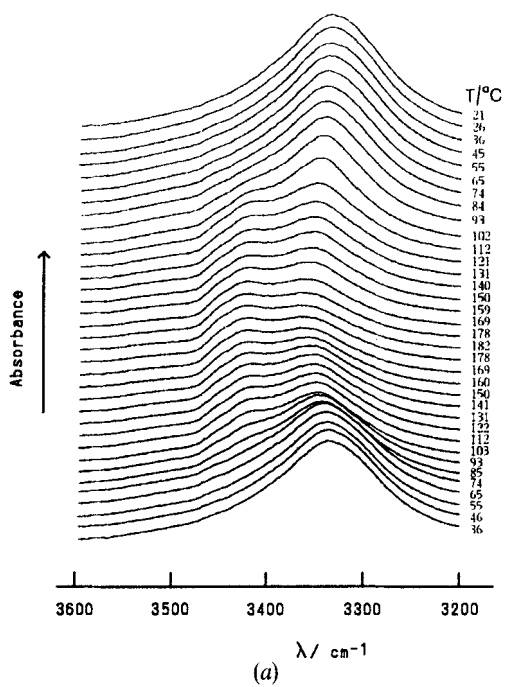


Figure 3. Infrared spectra of PU-a recorded as a function of increasing and decreasing temperature. (a) 3200–3600  $\text{cm}^{-1}$ ; (b) 1400–1800  $\text{cm}^{-1}$ .



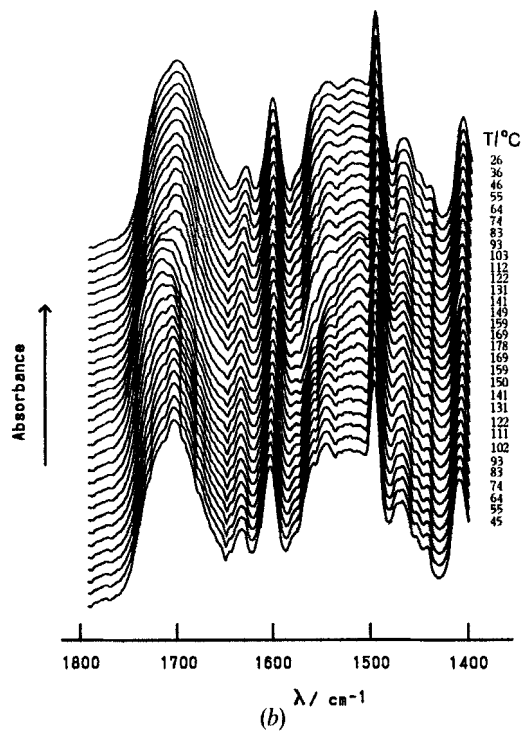
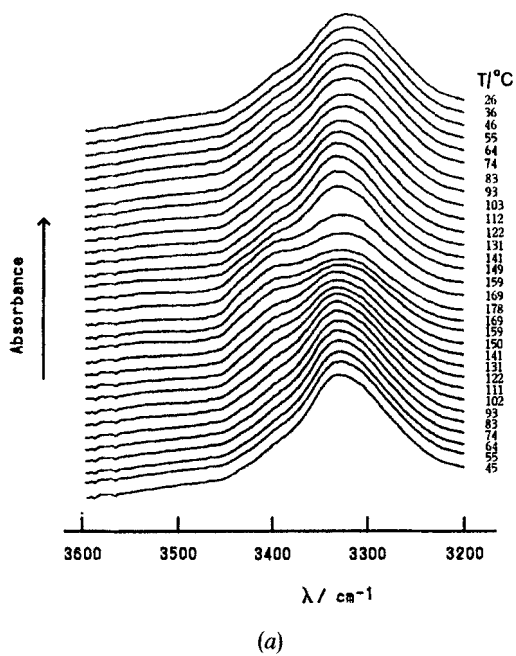


Figure 4. Infrared spectra of PU-b recorded as a function of increasing and decreasing temperature. (a) 3200–3600  $\text{cm}^{-1}$ ; (b) 1400–1800  $\text{cm}^{-1}$ .

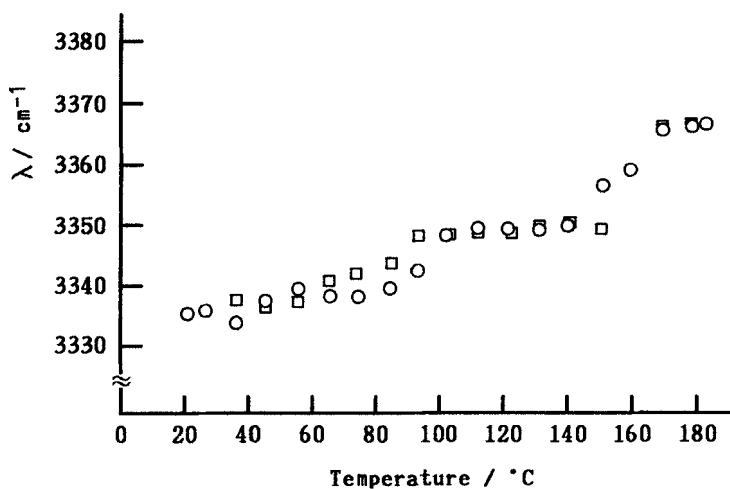


Figure 5. Effect of temperature on the band peak of the hydrogen-bonded N–H stretching vibration of PU-a. (○), heating; (□), cooling.

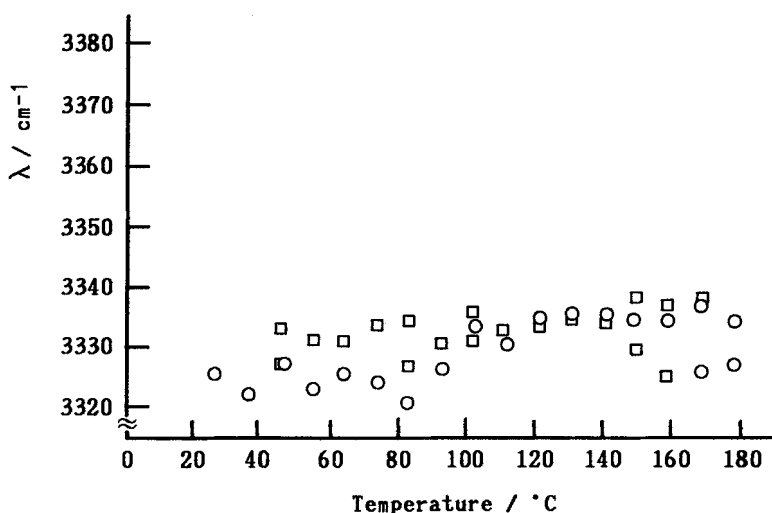


Figure 6. Effect of temperature on the band peak of the hydrogen-bonded N–H stretching vibration of PU-b. (○); heating, (□); cooling.

frequency of any band peak did not shift with temperature. These results suggest that the hydrogen bonding is formed among the polymer backbones of PU-b, but the strength of the hydrogen bonding is not alterned with temperature.

As shown in figure 5, the values of the frequency of the band peak derived from hydrogen-bonded N–H stretching vibration in the FT-IR spectra of PU-a are plotted against temperature. In each state, solid, smectic, nematic and isotropic phases, the band peak denoted the definite frequency values, respectively; however, it was shifted to higher frequency in the vicinity of the transition temperature with increasing temperature. A reversible change was observed for the shifting direction. In the case of PU-b, as shown in figure 6, no remarkable variation of the absorption was observed in the vicinity of the transition temperature. Two frequency plots at the same temperature

were due to the difficulty in determining the band peak, because the absorption bands were broad. This phenomenon exhibited by PU-a containing flexible alkyl chains in the polymer backbone is attributed to the idea that the energy state of the hydrogen bonding is transformed in accordance with each phase. However, for PU-b, containing rigid phenylene rings, this phenomenon was not observed.

The majority of LCPs contain flexible spacers in the main chains or side chains in order to lower the phase transition temperatures. However, as described here, a system which possesses interactions between its polymer backbones, such as polyurethane, is not always applicable. Actually, the mesophase thermal stability for PU-a was superior to that of PU-b in spite of the flexibility of the backbones, and the energy state of the hydrogen bonding was transformed at the phase transition temperature only for PU-a. It is concluded that variation of the energy state of the hydrogen bonding plays an important role in mesophase thermal stability.

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