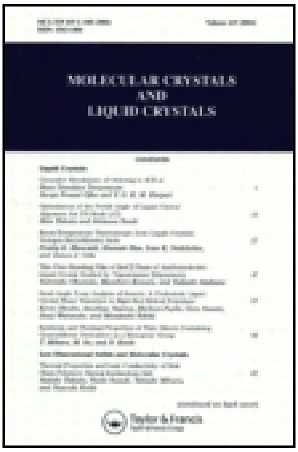

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Mesomorphic Properties and Intermolecular Interaction of Side-Chain Type Liquid Crystalline Polyurethanes

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MESOMORPHIC PROPERTIES AND INTERMOLECULAR INTERACTION OF SIDE-CHAIN TYPE LIQUID CRYSTALLINE POLYURETHANES

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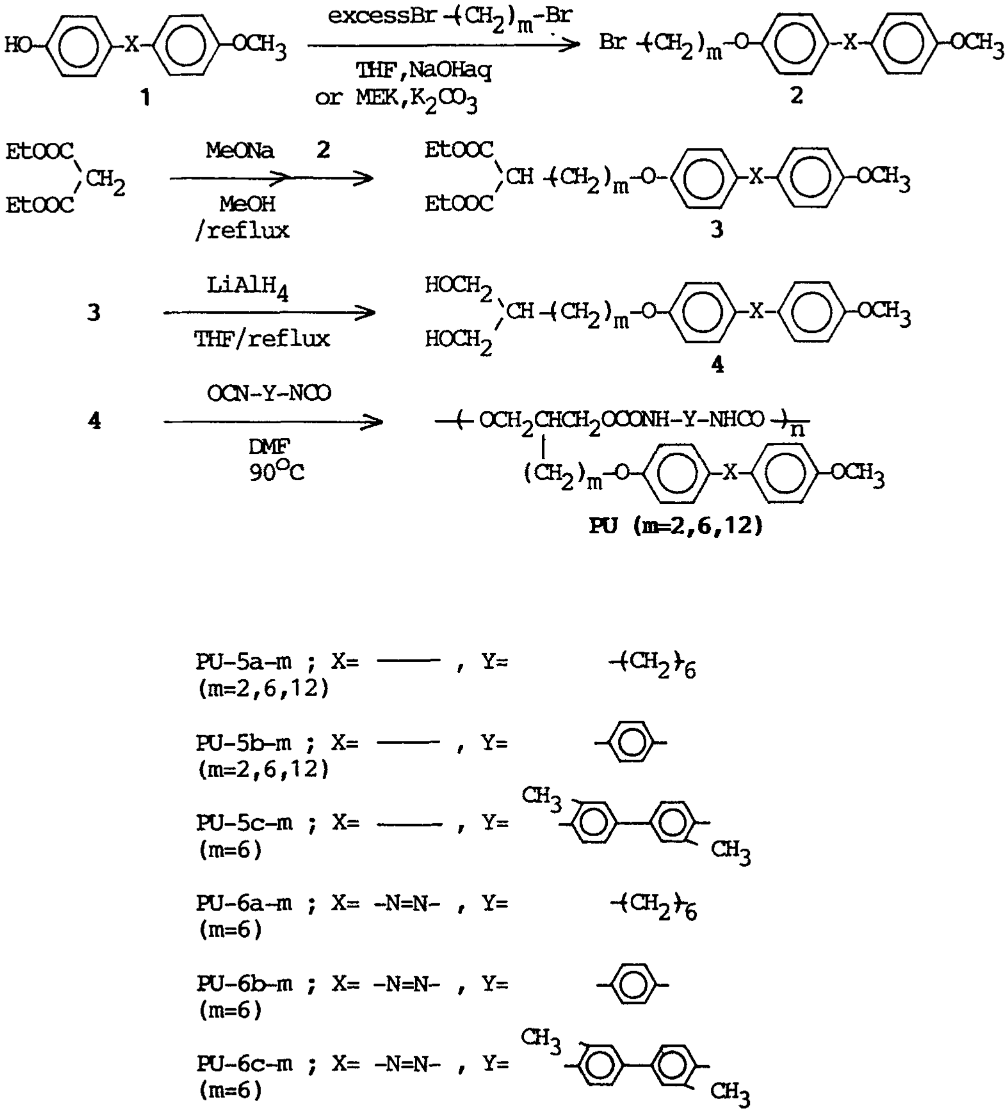
Abstract A series of side-chain type liquid crystalline polyurethanes have been synthesized from the mesogenic diol monomer with hexamethylene-, p-phenylene-, or bitolylene-diisocyanate. The mesomorphic properties has been investigated by differential scanning calorimeter DSC), wide angle X-ray scattering (WAXS), polarized light microscopy, and Fourier transfer infrared (FT-IR) spectroscopy. The polyurethanes exhibit an enantiotropic mesophase with nematic or smectic depending upon the flexibility of urethane bond in the polymer backbone. Thermal properties are deeply influenced by the hydrogen bonding among the polymer backbone.

INTRODUCTION

Side-chain type liquid crystalline polymers(SLCP) have been synthesized owing to their theoretical and technical aspects. The thermal properties of SLCPs are influenced by polymer backbone[1], polymer tacticity[2], molecular weight[3], molecular weight distribution, mesogen length[4], terminal group of mesogen[5], flexible spacer length[6], etc. As to the polymer backbone, a flexible polymer backbone mostly consists of polyacrylate[7], polymethacrylate[8], polychloroacrylate[9] and polysiloxane[10]. On the other hand, relatively rigid backbone such as polystyrene[11], polymaleimide[12], polyester[13], polyaminoacid[14] and polyurethane [15] is also used as a polymer backbone. Especially polyamide and polyurethane would become more rigid due to the formation of intermolecular interaction such as hydrogen bonding at the active hydrogen in the urethane bond with the adjacent atom like a carbonyl group. However, SLCPs having intermolecular interactions such as hydrogen bonding in the polymer backbone are little investigated.

Vibrational spectroscopy is one of the principle techniques for examining lateral interactions of the hydrogen bonding and conformational order in polymers. As to polyamide[16], polyurethane[17] and main-chain type liquid crystalline polyurethane[18], the lateral interaction with occurring by the hydrogen bonding among polymer backbones has been investigated with a thermally controlled FT-IR spectroscopy.



Scheme 1. Synthesis of diol-monomers and polyurethanes.

In the case of side-chain type polyurethane having flexible alkyl chains in the polymer backbones (flexible polyurethane), the absorption band arising from the hydrogen bonded N-H stretching vibration was shifted to higher frequency in the vicinity of the transition temperature, while polyurethanes with rigid moiety in the polymer backbones (rigid polyurethane), no remarkable variation of the absorption was observed in the neighborhood of the transition temperatures[19].

In this study various kinds of polyurethanes are synthesized as shown in Scheme 1 in order to clarify the relationship between the hydrogen bonding in the polymer backbone and the mesomorphic properties by FT-IR spectroscopy, WAXS, optical polarizing microscopy, and DSC measurements.

EXPERIMENTAL

Materials. The synthesis of diol monomers has been described elsewhere. The polymers we have studied are synthesized from diisocyanate (hexamethylene-, phenylene- or bitolylene-diisocyanate) and corresponding mesogenic diol in dry DMF at 90°C under a nitrogen atmosphere for 13h. The obtained polyurethanes were soluble in polar solvents such as tetrahydrofurane (THF) and dimethylformamide (DMF).

Characterization Techniques. DSC measurements were conducted with a Mettler 3000 series, employing a flow of dry nitrogen as a purge gas for the sample and reference cells.

WAXS patterns were recorded on a MAC Science MXP^3 X-ray diffractometer equipped with a thermal controller Model 5310.

Optical microscopy was performed on a Nikon optiphoto olalizing microscopy equipped with a Mettler FP80 controller and a FP82 hot stage.

Infrared spectroscopy were recorded on a JEOL JIR-100 spectrometer. Spectra were collected at 4-cm^{-1} resolution. A minimum of 20 scans was signal average, and the spectrum was stored on magnetic storage media.

The measurement of thermally-controlled FT-IR spectra were performed as follows. Elevated temperature spectra of

FT-IR were obtained by placing the cells made from two silicone wafers coated with rubbed polyimide in a temperature-controlled cell. Silicone bases were prepared by washing the silicone wafers with an aqueous solution of hydrogen fluoride in order to spray the polyimide solution easily on the surface. Polyimide was applied to the side in contact with the sample of the base in one direction. Polyurethane powder was inserted between the two silicone bases, and annealed above the isotropization temperature of the polyurethane. The edge of the cells was sealed with an epoxy compound. The temperature was monitored via a thermocouple placed adjacent to the cells.

Before each spectral acquisition the temperature was kept constant for 10 min to ensure complete temperature equilibration along the sample cell. At the end of the first heating scan, the sample was cooled very slowly to room temperature, followed by a second heating scan in a similar fashion.

RESULTS AND DISCUSSION

The phase transition temperatures of mesogenic diol monomers are summarized in Table I. The phase transition temperature and thermal stability of diol mesogenic

TABLE I Phase transition temperatures of diolmonomers

Diol monomer	Transition temp.(°C)[1]	R(°C)[2)]
Diol 2-MeOBi	$K \underset{99.5}{\overset{116.2}{\rightleftharpoons}} M \underset{151.7}{\overset{152.1}{\rightleftharpoons}} I$	52.2
Diol 6-MeOBi	$K \underset{65.0}{\overset{87.9}{\rightleftharpoons}} M \underset{133.3}{\overset{138.7}{\rightleftharpoons}} I$	68.3
Diol12-MeOBi	$K \underset{113.0}{\overset{117.9}{\rightleftharpoons}} M \underset{138.4}{\overset{140.8}{\rightleftharpoons}} I$	25.4
Diol 6-BuOBi	$K \underset{81.3}{\overset{77.2}{\rightleftharpoons}} M \underset{130.2}{\overset{131.4}{\rightleftharpoons}} I$	48.9
Diol 6-MeOAzo	$K \underset{112.9\ \mathrm{M?}\ 113.5}{\overset{117.3}{\rightleftharpoons}} N \underset{118.4}{\overset{119.9}{\rightleftharpoons}} I$	
Diol 6-NO_2Azo	$K \xrightarrow{243}$ decomposition	

K;crystal, M;mesophase, N;nematic, I;isotropic phase
1)Phase transition temperatures were determined by DSC.
2) R=(Ti-Tm)

monomers decrease with increasing spacer length.

The polymerization results for polyurethanes are summarized in Table II. The polymerization yield and molecular weight increase with increasing rigidity of polymer backbone component of urethane moiety.

TABLE II Results of synthesis of polyurethanes

Abbreviation	m	Yield(%)	Mwx10^{-3})	Mw/Mn
PU-5a	2	29.1	7.20	1.21
PU-5a	6	11.8	4.70	1.38
PU-5a	12	93.9	11.40	1.94
PU-5b	2	68.7		
PU-5b	6	76.3	7.30	1.42
PU-5b	12	85.0		
PU-5c	6	93.4	8.00	1.47
PU-6a	6	58.0	5.00	1.70
PU-6b	6	72.5	22.10	1.44
PU-6c	6	78.7	20.60	1.49

1)Determined by GPC(polystyrene standard)

DSC curves of PU-5 and PU-6 with same spacer length(m=6) were shown in Figure 1. Three transition points were observed in flexible polyurethanes such as PU-5a and PU-6a. A large endothermic peak originated from the mesophase-mesophase transition was detected for the flexible polyurethanes independent on the mesogenic group.

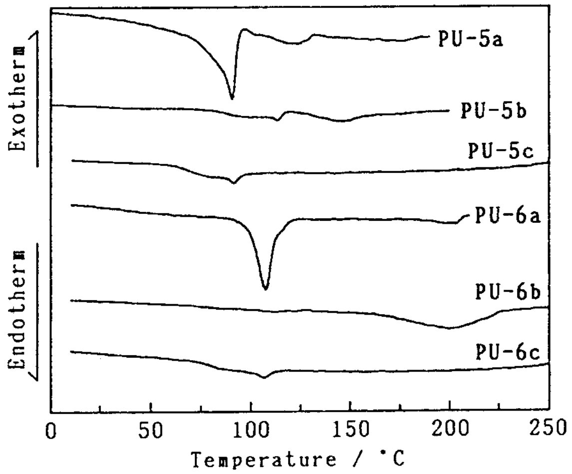


FIGURE 1 DSC curves of polyurethanes (m=6).
(heating scan)

Only glass transition temperature(Tg) was observed for the polyurethanes having bitolylene ring in the polymer backbone.

The thermal properties of obtained polyurethanes were summarized in Table III. All polyurethanes exhibited a mesomorphic behavior.

TABLE III Transition temperatures of side-chain type polyurethanes

Polyurethane	Transition temp.(^{o}C)	R(^{o}C)
PU-5a-2	$g \underset{64.0}{\overset{79.2}{\rightleftharpoons}} M \underset{125.0}{\overset{186.4}{\rightleftharpoons}} I$	107.2
PU-5b-2	$g \overset{128.0}{\rightleftharpoons} \underset{?}{M} \overset{191.0}{\rightleftharpoons} I$	63.0
PU-5a-6	$g \underset{60.7}{\overset{65.3}{\rightleftharpoons}} S \underset{82.0}{\overset{90.2}{\rightleftharpoons}} N \underset{165.2}{\overset{174.2}{\rightleftharpoons}} I$	108.9
PU-5b-6	$g \underset{92.7}{\overset{93.3}{\rightleftharpoons}} N \underset{107.5}{\overset{140.1}{\rightleftharpoons}} I$	46.8
PU-5a-12	$K \overset{107.8}{\rightleftharpoons} \underset{92.9}{S} \overset{126.0}{\rightleftharpoons} I$	18.2
PU-5b-12	$K \underset{117.5}{\overset{119.7}{\rightleftharpoons}} S \underset{?}{\overset{138.3}{\rightleftharpoons}} I$	18.6
PU-5c-6	$g \underset{70.0}{\overset{70.8}{\rightleftharpoons}} S \underset{93.7}{\overset{95.9}{\rightleftharpoons}} N \underset{?}{\overset{235.0}{\rightleftharpoons}} I$	144.2
PU-6a-6	$g \underset{58.2}{\overset{?}{\rightleftharpoons}} S \underset{88.4}{\overset{108.4}{\rightleftharpoons}} N \underset{143.1}{\overset{202.6}{\rightleftharpoons}} I$	84.9
PU-6b-6	$g \underset{77.8}{\overset{77.8}{\rightleftharpoons}} S \underset{119.8}{\overset{199.8}{\rightleftharpoons}} I$	42.0
PU-6c-6	$g \underset{80.4}{\overset{83.4}{\rightleftharpoons}} N \underset{99.3}{\overset{106.8}{\rightleftharpoons}} I$	18.9

K;solid, S;smectic, N;nematic, g;glassy, I;isotropic liquid, R=(Ti-Tm or Tg).

The isotropization temperatures and the mesomorphic temperature range for these polyurethanes decrease with increasing flexible spacer length. The thermal stability of the mesophase of flexible polyurethanes having methylene length(=m) of 2 or 6 was superior to that of rigid polyurethanes. However, with increasing spacer length (m=12) for flexible polyurethane the isotropization temperature became lower, and the mesomorphic temperature range was same value as rigid polyurethane.

Typical X-ray diffraction pattern of rigid and flexible polyurethanes with same spacer length and with different mesogenic group are shown in Figure 2. Sharp diffraction peaks are detected in both small angle and wide angle regions for PU-5a-6 and PU-6a-6 with flexible polyurethane below the second transition point confirmed by DSC measurements. These two sharp halos are originated by the smectic phase based on the DSC and polarized microscopy measurements, and also the lateral arrangement between the mesogenic groups would have higher ordering for these polyurethanes.

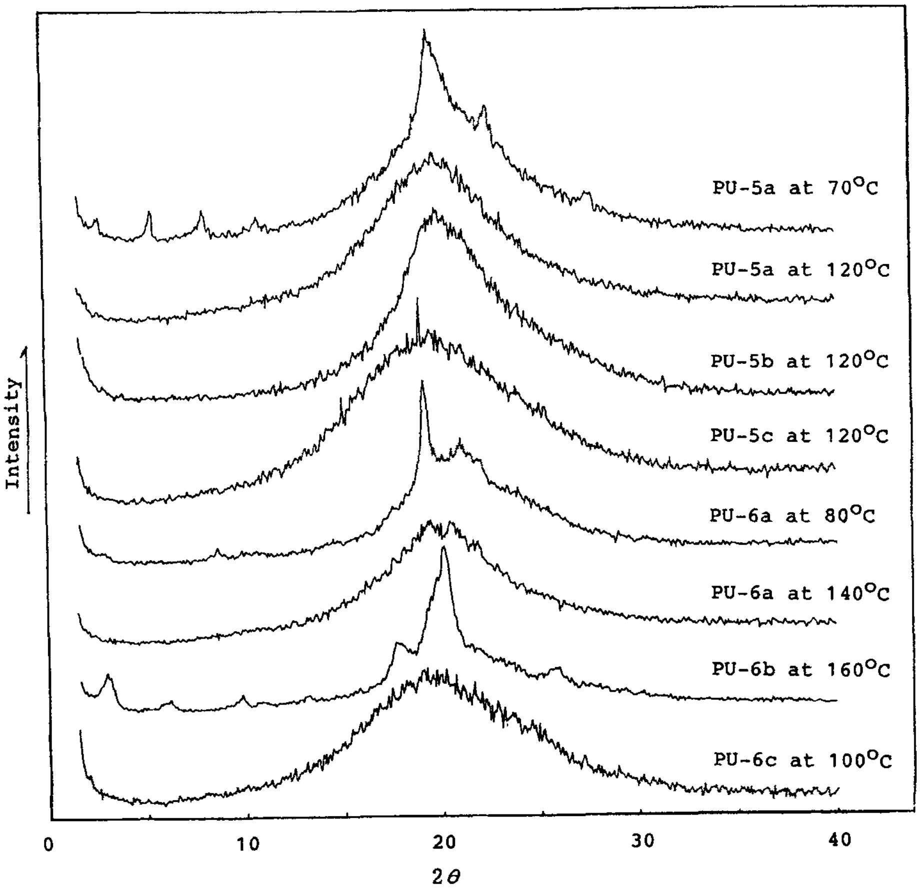


FIGURE 2 X-ray diffraction patterns of polyurethanes (m=6).

With increasing temperature, these two sharp halos disappeared, and only broad halo was detected in the wide angle regions below the isotropization temperature. The phase at this temperature range was assigned to the nematic phase supported also by DSC and polarized microscopy.

Only broad halo in the wide angle region was detected for flexible polyurethane having spacer length of 12, while sharp and broad halos were measured in the small angle and wide angle region, respectively, for the rigid polyurethane having spacer length of 12.

As shown in Table III, the thermal stability of the mesophase of PU-5a and PU-6a containing flexible alkyl chains in the polymer backbone was superior to that of polyurethanes with rigid phenylene or bitolylene rings except for PU-5c. These results showed that the difference of rigidity and bulkiness of the polymer backbones would affect on the thermal properties of these polyurethanes. We have expected that the thermal stability of rigid polyurethane is higher than that of flexible polyurethane before we measured the DSC. In order to confirm these differences, FT-IR spectra were measured at various temperatures using thermally-controlled FT-IR spectroscopy.

We have reported that 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 for having the spacer length of 6.[19]

Peak shifts and intensity changes were observed between 3200-3600cm^{-1}(N-H stretching vibration region), 1600-1800cm^{-1}(carbonyl stretching vibration, amide I region), and 1500-1570cm^{-1}(amide II region). The changes in intensity and peak shifts will be discussed in order to clarify the thermal properties of polyurethanes.

In the N-H stretching vibration region (3600-3200 cm^{-1}) of flexible polyurethane the peak observed around 3430 cm^{-1} is assigned to the ordered hydrogen-bonded N-H stretching vibration, while the new shoulder peak at 3410 cm^{-1} appeared with increasing temperature is assigned to the free N-H stretching vibration,[20] as shown in Figure 3.

The absorption band arising from hydrogen-bonded N-H of the flexible polyurethane with spacer length of 2,6 and 12, was shifted systematically to the higher wavenumber with increasing temperature. We interpret this phenomenon as a decrease in the average strength of the hydrogen bonds.

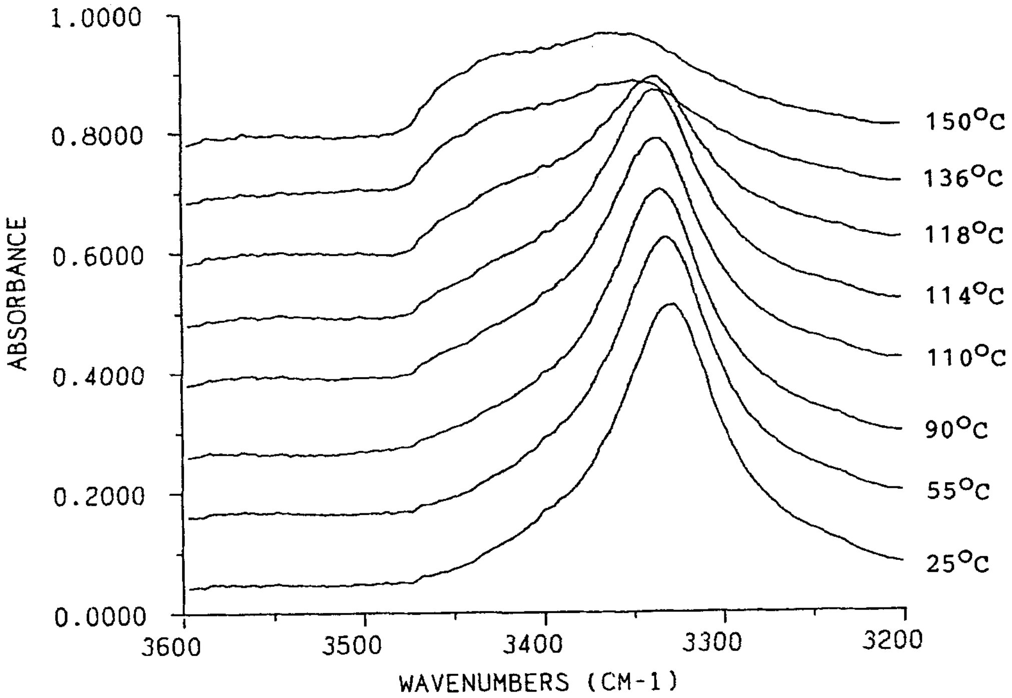


FIGURE 3 Variation of the N-H stretching vibration region ($3600\text{-}3200cm^{-1}$) of PU-5a-12 (heating scan).

In the case of rigid polyurethane with spacer length of 6 and 12, no remarkable variation of the absorption band for hydrogen-bonded N-H stretching vibration was observed at any temperatures. However, it was shifted to the higher frequency in the vicinity of the transition temperature with increasing temperature for rigid polyurethane with spacer length of 2.

On the other hand, the similar tendency was also observed for the absorption at nearly $1700cm^{-1}$, as shown in Figures

4 and 5. The spectra in these figures are shown on equal absorbance scale. The infrared absorbance of hydrogen-bonded urethane carbonyl appears at lower wavenumbers than that of free urethane carbonyl.[21)] With increasing temperature, the intensity of free carbonyl band increases and only free carbonyl band remains above the isotropization temperature.

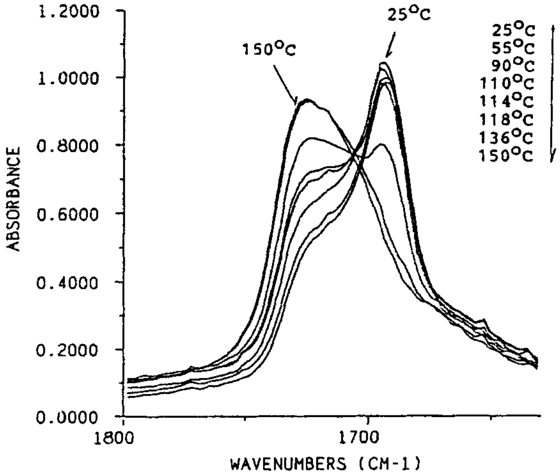


FIGURE 4 Variation of the C=O stretching vibration region (1800-1630cm^{-1}) of PU-5a-12 (heating scan).

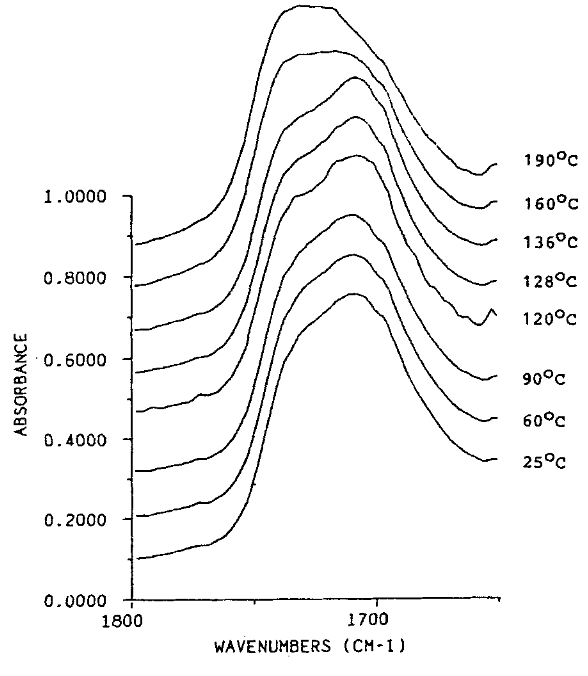


FIGURE 5 Variation of the C=O stretching vibration region (1800-1650cm^{-1}) of PU-5b-12 (heating scan).

In addition, the absorption band of deformation vibration at nearly 1530cm^{-1}(amide II) was shifted to the lower frequency with increasing temperature, and their intensities drastically decrease in the vicinity of the transition temperature detected by DSC measurement. These results indicate that the interaction among the polymer backbones varies with temperature.

The thermal properties of polyurethane are influenced by the hydrogen bonding of the polymer backbone, however as you can see in the Figures 4 and 5, the infrared spectra arising from the hydrogen-bonded are very broad. These broad band have originated from the degree of carbonyl hydrogen bonding reported by the amide I infrared spectra of semicrystalline samples such as nylons [22] and polyurethanes[17].

The presence of three major spectral components in the carbonyl region would be confirmed by second-derivative spectroscopy. So, it is necessary to separate these broad

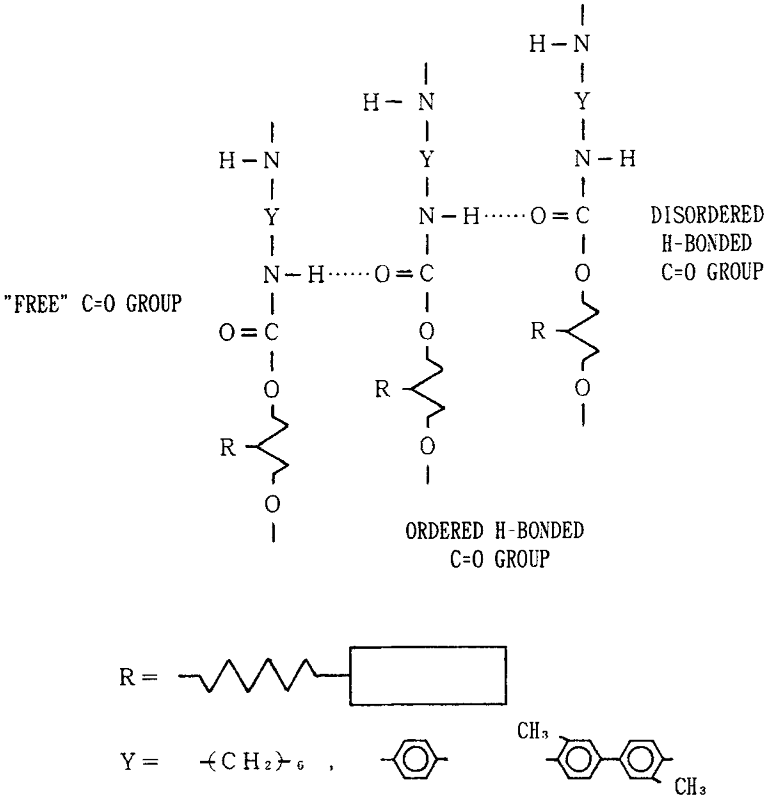


FIGURE 6 Intermolecular interactions involving the urethane group.

bands into three components, such as ordered(=crystalline) domains, disordered (=amorphous) conformations and non-hydrogen-bonded(=free) carbonyl groups as shown in Figure 6.[23] The spectra separation was carried out by step by step the well-established amide I deconvolution technique. Typical example of the least-squares fitting results is shown in Figure 7.

The curve-fitting analysis of the carbonyl stretching region of PU-5a-12 and PU-5b-12 as a function of decreasing temperature is given in Tables IV and V, respectively. The areas of the ordered hydrogen-bonded(A_o), disordered hydrogen-bonded(A_d) and non-hydrogen-bonded (A_f) peaks are also summarized in Tables IV and V. The mesomorphic properties of flexible polyurethane are deeply influenced by the A_o and A_f, while those of rigid polyurethane were not influenced by any hydrogen-bonded groups.

Although FT-IR spectroscopy would not measure directly the absolute degree of crystallinity, the ratio of the ordered amide I band to the total area of the amide I

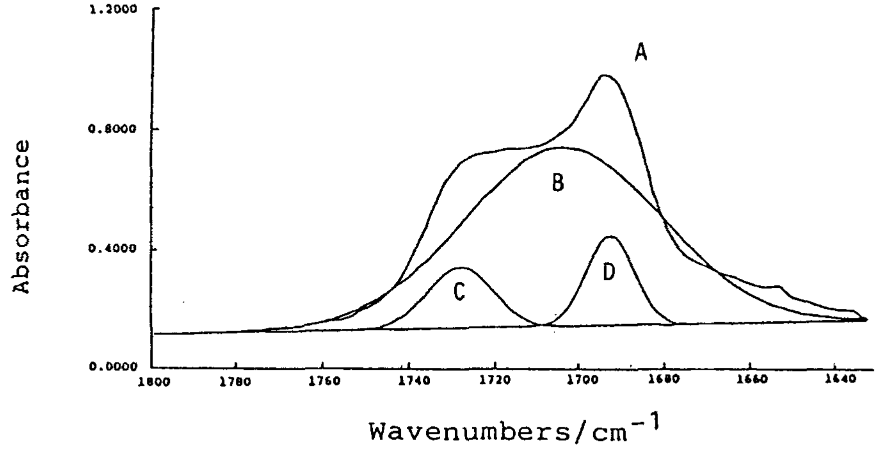


FIGURE 7 Least squares deconvolution of the C=O stretching vibration of PU-5a-12 at 114°C(heating scan). A, pure PU; B, disordered; C, free; D, ordered.

TABLE IV Deconvolution results for the amide I region of PU-5a-12 hydrogen bonded

	ordered			disordered			free				
temp (^{o}C)	λ (cm^{-1})	$W_{1/2}$	A_o	λ (cm^{-1})	$W_{1/2}$	A_d	λ (cm^{-1})	$W_{1/2}$	A_f	A_t	A_o/A_t
25	1691.7	14.9	5.93	1700.0	53.1	30.5	1725.9	15.7	1.93	38.3	0.155
55	1692.0	14.9	6.05	1700.8	54.8	31.5	1726.6	15.8	1.99	39.5	0.153
90	1692.7	14.2	5.62	1701.8	54.0	33.7	1727.2	17.0	2.88	42.2	0.133
110	1692.7	13.3	4.88	1703.4	53.9	34.1	1727.7	17.4	3.55	42.5	0.155
114	1692.5	12.7	4.15	1703.9	54.1	34.5	1727.8	17.5	3.88	42.5	0.098
136				1709.2	55.0	34.4	1727.0	23.6	9.06	43.5	
150				1707.2	59.1	29.2	1725.6	29.1	14.3	43.6	

A_o=area of band for ordered domains, A_d=area of band for mesophase and amorphous domains, A_f=area of band for free carbonyl groups, and A_t=total area=A_o + A_d + A_f. $W_{1/2}$=width at half-height of Gaussian curve.

TABLE V Deconvolution results for the amide I region of PU-5b-12 hydrogen bonded

	ordered			disordered			free				
temp (^{o}C)	λ (cm^{-1})	$W_{1/2}$	A_o	λ (cm^{-1})	$W_{1/2}$	A_d	λ (cm^{-1})	$W_{1/2}$	A_f	A_t	A_o/A_t
25	1688.7	33.6	5.75	1712.0	34.8	16.8	1736.0	22.7	6.99	29.5	0.195
60	1689.8	33.4	5.87	1713.0	34.9	16.6	1736.7	22.5	6.72	29.2	0.201
90	1690.8	33.0	6.05	1713.7	34.4	15.8	1737.2	22.6	6.56	28.4	0.213
110	1692.3	33.6	6.23	1714.5	35.0	15.7	1738.2	22.6	6.41	28.3	0.220
120	1692.3	32.9	5.18	1713.1	35.7	16.5	1738.4	22.3	6.59	28.2	0.184
128	1692.0	34.7	4.59	1712.5	36.8	17.1	1738.6	23.1	6.80	28.4	0.162
136	1693.5	34.7	4.19	1712.4	37.8	17.2	1738.9	23.4	6.97	28.3	0.148
160				1712.1	46.3	21.9	1739.9	24.7	7.37	29.3	

A_o=area of band for ordered domains, A_d=area of band for mesophase and amorphous domains, A_f=area of band for free carbonyl groups, and A_t=total area=A_o + A_d + A_f. $W_{1/2}$=width at half-height of Gaussian curve would give the information of crystallinity supported by the nylon 6,6.[22]

The total area of the amide I region (A_t) did not vary appreciably with temperature. The ratio of A_o/A_t for flexible polyurethanes with spacer length of 2 and 6 is larger than that for rigid polyurethanes with spacer length of 2 and 6. On the other hand the ratio of A_o/A_t for rigid polyurethane with spacer length of 12 is larger than that for flexible polyurethane.

The disordered hydrogen bonded carbonyl band is about 2.5 times as broad as its ordered counterpart for PU-5a-2, PU-5a-6, PU-5b-6 and PU-5a-12, while the same breadth value was obtained for PU-5b-2 and PU-5b-12. As you can seen in Table III, the Tis of these two rigid polyurethanes were higher than those of flexible polyurethanes. The area of the ordered hydrogen bonded carbonyl bands would be reflected the degree of order.

CONCLUSIONS

The side-chain type polyurethanes exhibit smectic or nematic phase at the mesomorphic temperature range depending upon the spacer length or rigidity of polymer backbone.

The difference of thermal properties of the polyurethanes would be explained by internal hydrogen bonding supported by thermally controlled FT-IR spectroscopy measurements. The hydrogen bonding can be divided into three components, ordered-, disordered- and non-hydrogen-bonded carbonyl groups.

The ordered hydrogen-bonded N-H stretching band shifts to the higher wavenumber in the vicinity of transition temperature for flexible polyurethanes, while no remarkable shifts of the ordered hydrogen-bonded N-H stretching band was observed for rigid polyurethanes.

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