

Synthesis of Thermotropic Polyurethanes Containing Imide Units and Their Mesophase Behavior

Dong-Jin Lee¹, Ju-Shik Kong, and Han-Do Kim*

Department of Textile Engineering, Pusan National University, Pusan, Korea

¹R & D Center for Chemical Technology, Hyosung Corp., Kyonggi-do, Korea

(Received June 29, 2000 ; Revised August 16, 2000 ; Accepted August 21, 2000)

Abstract : Thermotropic polyurethanes were synthesized from 1,6-hexane diisocyanate (HDI) as a diisocyanate, 1,6-hexane diol (HD), and rigid diols containing imide unit such as N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyl-dicarboxyimide (BPDI) or bis-N-(4-hydroxyphenyl)-4,4'-oxydiphthalimide (ODPI). The effects of structure difference between BPDI and ODPI and composition of HD/BPDI (ODPI) on the thermal and liquid crystalline behavior were studied. Thermotropic polyurethanes with an inherent viscosity of 0.59~0.70 were obtained. The melting temperature of BPDI-based polyurethanes were in the range of 150~290°C, however, those of ODPI-based polyurethanes were in the range of 150~190°C. All the polyurethanes based on ODPI (25~100 mole %) clearly exhibited a stable liquid crystalline phase, and BPDI-based polyurethane having 5-25% of BPDI showed a mesophase. The melting and isotropization temperatures (T_m , T_i) and $\Delta T(T_i - T_m)$ increased with increasing BPDI and ODPI content. The polyurethanes based on BPDI has higher melting points and thermal stability compared to ODPI-based polyurethanes.

Introduction

Thermotropic liquid crystalline (LC) polymers having mesogenic units along the main chain have attracted attention as a result of their good mechanical properties and ease of processing. To obtain a useful thermotropic polymer, careful attention must be given to monomer composition. To reduce the melting point of the intractable homopolymer, monomer must be introduced that disrupt the order or regularity of the backbone. Generally, processing temperature can be lowered by copolymerizing the rigid backbone moieties with controlled amounts of a moiety having flexible linkages and/or dissymmetrical units having bulky side groups or kinks.

The mesogenic unit was defined as the part of the polymer chain that is composed of the aromatic or cycloaliphatic segment. Simply for convenience, we have defined the remainder of the polymer repeating unit as the flexible spacer. What is important, however, is the different structural nature of the spacer and the mesogenic unit, and unfortunately the separate roles of these two groups are not yet fully understood.

Studies on the effect of flexible spacers include the use of either poly(ethylene oxide) or polysiloxane segments. It is clear that the role of the spacer is more complex than simply that of decoupling the mesogenic groups. The first reported main chain thermotropic LC polymer contained a polymethylene flexible spacer. The effect of increased polymethylene flexible spacer length on the properties of main chain LC polymers has been very well documented

in a number of publications. Essentially three effects can be observed in all such series: (1) reduction of the transition temperatures (both melting temperature T_m and clearing (isotropization) temperature, T_c (T_i) with increased spacer length. (2) an even-odd relationship for the transition temperatures, in which polymers with an even number of atoms in the spacer generally have higher transition temperatures than those in the same series with an odd number of atoms, and (3) in some cases, a smectic mesophase is formed by polymers containing very long spacers (approximately eight atoms or more).

Recently, in earlier investigations[1-4] of synthesis and properties of thermotropic polyurethanes, D. J. Lee *et al.* used techniques of (i) the introduction of bulky substituent group in the aromatic ring to decrease the degree of lateral packing, (ii) the copolymerization of two kinds of monomers having different alkylene lengths to lower the regularity of the polymer structure, and (iii) the use of nonlinear monomers to lower the persistence length of the polymer chain in the liquid crystalline phase and to decrease the lateral interactions in the solid state.

Aromatic imide groups are planar, rigid, and polar, but they proved to be rather poor mesogens[5-7]. In particular, it was found that many polyesters derived from highly symmetric imide units such as those pyromellitic anhydride, naphthalene-1,4,5,8-tetracarboxylic anhydride, or perylene tetracarboxylic acid anhydride, are not liquid crystals[8-10]. Polyurethanes having imide unit were synthesized by several authors[11-13]. H. Sato *et al.*[14] investigated the influence of hydrogen bonding of the urethane linkages on the stability of the mesophase of the polymers, but the liquid crystallinity of the polymers was not observed.

*To whom correspondence should be addressed:
kimhd@hyowon.pusan.ac.kr

In our previous study[15], BPDI and N,N-bis [4-(hydroxyhexyloxy)phenyl]-3,4,3',4'-biphenyldicarboxyimide(BHDI) was used as a chain extender to synthesize thermotropic polyurethane based on isocyanate MDI/ polyol PTMG (MW:1,000). Any melting behavior was not shown in the BPDI-based polyurethane because of higher melting temperature than decomposition temperature. However, when BHDI-based polyurethane has above 50 wt% of hard segment content, it exhibited nematic LC behavior. The structure difference between BHDI and BPDI is that BHDI has a flexible spacer of 6-methylene units but BPDI does not.

In this study, to reduce melting point, we used flexible diisocyanate HDI and diol HD having 6-methylene units with mesogenic monomers BPDI and bis-N-(4-hydroxyphenyl)-4,4'-oxydiphthalimide (ODPI). The effects of composition of HD/BPDI (or ODPI) and structure difference between BPDI and ODPI on the thermal and liquid crystal behaviors of polyurethanes were examined. Structure, thermal properties and liquid crystalline behaviors were characterized by ^1H NMR spectroscopy, FT-IR spectroscopy, polarized optical microscope observation, and differential scanning calorimetry.

Experimental

Material

1,6-Hexane diisocyanate (HDI, Aldrich Co.) was used as a diisocyanate monomer. 4,4'-Biphenyl dianhydride (BPDA, TCI Co.), 4,4'-oxydiphthalic anhydride (ODPA, TCI Co), 1,6-hexane diol (HD, Aldrich Co.), and *p*-aminophenol (PAP, Aldrich Co.) were used without further purification. N,N'-Dimethylformamide (DMF) was purified by distillation under reduced pressure before use.

Synthesis of BPDI and ODPI

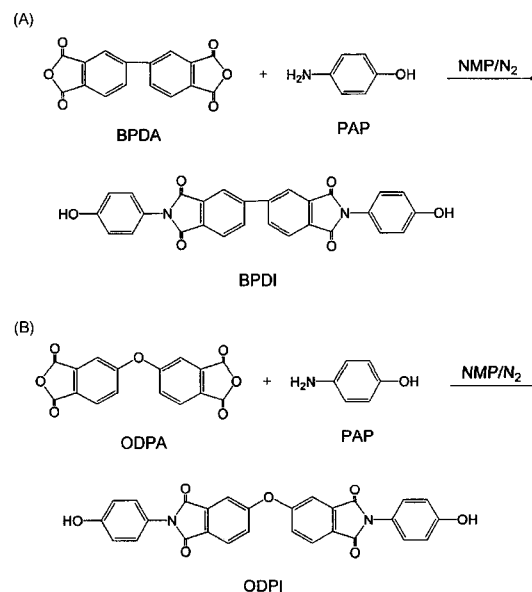
1,4-Aminophenol (0.05 mol) and 4,4'-biphenyl dianhydride (0.025 mol) or 4,4'-oxydiphthalimide (0.025 mol) were mixed in 35 ml of N-methyl-2-pyrrolidone (NMP). The reaction mixture was reacted for 14 hr at 90°C, then poured into methanol. The precipitates BPDI and ODPI were filtered off and recrystallized from DMF. The yield of BPDI was 65%, and that of ODPI was 88%. The reaction was shown in Scheme 1.

Polyurethanes

The copolyurethanes with various compositions were synthesized by copolyaddition of 1,6-hexane diisocyanate (HDI) with different molar ratios of both diols, i.e., 1,6-hexane diol (HD) and BPDI or ODPI by the method previously reported[1-3].

Characterization

The structure analysis of the polymers and their inter-



Scheme 1. Synthesis of dihydroxy compound (A) N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyl-dicarboxyimide (BPDI) and (B) N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-oxybisphenyl-dicarboxyimide (ODPI).

mediates was performed by ^1H NMR spectroscopy using a Varian Unity Plus 300 spectrometer with 3-(trimethylsilyl) propanesulfonic acid sodium salt (DSS) or tetramethylsilane (TMS) as an internal standard. The thermal properties of the polymers were examined using a DSC 220C differential scanning calorimeter. Optical textures of the mesophases were observed using an Olympus BH2 polarized microscope equipped with a Mettler FP84 hot stage. To confirm the structure of the synthesized polyurethanes, infrared spectroscopy was performed using a FTIR spectrometer (Impact 400D; Nicolet, Northvale, NJ). For each sample, 32 scans at 2 cm^{-1} resolution were collected in the absorption mode. The measurements of thermostabilities were performed on a Du Pont 9900 TGA at a heating rate of 10°C/min under a nitrogen atmosphere.

Results and Discussion

The dihydroxy compounds containing the imide moiety, N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboxyimide (BPDI) or bis-N-(4-hydroxyphenyl)-4,4'-oxydiphthalimide (ODPI), were synthesized from 4,4'-biphenyl dianhydride (BPDA) or 4,4'-oxydiphthalic anhydride (ODPA), respectively, as shown in Scheme 1. The structure of BPDI was confirmed by ^1H NMR spectroscopy in the previous papers[15]. Figure 1 shows the structure of ODPI confirmed by ^1H NMR spectrum in a DMSO-*d*₆ solution at 50°C. The ^1H NMR spectrum showed the proton signals for the aromatic rings at 7.19-8.28 ppm. And

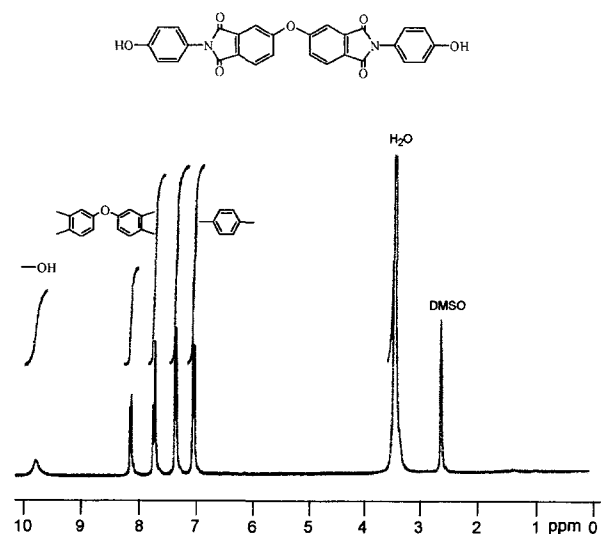
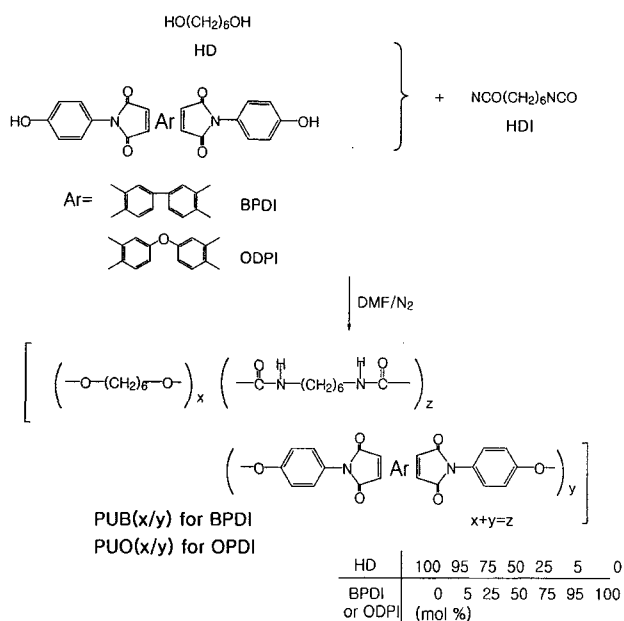


Figure 1. 300 MHz ^1H NMR spectrum of dihydroxy compound ODPI in $\text{DMSO}-d_6$ at 50°C .



Scheme 2. Synthesis of copolyurethanes PUB containing BPDI unit and PUO samples containing OPDI unit.

absorptions due to hydroxy group was also seen at 9.95 ppm.

The polyurethanes were synthesized from 1,6-hexane diisocyanate (HDI), 1,6-hexane diol, and rigid diols BPDI or ODPI containing imide unit as shown in Scheme 2. The polyurethanes with different compositions of HD/BPDI (or ODPI) such as 100/0, 95/5, 75/25, 50/50, 25/75, 5/95, and 0/100 mole % were synthesized. These two kind of polyurethanes were designated as a PUB series

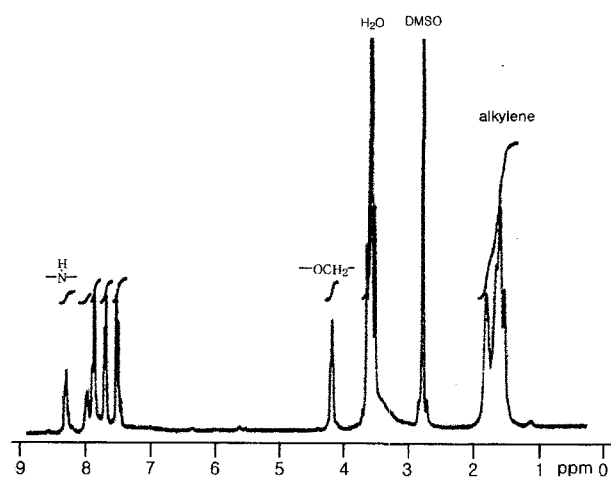
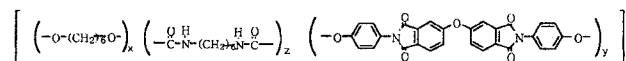


Figure 2. 300 MHz ^1H NMR spectrum of polyurethane PUO (50/50) in $\text{DMSO}-d_6$ at 50°C .

Table 1. Description of PUB series obtained by copolyaddition reaction^{a)} of 1,6-hexane diisocyanate (HDI) with hexane diol (HD) and N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboximide (BPDI)

Designation	Composition		Diisocyanate	Yield	η inh ^{b)}
	HD (mol%)	BPDI (mol%)			
PUB (100/0)	1.182 (10.0)	-	1.682 (10.0)	1.378 (48)	
PUB (95/5)	1.123 (9.5)	0.238 (0.5)	1.682 (10.0)	1.995 (66)	
PUB (75/25)	0.886 (7.5)	1.191 (2.5)	1.682 (10.0)	3.349 (89)	
PUB (50/50)	0.473 (4.0)	1.906 (4.0)	1.346 (8.0)	3.167 (85)	0.59-0.70
PUB (25/75)	0.118 (1.0)	1.429 (3.0)	0.673 (4.0)	1.837 (83)	
PUB (5/95)	0.024 (0.2)	1.811 (3.8)	0.673 (4.0)	2.409 (96)	
PUB (0/100)	-	1.144 (2.4)	0.404 (2.4)	1.474 (95)	

a) Solvent: DMF; reaction time: 24 hr; reaction temperature: 80°C .

b) Solvent: DMF, concentration: 0.5 g/dl.

for the samples containing BPDI and a PUO series samples containing ODPI. As a representative case, PUO (50/50) is a polyurethane consisting of HD/ODPI (50/50 mol%). The structure of a typical polyurethane PUO (50/50) was confirmed by ^1H NMR spectrum in a $\text{DMSO}-d_6$ solution at 50°C (see Figure 2). The ^1H NMR spectrum

indicated that there was NH proton absorptions due to the urethane linkage at 8.32 ppm, absorptions assignable to oxydiphenylene and benzene protons at 7.42-7.96 ppm. The polyurethanes with inherent viscosities of 0.59-0.70 dl/g that have yields in the range of 76-80% were obtained (see Tables 1 and 2).

The structure of the resulting polyurethane was identified with FT-IR spectroscopy. As shown in Figure 3, the typical IR spectrum of the sample PUB (25/75) at room temperature showed the bands near 3330 cm^{-1} (N-H stretching), 1700 cm^{-1} (C=O stretching), 1540 cm^{-1} (C-N-

H bending), and 1280 cm^{-1} (N-C-O stretching).

In an earlier investigation[15], we used BPDI and N,N'-bis[4-(6-hydroxyhexyloxy)phenyl]-3,4,3',4'-biphenyldicarboximide (BHDI) as a chain extender to prepare polyurethane based on isocyanate MDI/PTMG (MW: 1,000). Structure difference is that BHDI has a flexible spacer of 6-methylene units but BPDI does not. When BHDI-based polyurethane has above 50 wt% of hard segment content, the obtained thermotropic polyurethanes exhibited nematic LC behavior. However, any melting behavior was not shown in the BPDI based polyurethane because of higher melting temperature than decomposition temperature. This indicates that the thermotropic LC polymers need the adequate contents of flexible spacer and mesogenic units to give LC behavior.

From 3-dimensional molecular model of BPDI and ODPI calculated by the molecular force field method (chem 3D), it was found that the molecular shape of BPDI is linear, while the ODPI molecule is bent. BPDI and OPDI seem to be stiff and long enough to form a mesophase. In this study, we used BPDI (or ODPI) as a rigid monomer, and diisocyanate HDI and diol HD having 6-methylene units to give flexibility. The influences of composition and structure difference between BPDI and ODPI on the thermal and liquid crystal behaviors of polyurethanes synthesized in this study were examined.

A phase diagram can be drawn by combining the ther-

Table 2. Description of PUO series obtained by copolyaddition reaction^{a)} of 1,6-hexane diisocyanate (HDI) with hexanediol (HD) and N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-oxybiphenyldicarboximide (ODPI)

Designation	Composition		Diisocyanate HDI	Yield g(%)	η inh ^{b)} (dl/g)	
	PU (mol%)	HD g (mmol)				ODPI g (mmol)
PUO (100/0)		1.182 (10.0)	1.682 (10.0)	1.378 (48)		
PUO (95/5)		0.674 (5.7)	0.148 (0.3)	1.009 (6.0)	1.407 (77)	
PUO (75/25)		0.461 (3.9)	0.640 (1.3)	0.875 (5.2)	1.639 (83)	
PUO (50/50)		0.236 (2.0)	0.985 (2.0)	0.673 (4.0)	1.681 (89)	0.59~ 0.70
PUO (25/75)		0.059 (0.5)	0.739 (1.5)	0.336 (2.0)	0.871 (77)	
PUO (5/95)		0.012 (0.1)	0.985 (2.0)	0.353 (2.1)	1.312 (97)	
PUO (0/100)		-	0.985 (2.0)	0.336 (2.0)	1.258 (95)	

a) Solvent: DMF; reaction time: 24 hr; reaction temperature: 80°C.

b) Solvent: DMF, concentration: 0.5 g/dl.

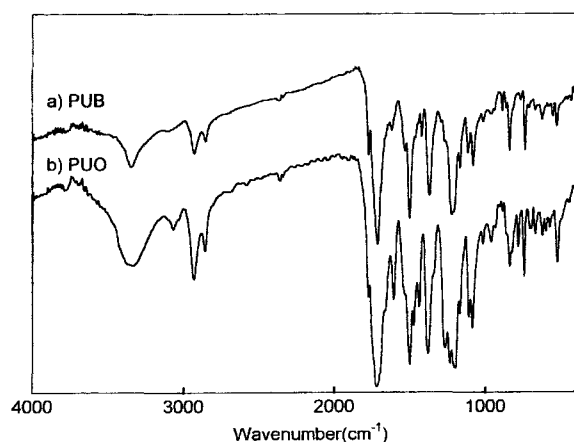


Figure 3. FT-IR spectrum of typical polyurethanes PUB (25/75) and PUO (25/75).

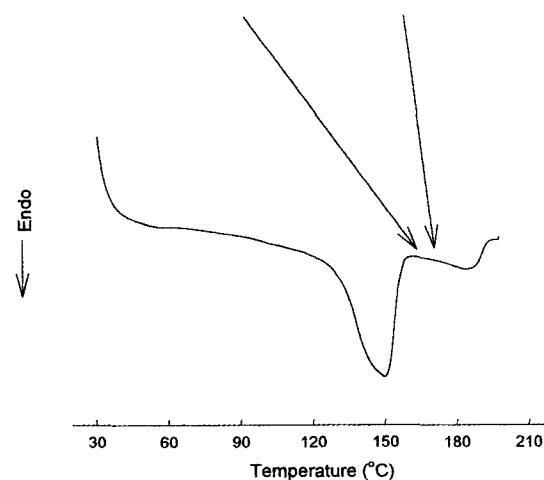
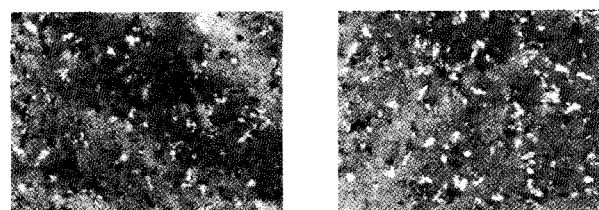


Figure 4. DSC thermogram and polarized microphotographs of polyurethane PUB (95/5).

mal observations with the microscopy observations. For a typical sample PUB (95/5), polarized photomicrographs taken at two temperatures and DSC thermogram during the heating experiments are shown in Figure 4. The crystalline (K) melting temperature (T_m) of the sample PUB (95/5) was near 150°C and its isotropic (I) temperature (or clearing temperature, T_i) was about 187°C. PUB (95/5) exhibits a nematic mesophase in between T_m 150°C and T_i 187°C. The phase behaviors of BPDI-based polyurethanes (PUB series samples) are shown in Table 3 and Figure 5. Only two samples PUB (95/5) and PUB (75/25) in PUB series showed the mesophase behavior. T_m , T_i and ΔT ($T_i - T_m$) increased with increasing content of mesogenic units (BPDI). The polyurethanes PUB (50/50), PUB (25/75), PUB (95/95) and PUB (0/100) having above 50 mol% of BPDI units have very high T_m in the range of 279-288°C but do not show mesophase.

Table 4 and Figure 5 show phase behaviors of PUO series samples. All the samples containing ODPI units exhibit mesophases. The melting temperature of PUO series polyurethanes samples was in the range of 150-190°C, and their isotropic temperature was 160-250°C. T_m , T_i and ΔT ($T_i - T_m$) increased with increasing content

Table 3. Thermal properties of polyurethane PUB samples

PUB(mol%) (HD/BPDI)	Transition temperature ^{a)} /phase ^{b)}			ΔT $T_i - T_m$ (°C)
	K	T_m (°C)	I	
PUB(100/0)	K	147	I	
PUB(95/5)	K	150	M	37
PUB(75/25)	K	184	M	76
PUB(50/50)	K	279	I	
PUB(25/75)	K	286	I	
PUB(5/95)	K	287	I	
PUB(0/100)	K	288	I	

a)Determined by DSC measurement at a heating rate of 10°C/min under nitrogen atmosphere.

b)K: crystalline; M: mesophase; I: isotropic.

Table 4. Thermal properties of polyurethane PUO samples

PUO(mol%) (HD/OPDI)	Transition temperature ^{a)} /phase ^{b)}			ΔT $T_i - T_m$ (°C)
	K	T_m (°C)	I	
PUO(100/0)	K	147	I	
PUO(95/5)	K	150	M	14
PUO(75/25)	K	169	M	51
PUO(50/50)	K	180	M	52
PUO(25/75)	K	184	M	52
PUO(5/95)	K	185	M	53
PUO(0/100)	K	187	M	62

a)Determined by DSC measurement at a heating rate of 10°C/min under nitrogen atmosphere.

b)K: crystalline; M: mesophase; I: isotropic.

of mesogenic units (ODPI) for PUO series samples. The ODPI-based polyurethanes (PUO series samples) clearly exhibited a stable liquid crystalline phase with a low mesophase range and high clearing temperature. This may be attributed to the bent structure and mobility of ODPI having ether group and the abundant flexible units supplied by HDI and HD.

The PUB samples based on BPDI have higher T_m and T_i

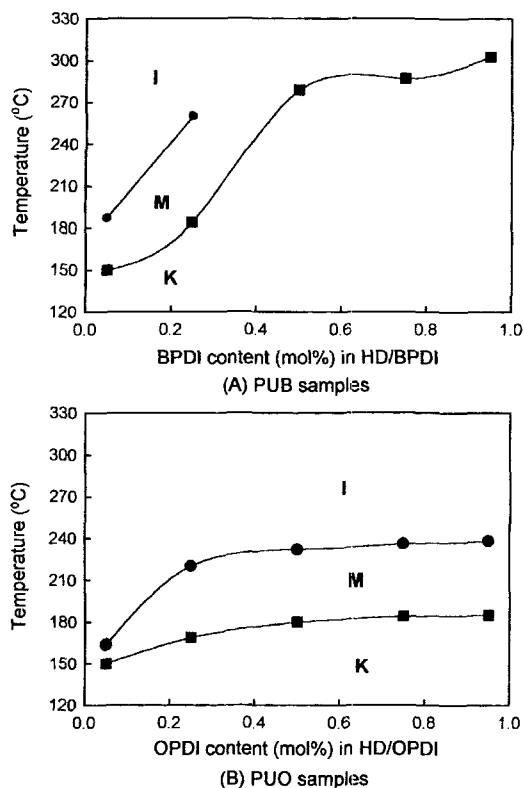


Figure 5. Phase diagrams for polyurethanes (A) PUB and (B) PUO samples.

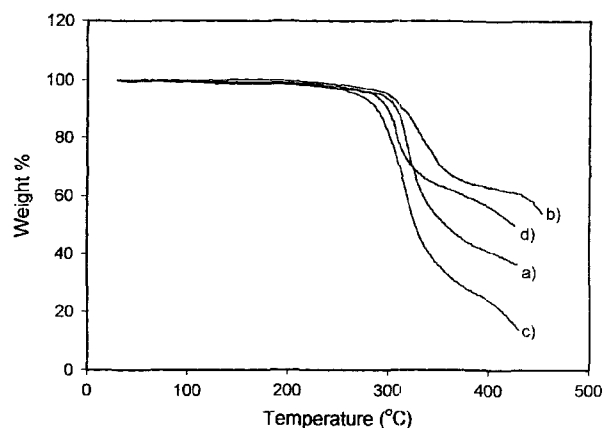


Figure 6. TGA curve for typical polyurethanes: a) PUB (75/25), b) PUB (25/75), c) PUO (75/25) and d) PUO (25/75).

compared to PUO samples based on ODPI at the same compositions. This may be attributed to the structural difference of BPDI and ODPI described above.

An assessment of the thermal degradation characteristics of the typical polyurethanes was made by TGA. As shown in Figure 6, the weight loss (5 and 10%) temperatures of polyurethanes seems to be dependent on structure of rigid diol and composition. The weight loss temperature increased with increasing mesogenic units. The BPDI-based polyurethanes have higher weight loss temperature than those of ODPI-based polyurethanes at the same composition.

Conclusions

Two series of thermotropic polyurethanes that form liquid crystalline order were synthesized from 1,6-hexane diisocyanate (HDI) as a diisocyanate, 1,6-hexane diol (HD), and rigid diols such as N,N'-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboxyimide (BPDI) or bis-N-(4-hydroxyphenyl)-4,4'-oxydiphthalimide (ODPI) containing imide unit to achieve low melt processing temperatures while having liquid crystalline behaviour. Studies have been made on the effects of the chemical structure difference between BPDI and ODPI and overall composition of HD/BPDI (or ODPI) on the thermal and liquid crystalline behavior.

Their properties are summarized as follows. Thermotropic polyurethanes with inherent viscosities of 0.59~0.70 were obtained. BPDI-based polyurethane have melting points in the temperature range of 150~290°C, and the melting points of ODPI-based polyurethanes was in the range of 150~190°C. All the polyurethanes based on ODPI (25~100 mole %) clearly exhibited a stable liquid crystalline phase, however, BPDI-based polyurethanes having 5-25 mol% of BPDI showed a mesophase. The melting and isotropic temperatures (T_m , T_i) and

$\Delta T(T_i - T_m)$ increased with increasing BPDI and ODPI content. The BPDI-based polyurethanes have higher melting point and thermal stability than those of ODPI-based polyurethane at the same composition.

References

1. D. -J. Lee, J. -B. Lee, N. Koide, E. Akiyama, and T. Uryu, *Macromolecules*, **31**, 975 (1998).
2. D. -J. Lee and T. Uryu, *Macromolecules*, **31**, 7142 (1998).
3. D. -J. Lee and T. Uryu, *Sen-i Gakkaishi*, **54**, 246 (1998).
4. J. -B. Lee, D. -W. Choi, and D. -J. Lee, *J. Ind. & Eng. Chem.*, **3**, 277 (1997).
5. H. R. Kricheldorf, R. Pakull, and G. Schwarz, *Makromol. Chem.*, **194**, 1209 (1993).
6. E. Bialecka-Florjanczyk and A. Orzeszko, *Liq. Cryst.*, **15**, 255 (1993).
7. R. Pardey, A. Zhang, P. A. Gabori, F. W. Harris, S. Z. D. Cheng, J. Adduci, J. V. Facinelli, and R. W. Lenz, *Macromolecules*, **25**, 5060 (1992).
8. H. R. Kricheldorf and D. Jahnke, *Eur. Polym. J.*, **26**, 1009 (1990).
9. A. Orzeszko and K. Mirowski, *Makromol. Chem.*, **191**, 701 (1990).
10. A. Orzeszko and K. Mirowski, *Makromol. Chem.*, **192**, 1841 (1991).
11. K. Kurita, H. Imajo, T. Nakada, and Y. Iwakura, *Makromol. Chem.*, **182**, 2577 (1981).
12. H. S. Patel and H. S. Vyas, *Eur. Polym. J.*, **27**, 93 (1991).
13. H. Imajo, K. Kurita, and Y. Iwakura, *J. Polym. Sci., Polym. Chem. Ed.*, **19**, 1855 (1981).
14. T. Hirata, H. Sato, and K. I. Mukaida, *Makromol. Chem. Phys.*, **195**, 2267 (1994).
15. T. J. Lee, D. J. Lee, and H. D. Kim, *J. Appl. Polym. Sci.*, **77**, 577 (2000).