

## Synthesis and Liquid Crystallinity of Polyurethanes, Poly(imide-urethane)s

Dong-Jin Lee, Han-Do Kim, and Toshiyuki Uryu\*

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

*\*Institute of Industrial Science, University of Tokyo, Tokyo, Japan*

### INTRODUCTION

A number of papers concerning the preparation and physical properties of thermotropic polyurethanes have been reported,<sup>1,2</sup> since thermotropic polyurethanes were first reported by Iimura and coworkers.<sup>3</sup> We have been studying the synthesis of thermotropic para-type aromatic polyurethanes containing alkylene spacers.<sup>4,7</sup> The para-type polyurethanes had a tendency to readily crystallize both by mesogenic interactions and by intermolecular hydrogen bondings originating from urethane bonds.

An importance of the orientation formed by intermolecular or intramolecular interaction was found out in the case of main-chain<sup>8</sup> and side-chain liquid crystalline polymers.<sup>9</sup> Thus in order to examine the effects of the mesogenic interaction, para-type polyurethanes without any mesogen were prepared.<sup>5,6</sup> It was revealed that those polyurethanes exhibited monotropic liquid crystallinity induced by the intermolecular hydrogen bondings alone. And, the introduction of bulky substituent groups in the aromatic ring to decrease the degree of lateral packing was considerably responsible for the formation of liquid crystalline phase.

In this study, first, we wish to report the synthesis of monotropic liquid crystalline para-type homo- and copolyurethanes which contain a biphenylene mesogen and alkylene spacers in order to decrease the intermolecular hydrogen bondings. Although several para-type homopolyurethanes containing the biphenylene mesogen were previously reported by us to have enantiotropic liquid crystallinity,<sup>4</sup> we report that the liquid crystallinity depends on the molecular weight of the polyurethanes and high-molecular-weight ones exhibit monotropic liquid crystallinity rather than the enantiotropic by using a detecting method suitable for such polymers as polyurethanes possessing high rate of chain orientation. Second, we report that enantiotropic liquid crystalline copolyurethanes were successfully synthesized by copolyaddition of both meta- and para-type diisocyanates with 4,4'-bis( $\omega$ -hydroxyalkoxy)biphenyls. Third, we wish to describe the synthesis and liquid crystallinity of poly(imide-urethane)s containing symmetric imide unit in the backbone in order to increase the thermal stability of the polymers. Thermal

properties and structure of the polymers were characterized by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopies, FT-IR spectroscopy, polarized optical microscope observation, differential scanning calorimetry, and X-ray diffraction measurements.

## **EXPERIMENTAL**

### **Synthesis of 4,4'-bis( $\omega$ -hydroxyalkoxy)biphenyls (BPn; n=2, 6, 8, 11)**

The reaction of 4,4'-dihydroxybiphenyl with  $\omega$ -halogenated alkanols is described in detail elsewhere.<sup>4,7,10</sup>

### **Synthesis of 2-methyl-4-( $\omega$ -hydroxyalkoxy)anilines (MHAn; n=5, 6, 8, 11)**

The reaction of 4-nitro-3-methyl phenol with  $\omega$ -halogenated alkanols and hydrogenation of the nitro compounds are described according to a modified procedure reported in the literature.<sup>9</sup>

### **Synthesis of N,N'-bis[2-methyl-4-( $\omega$ -hydroxyalkoxy)phenyl]-2,3,6,7-naphthalene dicarboximides (BMNDIn; n=5, 6, 8, 11)**

The reaction of 2-methyl-4-( $\omega$ -hydroxyalkoxy)anilines (MHAn) with 2,3,6,7-naphthalenetetracarboxylic dianhydride (NTCDA) is described in the literature.<sup>11</sup>

### **Polyurethanes**

The homopolyurethanes were synthesized by a polyaddition reaction as described in the previous paper.<sup>4</sup> The copolyurethanes with different compositions were prepared using the same method described for the homopolyurethanes.

### **Poly(imide-urethane)s**

The poly(imide-urethane)s were synthesized by polyaddition as described in the literature.<sup>4-7,10</sup>

### **Characterization**

The structure analysis of the polymers and their intermediates was performed by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy using a JEOL Lambda-400 spectrometer on a DMSO- $d_6$  solution at 90°C or  $\text{CDCl}_3$  at room temperature with 3-(trimethylsilyl)propanesulfonic acid sodium salt (DSS) or tetramethylsilane (TMS) as an internal standard. FT-IR spectra ranging from 4600-400  $\text{cm}^{-1}$  of the polymers were measured with a Perkin Elmer FT-IR 1600 spectrometer by the KBr method. The thermal properties of the polymers

were examined using a Mettler DSC 30 differential scanning calorimeter. All samples were heated to a temperature above the isotropic temperature to eliminate thermal history, then cooled to room temperature and scanned for the second time. Optical textures of the mesophases were observed using an Olympus BH2 polarized microscope equipped with a Mettler FP84 hot stage. Measurements on the thermal stability of polymers were carried out with a TG8120 thermogravimeter at a heating rate 5°C/min under nitrogen atmosphere. X-Ray diffraction measurements were performed with a Rigaku RINT 1500 X-ray diffractometer.

## RESULT AND DISCUSSION

As shown scheme 1, homopolyurethanes were prepared by polyaddition of 4,4'-bis( $\omega$ -hydroxyalkoxy)biphenyls (BPn) with a para-type 2,5-tolylene diisocyanate (2,5-TDI). Four kinds of copolyurethanes (PU $m$ nT), i.e., PU68T, PU211T, PU611T, and PU811T, were synthesized by polyaddition of two different BP $x$ 's ( $x=m, n$ ) with 2,5-TDI.

In order to examine liquid crystallinity of para-type homopolyurethanes containing biphenylene mesogen, the polyurethanes with different molecular weights were prepared. Results of polymerizations and intrinsic viscosities of the polyurethanes are summarized in Table 1. Liquid crystallinity of para-type homopolyurethanes seemed to be caused by disordering to some extent the spontaneous orientation of segments in high-molecular-weight polymers. It is supposed that such disordering can be produced by formation of copolyurethanes.

Copolyurethanes containing the biphenylene mesogen, an alkylene moiety, and two different diisocyanates, i.e., meta- and para-type tolylene diisocyanates were synthesized in order to induce enantiotropic liquid crystallinity by decreasing to some extent both intermolecular hydrogen bondings and mesogenic interactions, as shown in Scheme 2. Three kinds of copolyurethanes with different compositions, i.e., PU6T(m/p)s, PU8T(m/p)s, and PU11T(m/p)s, were synthesized.

There are a number of studies which dealt with the introduction of nonlinear monomer units into thermotropic aromatic polyesters.<sup>12,13</sup> In general, when the proportion of nonlinear monomers in the polyesters increased beyond a certain critical value, the liquid crystallinity was not induced. However, the present results indicate that although the incorporation of nonlinear meta units in the polyurethanes decreased the  $T_m$  and the temperature range, the liquid crystallinity was induced with high proportions of the nonlinear units.

The 2-methyl-4-( $\omega$ -hydroxyalkoxy)anilines (MHAn) were prepared in a two step

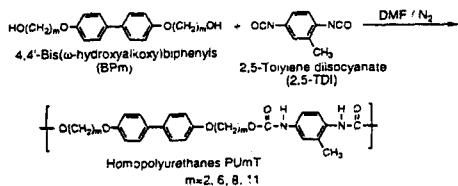
procedure starting from 4-nitro-3-methyl phenol. The model compounds were obtained in 59-81% yield. The substituted dihydroxy compounds containing the (2,3,6,7-naphthalenetetracarboximido)-N,N'-di-2-methylphenylene moiety were prepared by reacting naphthalene-2,3,6,7-dianhydride with 2-methyl-4-(w-hydroxyalkoxy)anilines according to a procedure reported in the literature, the yield was 50-72%. In order to prevent thermal degradation below the melting points and to increase the solubility, a substituent group in the aromatic ring was introduced. The poly(imide-urethane)s containing an imide unit, a meta- or a para-type tolylene diisocyanate, and an alkylene moiety were synthesized, as shown in Scheme 3. These polymers were designated as PIUnTp or PIUnTm.

Like thermotropic polyurethanes without mesogen, it was assumed that in these poly(imide-urethane)s containing no mesogenic unit, the liquid crystallinity was induced by intermolecular hydrogen bondings and that the (2,3,6,7-naphthalenetetracarboximido)-N,N'-di-2-methylphenylene moiety had a function to form coplanar structure including the plane made by the tolylene inserted the urethane groups.

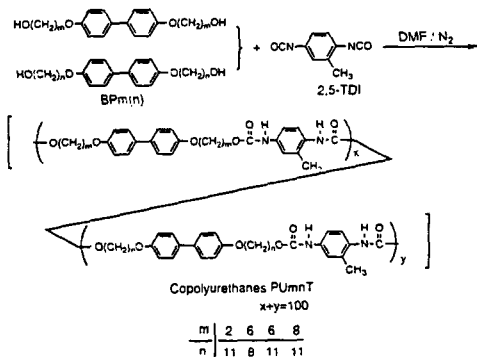
## REFERENCES

1. M. T. Cidade, J. C. M. Bordado, J. Figueirinhas, and A. F. Martins, *Liquid Crystals*, **13**, 295 (1993).
2. H. R. Kricheldorf and J. Awe, *Makromol. Chem.*, **190**, 2579 (1989).
3. K. Iimura, N. Koide, H. Tanabe, and M. Takeda, *Macromol. Chem.*, **182**, 2569 (1981).
4. J.-B. Lee, T. Kato, T. Yoshida, and T. Uryu, *Macromolecules*, **26**, 4989 (1993).
5. J.-B. Lee, T. Kato, K. Iimura, and T. Uryu, *Macromolecules*, **28**, 2165 (1995).
6. J.-B. Lee, T. Kato, and T. Uryu, *Polym. J.*, **27**, 664 (1995).
7. D.-J. Lee, J.-B. Lee, N. Koide, E. Akiyama, and T. Uryu, *Macromolecules*, in press.
8. S. M. Aharoni, *Macromolecules*, **21**, 1941 (1988).
9. Y. Kosaka and T. Uryu, *Macromolecules*, **28**, 870 (1995).
10. D.-J. Lee and T. Uryu, *Macromolecules*, submitted.
11. M. Sato, T. Hirata, and K. Mukaida, *Makromol. Chem.*, **193**, 1729 (1992).
12. A. B. Erdemir, D. J. Johnson, and J. G. Tomka, *polymer*, **27**, 441 (1986).
13. R. W. Lenz and J.-I. Jin, *Macromolecules*, **14**, 1405 (1981).

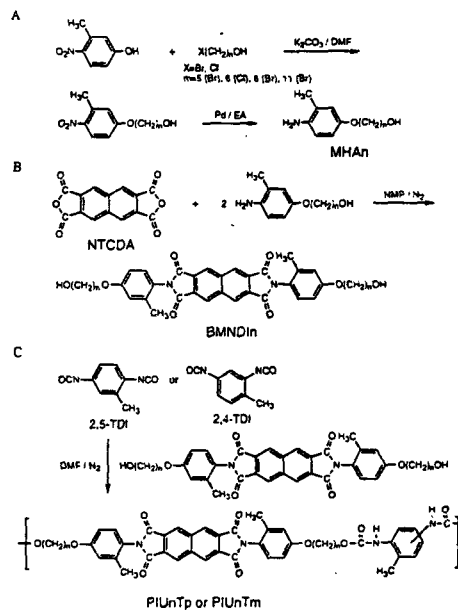
### Homopolyurethanes



### Copolyurethanes

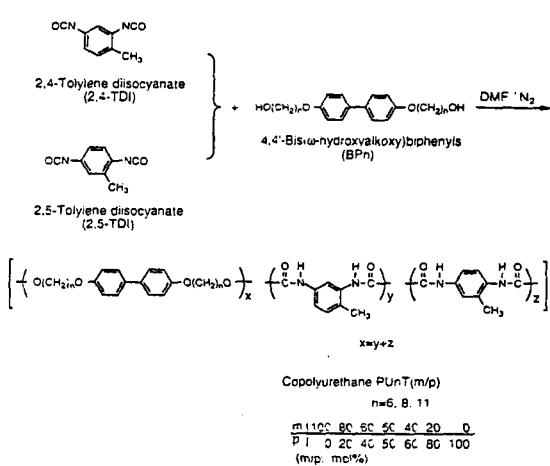


**Scheme 1.** Synthesis of Para-Type Homo- and Copolyurethanes



**Scheme 3.** Synthesis of Intermediates MHAn, BMNDIn, and Poly(imide-urethane)s

### Copolyurethanes



**Scheme 2.** Synthesis of Copolyurethanes

**Table 1.** Polyaddition Reaction of 2,5-Tolylene Diisocyanate (2,5-TDI) with 4,4'-Bis(6-hydroxyhexyloxy)biphenyls (BP6)

PU designation	BP6 g (mmol)	2,5-TDI g (mmol)	yield g (%)	$[\eta]_{\text{DMF}}$ dL/g
PU6T-1	0.883 (2.29)	0.398 (2.29)	0.877 (69)	0.16
PU6T-2	0.883 (2.29)	0.398 (2.29)	0.969 (76)	0.17
PU6T-3	0.883 (2.29)	0.398 (2.29)	0.814 (64)	0.23
PU6T-4	0.442 (1.14)	0.205 (1.18)	0.559 (86)	0.64
PJ6T-5	0.338 (0.87)	0.153 (0.88)	0.475 (97)	0.77
PU6T-6	1.330 (3.44)	0.600 (3.45)	1.812 (94)	0.82

a; Solvent: DMF; reaction time: 24 hr; temperature: 80°C. b) Measured in 1,1,2,2-tetrachloroethane-phenol (1:1, v/v) solution at: 30°C.