

Synthesis of Liquid Crystalline Copolyurethanes Containing Imide Unit

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INTRODUCTION

We have been studying the synthesis of thermotropic polyurethanes,¹⁻⁴ based on structural modifications by means 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. As the resulting polyurethanes clearly exhibited a stable liquid crystalline phase with a low mesophase range and high clearing temperature, it was concluded that the incorporation of the modified units into polymer backbone caused an increase in the mobility in liquid crystalline state by lowering intermolecular interactions to a certain critical level.

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 M. 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.

In the previous work, we prepared liquid crystalline polyurethanes containing non-mesogenic imide units. Their liquid crystallinity was in detail examined. In this study, we wish to describe the synthesis of copolyurethanes containing symmetric imide unit in the backbone in order to increase the thermal and mesomorphic stability of the polymers. Thermal properties and structure of the polymers 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.), 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 *N,N'*-Bis(4-hydroxyphenyl)-3,4,3',4'-biphenyldicarboximide

1,4-Aminophenol (0.05mol) and 4,4'-biphenyl dianhydride (0.025mol) were stirred in 35 ml of *N*-methyl-2-pyrrolidone (NMP). The mixture was reacted for 14hr at 90°C, then poured into methanol. The precipitate was filtered off and recrystallized from DMF. The yield was 65%.

Copolyurethanes

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 *N,N'*-bis(4-hydroxyphenyl)-3,4,3',4'-biphenyl dicarboximide (BPDI) as described in the previous papers.¹⁻³

Characterization

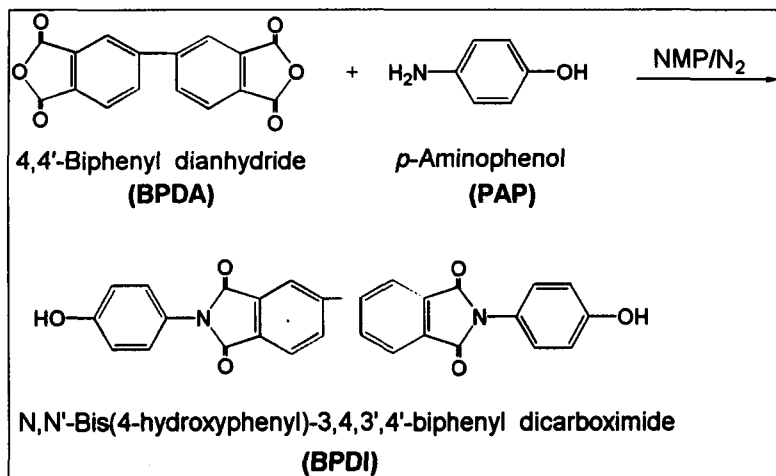
The structure analysis of the polymers and their intermediates was performed by ¹H NMR spectroscopy using a Varian Unity Plus 300 spectrometer with 3-(trimethylsilyl) propanesulfonic acid sodium salt (DSS) or tetramethylsilane (TMS) as an internal standard. The thermal properties of the polymers were 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.

RESULT AND DISCUSSION

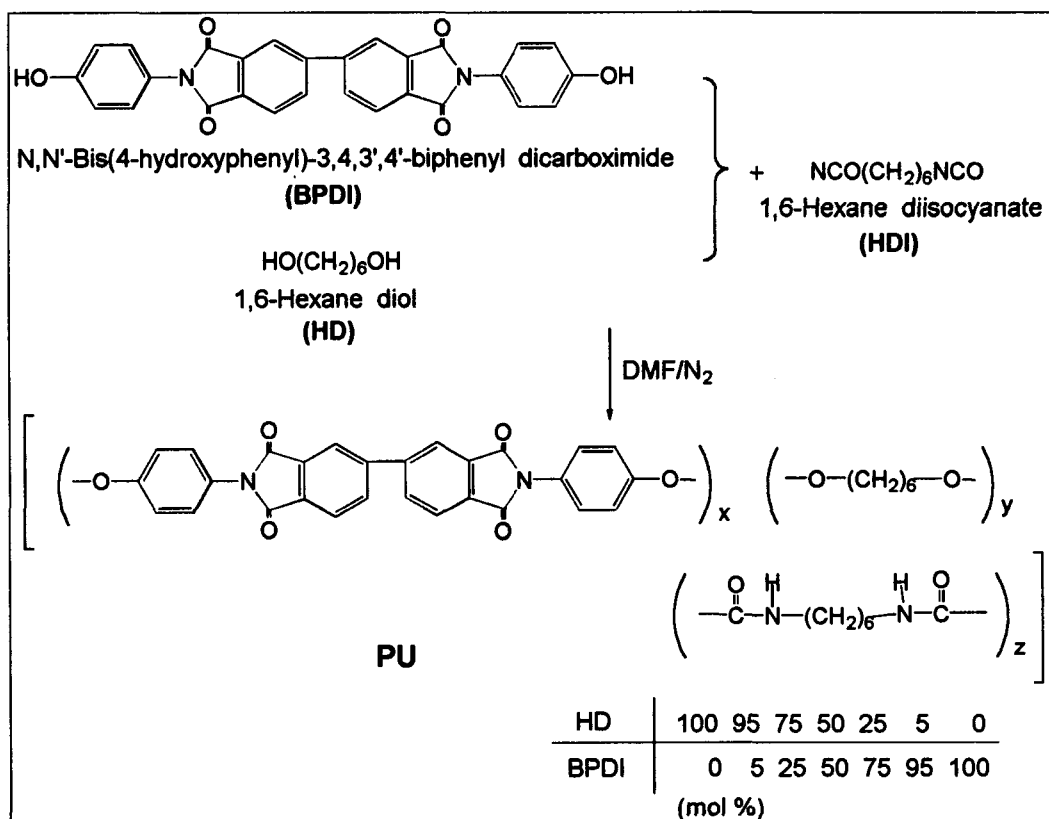
As shown scheme 1, dihydroxy compound having symmetric imide group was prepared from 4,4'-biphenyl dianhydride (BPDA) and *p*-aminophenol (PAP). The model compound was obtained in 65% yield.

In the copolyurethanes, the imide group in the backbone was introduced in order to increase the thermal and mesomorphic stability of the polymers, as shown in Scheme 2. The copolyurethanes with different compositions, i.e., PU(HD/BPDI)=100/0, 95/5,

75/25, 50/50, 25/75, 5/95, 0/100)s, were synthesized.



Scheme 1. The Structure and Synthetic Route of Monomer



Scheme 2. The Structure and Synthetic Route of Copolyurethanes

A polarized microphotograph for the copolyurethane PU(95/5) is shown in Figure 1. The photo is microphotograph taken at 180°C in the heating stage, having both liquid

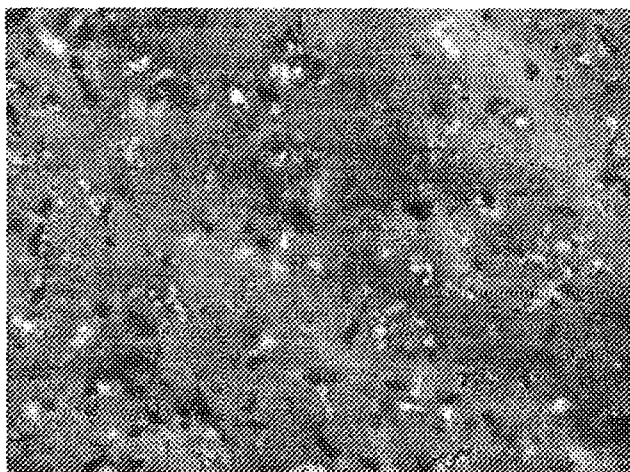


Fig. 1

crystalline texture and mobility. In the main chain poly(ester-imide)s, symmetric imide units such as pyromellitimide, naphthalene-1,4,5,8-tetracarboxydiimide, or perytetracarboxydiimide seem to be stiff and long enough to form a mesophase, but the mesophase was not observed for the polymers based on the symmetric imide moiety. The polyurethanes prepared by introducing imide unit in the backbone exhibited liquid crystallinity.

It could be concluded that the presence of urethane linkages in the polymer chains plays an important role in the formation of liquid crystalline phases, which may be attributable to intermolecular interaction originating from the hydrogen bonding of urethane linkages.

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*, accepted.
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).