

# Synthesis and Liquid Crystallinity of Polyurethane Elastomers

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## Introduction

Segmented polyurethane elastomers are an important class of polymeric materials consisting of thermodynamically incompatible hard and soft segments. Due to the chemical structural difference between the hard and soft segments, a microphase separation occurs, consisting of crystalline hard domains and amorphous soft domains.

In a liquid crystalline polyurethane elastomer (LCPUE), it was revealed that the incorporation of low molecular weight mesogenic diol as a chain extender in the backbone could produce liquid crystalline character.<sup>1-2</sup> Such a polyurethane possess characteristics of liquid crystalline (LC) polymer and a thermoplastic elastomer. They are prepared by chemically linking mesogenic groups into slightly crosslinked polymer networks that add rubber elasticity. At high elongations, the amorphous soft segments will tend to become anisotropic as well. Thus, this kind of elastomer may exhibit unusual anisotropic electrical, mechanical properties, leading to future technological application.

In recent years, various type of liquid crystalline polymers such as polyesters, polyamides, poly(ester-imide)s, and polyurethanes have gained growing interest as new materials, especially as a high strength and high modulus fiber. In the case of LCPUEs, because of the strong intermolecular interaction resulting from the hydrogen bonding of urethane linkage, the main troubles of processing LCPUEs are the high melting point, sometimes exceeding the decomposition temperature, and limited solubility, being an effect of high molecular cohesion and low mixing entropy of the polymers. Generally, to decrease the phase transition temperatures and to improve the solubility, various methods have been applied: (1) insertion of flexible chain spacer

between rigid mesogen segments,<sup>3-6</sup> (2) addition of a pendent flexible chain or a voluminous substituent to the rigid aromatic skeleton,<sup>7-8</sup> or using a secondary amine reacted with dichloroformates,<sup>9</sup> and (3) the introduction of unsymmetric comonomers, which disorder the linearity of the macromolecules.

In this study, we selected a method that insertion of a flexible chain spacer between rigid mesogen segments and investigated syntheses and properties of novel LCPUEs from PTMG ( $M_w$  1000), 2,4-TDI, and mesogenic diol containing imide linkage. The effects of the hard segment content on the liquid crystallinity and tensile properties were investigated. The structures and the thermal properties of all synthesized LCPUEs were examined by using FT-IR spectroscopy, <sup>1</sup>H-NMR, differential scanning calorimetry (DSC), polarized microscope with a hot stage, dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). Mechanical properties were also examined by using a Instron.

## Experimental

### Materials

Poly(tetramethylene)glycol (PTMG,  $M_w$  1000, BASF) was used after purification by distillation. 2,4-Toluene diisocyanate (2,4-TDI, Aldrich), 4,4'-biphtalic dianhydride (Tokyo Kasei. Co.), 6-chloro-1-hexanol (Aldrich), and 4-nitrophenol (Tokyo Kasei. Co.) were used without purification. Dimethylformamide (DMF) and N-methyl-2-pyrrolidone (NMP) were dried over molecular sieves and distilled under reduced pressure.

### Measurements

To confirm the structure of the synthesized mesogenic chain extenders and polymers, infrared spectroscopy was performed using Fourier transform infrared spectrometer (Impact 400D, Nicolet). From FT-IR spectra, the degree of hydrogen bonding of hard segments was examined. The spectra were analysed employing a curve-resolving technique based on a linear least-squares analysis to fit a combination of the Lorentzian and Gaussian curve shape. The thermal behavior of samples was examined by using DSC 220C (Seiko) at a heating rate of 10°C/min under a nitrogen atmosphere. Optical textures were observed with an Zeiss polarizing optical microscope equipped with a Linkam THMS 600 hot stage. The dynamic mechanical

thermal behaviors of polymers were measured by DMTA (MkIII, Rheometric Scientific). The DMTA was operated from -80 to 250°C at a heating rate of 3°C/min. The analysis frequency was utilized at 2 Hz and the films with dimensions of 8×3×0.5 mm<sup>3</sup> were prepared for all DMTA measurement. Tensile test was carried out with a Tinius Oslen 1000 on dumbbell specimens of cross-sectional area 3×0.5 mm<sup>2</sup> at room temperature. The cross-head speed was 20 mm/min.

#### **Synthesis and identification of chain extender**

4-Nitrophenol (0.65 mol, 8.34 g) and sodium carbonate (0.66 mol, 6.359 g) were mixed in 35 ml of DMF. Then, 6-chloro-1-hexanol (0.67 mol, 0.92 g) was added dropwise. The mixture was reacted for 14 hr at 90°C, then poured into cool water. The precipitate was filtered off and recrystallized from DMF. Dried yellow powder was reacted on hydrazine to synthesize amino compound. Then, this material and 4,4'-bipthalic dianhydride were mixed in 40 ml of DMF at 80°C. The reaction was continued by refluxing for 15 hr and poured into methanol. The precipitated material was filtered off and recrystallized from DMF. Yield 70%.

#### **Synthesis of liquid crystalline polyurethane elastomers**

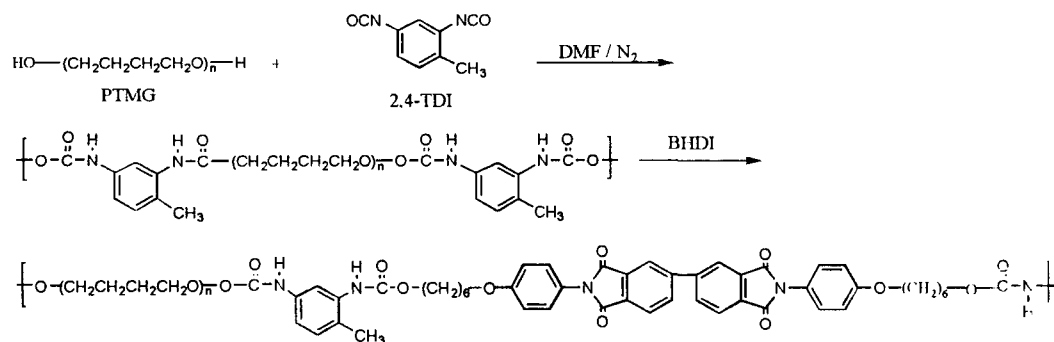
The general reaction routes for two types of the liquid crystalline polyurethane elastomers (LCPUEs) in this study are shown in Scheme 1. To a 250ml four-necked flask equipped with a condenser, thermometer, magnetic stirrer, and nitrogen inlet-outlet were added PTMG (M<sub>w</sub>, 1000)(0.00023 mol), 2,4-TDI (0.00066 mol) and DMF (15-20 ml). The reaction mixture was stirred at 80°C under nitrogen gas for 2 hr. Then DMF (15ml) and mesogenic diol (BHDI)(0.00043 mol) were added, and the reaction was continued at 100°C for 24 hr. DMF was added as the reaction proceeded to keep the solution viscosity low enough to allow stirring. The yellow polymer was precipitated out by pouring the reaction mixture into methanol. The precipitated polymer was filtered off and dried in vacuum at 60°C.

#### **Result and Discussion**

Liquid crystalline polyurethane elastomers based on PTMG (M<sub>w</sub> 1000) as soft segment, 2,4-TDI as diisocyanate, and BHDI containing imide linkage as mesogenic chain extender were synthesized and characterized by FTIR, <sup>1</sup>H-NMR, DSC, TGA,

DMTA, and polarizing microscopy.

The liquid crystalline polyurethane elastomers synthesized in this study showed a nematic textures by polarized optical microscopy. As increasing hard segment content, the value of K (area of hydrogen bonded C=O/area of free C=O) increased. Polyurethane elastomers containing higher hard segment content had higher tensile strength and Young's modulus (E) due to the reinforcement effects of hard segments.



Scheme 1. Synthesis of liquid crystalline polyurethane elastomer

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