

Synthesis and Properties of Liquid Crystalline 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 order to achieve an anisotropic mesophase in the hard domains, the mesogenic units are introduced as chain extender. Due to the liquid crystalline nature of the hard domains, their response to an applied strain should be different than that in a system with crystalline domains, and such an applied strain may result in a highly oriented and perfect structure.

Studies concerning liquid crystalline polyurethane elastomers (LCPUE) were published by Lorentz et al.,¹ Penczek et al.,²⁻³ MacKnight et al.,⁴ and Chang et al.⁵ Lorentz and co-workers reported the mechanical and thermal properties of segmented polyurethanes prepared from 4,4'-(ω -hydroxyalkoxy)biphenyl, hexamethylene diisocyanate (HDI), or isophorone diisocyanate (IPDI), respectively, and poly(tetramethyleneoxide)diol (PTMG) or polycaprolactone diol as soft segment. Penczek and co-workers investigated segmented polyurethanes based on 2,4-TDI, PTMG soft segment and 2,2'-bis-(2-hydroxyethoxy)biphenyl (BHEBP) as chain extender. MacKnight and co-workers studied the synthesis and the phase behavior of LCPUEs prepared from PTMG with different chain length, 2,4-TDI, or 2,6-TDI respectively, and chain extender BHEBP. Chang and coworkers investigated LCPUEs based on 1,10-decanediol, PTMG (Mn 1000, 2000) as soft segment, HDI, 4,4'-methylenecyclohexyl diisocyanate- (H₁₂MDI) and benzene-1,4-di(4-iminophenoxy-n-hexanol) as mesogenic diols.

The purpose of this investigation is to synthesize novel LCPUEs with new mesogenic diol and to study the effect of soft segment with different chain length,

two diisocyanate, and the hard segment content on the properties of liquid crystallinity. Liquid crystalline polyurethane elastomers composed of PTMG(Mn 1000, 2000), HDI, H₁₂MDI and mesogenic diol containing imide linkage. The structures and the thermal properties of all synthesized LCPUEs were investigated by using FT-IR spectroscopy, ¹H-NMR and DSC measurement, a 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, Mn 1000, 2000, BASF) was used after purification by distillation. Hexamethylene diisocyanate(HDI, Aldrich), 4,4'-methylenebiscyclohexyl diisocyanate(H₁₂MDI, Adrich), and 1,6-hexanediol(HD, Aldrich) were used without purification. 1,4-amino phenol(Adrich), 4,4'-biphthalic anhydride(Tokyo Kasei. Co.) and 6-chlorohexanol(Aldrich) were used as received.

Synthesis

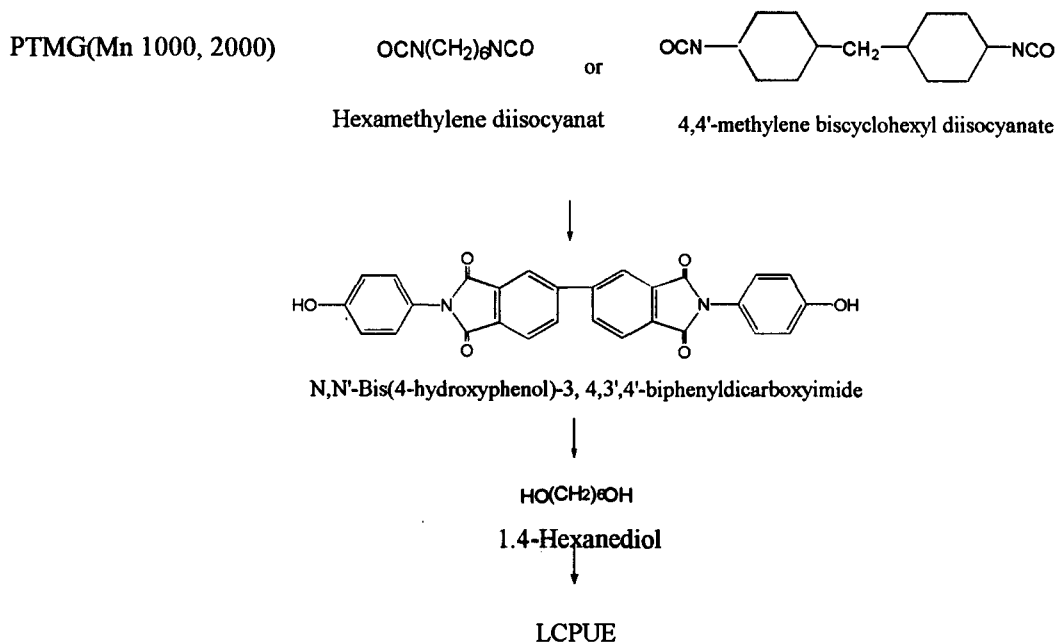
N, N'-Bis(4-hydroxyphenol)-3, 4, 3',4'-biphenyldicarboximide

1,4-aminophenol(0.05mol) and 4,4'-biphthalic anhydride(0.025mol) were stirred in 35ml 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 DMF. The yield was 65%. ¹H NMR (DMSO-*d*₆, 300 MHz): BPDI, δ 6.87-6.91 (4H, d), 7.19-7.23 (4H, d), 8.00-8.03 (2H, d), 8.26-8.29 (4H, d), 9.69 (2H, s).

Polymer 1HHI-65

A solution of PTMG(Mn, 1000)(0.001mol, 1g), HDI(0.005mol, 0.841g), dibutyl tin dilaurate(25mg) in 15mL of dimethylformamide(DMF) was stirred at 80°C for 2hr. To this solution, N, N'-Bis(4-hydroxyphenol)-3, 4, 3',4'-biphenyldicarboximide (0.0015mol, 0.71g) was added in a period of 2hr, then HD(0.0025mol, 0.295g) was added. The polymerization was continued at 80°C for another 20hr, reaction mixture was poured into methanol. The precipitated product was filtered and dried at 60°C in vaccum.

Other polymers were prepared according the procedure described above.



Scheme 1. Liquid crystalline polyurethane elastomer

Characterization

The thermal behavior of samples was examined by using DSC 220C(Seiko) at a heating rate $10^\circ\text{C}/\text{min}$ under a nitrogen atmosphere. Optical textures were observed with an Zeiss polarizing optical microscope equipped with a hot stage. $^1\text{H-NMR}$ spectra were recorded Varian Unity Plus 300 spectrometer. The dynamic mechanical thermal behavior were obtained by DMTA measurement by using DMTA MkIII (Rheometric Scientific) at a heating rate of $3^\circ\text{C}/\text{min}$ at 2Hz frequency. Tensile test was carried out with a Tinius Oslen 1000 on dumbbell specimens of cross-sectional area $3 \times 0.5\text{mm}^2$ at room temperature.

Result and Discussion

Novel liquid crystalline polyurethane elastomers were synthesized by polyaddition of HDI with N,N'-bis(4-hydroxyphenol)-3,3',4',4'-biphenyldicarboximide, PTMG(Mn 1000, 2000), and HD in the presence of dibutyl tin dilaurate as the catalyst by three step process. The mesogenic unit, N,N'-bis(4-hydroxyphenol)-3,3',4',4'-biphenyldicarboximi-

de was used as a chain extender in order to increase the thermal and mesomorphic stability for preparing polyurethane elastomers.

Thermal properties of all synthesized polyurethanes were determined by DSC measurement. Figure 1 shows the DSC trace of 1HHI-50 sample. On second run, two endotherms and one shoulder were detected at 206, 236, and 264°C owing to two melting transitions and isotropic transition of hard segment, respectively. Figure 2 shows microphotograph of the 1HHI-50 sample, which shows nematic texture taken at 240°C. The synthesized polyurethanes showed high mesophase stability.

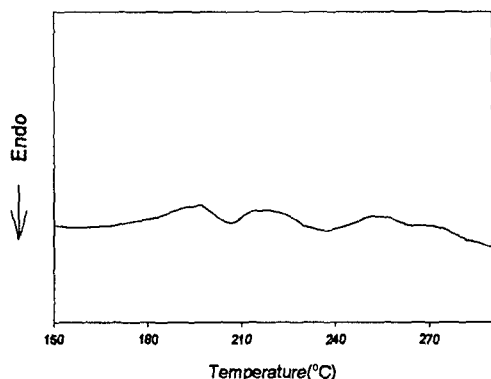


Fig 1. DSC measurement of sample 1HHI-50, the second heating, at a heating rate of 10°C/min.

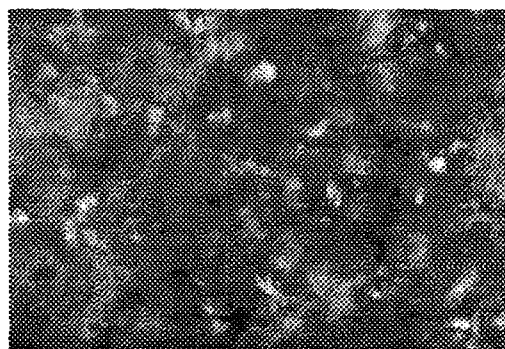


Fig 2. Polarized microphotograph of sample 1HHI-50 at a 200°C

Reference

1. R. Lorenz, M. Els, F. Haulena, A. Schmitz, and O. Lorenz, *Angew. Makromol. Chem.*, **180**, 51 (1990).
2. P. Penczek, K. C. Frisch, B. Szczepaniak, and E. Rudnik, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 1211 (1993).
3. B. Szczepaniak, K. C. Frisch, P. Penczek, E. Rudnik, and M. Cholinska, *J. Polym. Sci., Part A: Polym. Chem.*, **31**, 3231 (1993).
4. W. Tang, R. J. Farris, W. J. MacKnight, and C. D. Eisenbachs, *Macromolecules*, **27**, 2814 (1994).
5. Sun, Hsu, Chang., *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 787 (1995).