

Synthesis and Characterization of Rotaxane Crosslinked Polyurethanes

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Abstract

Three polyurethanes (PU0, PU11 and PU33) where azobis(dibenzo-24-crown-8 ether) **1** acts as a crosslink point with a [3]rotaxane structure except PU0 were synthesized and characterized by ¹H NMR and ATR-FT-IR spectroscopies, and DSC.

Introduction

One of the most interesting properties of a rotaxane, in which a ring molecule connects to a dumbbell-shaped axis molecule without any covalent bond in-between, is that the ring molecule can move freely along the axis molecule (Fig. 1).^{1,2)} Thus, it is expected that introduction of the rotaxane crosslink instead of the hydrogen bonding one into the hard segments of PU elastomers (PUEs) leads to control the mechanical properties and development of novel functions of PUEs.

In this presentation we describe the synthesis of three PUs with and without a [3]rotaxane as a rotaxane crosslink point and characterization of the PUs by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) and differential scanning calorimetry (DSC).

Experimental

The ring **1**³⁾ and axis **2** were synthesized according to literatures. The synthesis of PUs was as follows. The reaction of diphenylmethane diisocyanate (MDI, Mitsui Chemical Co., Ltd., Japan) and poly(tetramethyleneoxide) (PTMG, Mn = 1000, Nippon Polyurethane Industry Co., Ltd., Japan) in dry acetonitrile (the ratio of [NCO]/[OH] = 3)

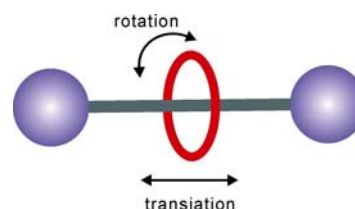
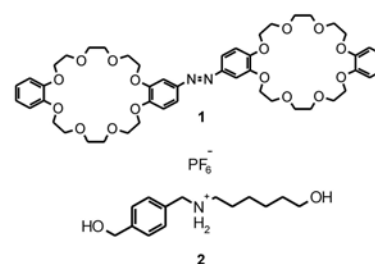


Figure 1. Schematic draws of a rotaxane.



gave a prepolymer. The prepolymer was reacted with the pseudo[3]rotaxane prepared from **1** and **2** (the ratios of $[1]/[2] = 1/6$ for **PU11** or $1/2$ for **PU33**) in dry acetonitrile (the ratios of $[NCO]/[OH] = 1.05$) to obtain **PU11** and **PU33**. **PU0** was also prepared by similar manner without **1**. **PU0** and **PU33** were obtained as a brownish yellow solid and **PU11** was obtained as a brown solid.

Results and Discussion

From the ^1H NMR spectra the content ratios of **1** to **2** in **PU11** and **PU33** were estimated to be 11, and 33 %, respectively.

Figure 2 shows ATR-FT-IR spectra of C=O stretching ($\nu(\text{C}=\text{O})$) band region for the PUs. Two peaks were observed 1704-1708 and 1726-1729 cm^{-1} , assignable to hydrogen bonded carbonyl stretching bands ($\nu(\text{C}=\text{O})_{\text{H-bond}}$) and free ones ($\nu(\text{C}=\text{O})_{\text{free}}$), respectively. Relative intensity of the carbonyl group ($I_{\nu(\text{C}=\text{O})_{\text{H-bond}}}/I_{\nu(\text{C}=\text{O})_{\text{free}}}$) of **PU0**, **PU11** and **PU33** were 1.45, 0.84 and 0.73, respectively. These values increased with increase in the content ratio of **1** due to the steric hindrance of **1** forming the rotaxane structure. This behavior suggests that the formation of the hydrogen bonds in the PUs could be controllable by the introduction of **1**.

Fig. 3 shows DSC thermograms of the PUs. Glass transition temperatures (T_g) of the soft segment chains in **PU0**, **PU11** and **PU33** were observed at -68.3 , -60.5 and -59.0 $^{\circ}\text{C}$, respectively. The shift of T_g to lower temperature could be also due to decrease in the formation of hydrogen bonds arising from the steric hindrance of **1** forming the rotaxane structure. All the PUs also gave an endothermic peak around 30 $^{\circ}\text{C}$, suggesting the existence of another soft segment domain in different microenvironment.

References

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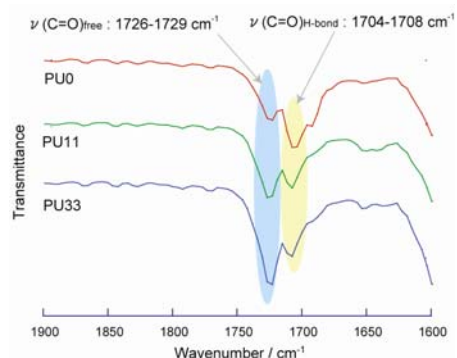


Figure 2. ATR-FT-IR spectra of the carbonyl stretching band region for **PU0**, **PU11** and **PU33**.

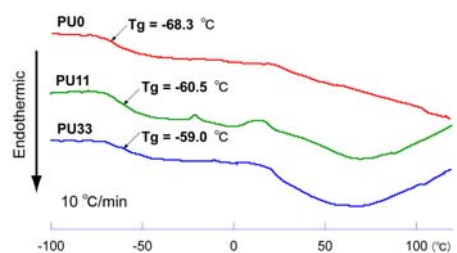


Figure 3. DSC thermograms of **PU0**, **PU11** and **PU33**.