

Physical and Mechanical Properties of Polyurethanes Crosslinked by [3]Rotaxane

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Abstract

We report here physical and mechanical properties of three polyurethanes (**PU11**, **PU33** and **PU0**) with and without azobis(dibenzo-24-crown-8 ether) **ABC**, which acts as a mechanical bonding cross-link point possessing a [3]rotaxane structure.

Introduction

One of the most interesting properties of rotaxanes arising from a mechanical bond is that the ring molecule can move freely along the axis molecule since no covalent bond exists between the ring and axis molecules (Fig. 1).^{1,2)} It is

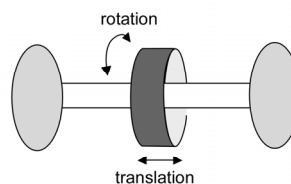


Figure 1. Schematic draws of a rotaxane.

expected that introduction of the mechanical bonding 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 characterization of three PUs with and without a [3]rotaxane as a mechanical bonding crosslink point by spectral, thermal, and mechanical measurements.

Results and Discussions

Glass transition temperatures (T_g) of the soft segment chains in **PU0**, **PU11** and **PU33** were observed at -62 , -61 and -59 °C, respectively. The T_g values are gradually shifted to higher temperature with increasing the content of **ABC** while the difference was small. The shift would be expected that the decrease of the formation of hydrogen

bonding between the PU chains induced by the introduction of **ABC** would involve decreasing both the hard-segment and pure soft-segment phases. In fact, the ATR-FT-IR spectra of the PUs revealed that relative intensity ratios of the carbonyl groups ($I_{\nu(\text{C}=\text{O})\text{H-bond}}/I_{\nu(\text{C}=\text{O})\text{free}}$) of the PUs decreased with increasing the content of **ABC**.

Figure 2 shows the stress-strain curves for the **PU0**, **PU11** and **PU33**. Young's moduli for **PU0** and **PU33** were 11.1 and 10.8 MPa, respectively, whereas that for **PU11** was 1.8 MPa. Remarkably, **PU33**

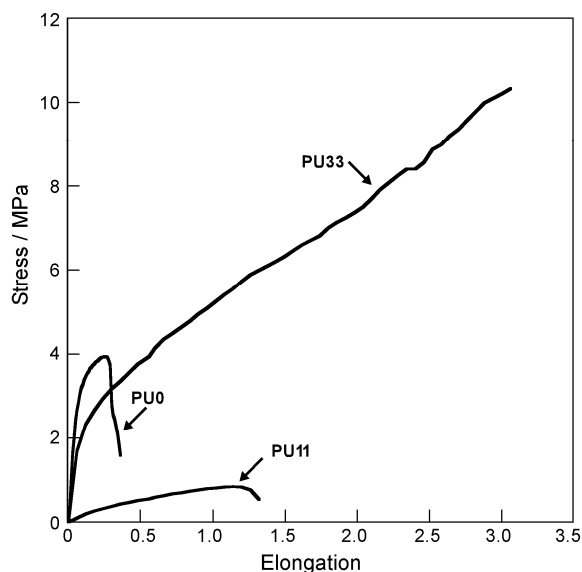


Figure 2. Stress vs. elongation curves for **PU0**, **PU11** and **PU33** at 20 °C.

possesses the best tensile strength and strain at break. Even if the interaction between a crown unit of **ABC** and an ammonium unit of **Ax** is broken by tension, the crown unit can slide on the chain and interact with neighbor ammonium unit of **Ax**. Therefore, we believe that this sliding behavior causes the unique tensile properties. These tensile strength and elongation properties are the evidence for the existence of the mechanical bond crosslink point via the rotaxane in the structure of **PU33**.

Conclusions

The content of 33 % for **ABC** in **PU33**, in which some of them act as the mechanical bond crosslink point, is enough to develop the properties originated from the mechanical bond crosslink point. In fact, incorporation of the enough amount of the mechanical bond crosslink point via the rotaxane structure causes the best tensile strength and elongation among the PUs. In contrast, the content of 11 % for **ABC** in **PU11** is unsatisfying to form the network structure.

References

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