

Study on Synthesis and Physical Properties of Polyurethanes Crosslinked by Polyrotaxanes

ポリロタキサン架橋ポリウレタンの合成と物性評価に関する研究

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Polyurethanes (PUs) made up of isocyanates, alkylene glycols, and curing agents are one of the most important macromolecules. The use of PUs covers a lot of industrial and commercial products such as rubbers, films, fibers, paints, forms, adhesion, and so on. The various applications are based on the characteristic properties derived from the variety of chemical structures of PUs. For instance, a microphase-separated structure consisting of a hard segment domain and soft segment domain affects the thermal and elastic properties of PU. Especially, the hard segment domain plays a critical role in appearing the mechanical property due to acting as physical crosslinks. Therefore, designing a novel crosslink structure instead of the hard segment enable us to develop a unique PU elastomer.

Polyrotaxanes (PRXs) are among the topological macromolecules in which plural ring molecules are interlocked by a long axle molecule bearing bulky end cap groups that prevent the ring molecules from being released. The most interesting property of PRXs is the free sliding of the ring molecules along the axle molecule because of the absence of covalent bonds between the ring molecules and axle molecule. Since the first report of PRX consisting of α -cyclodextrins (CyD) as a ring molecule and poly(ethylene glycol) (PEG) as a long axle molecule by Harada, *et. al.*, many studies on PRXs that make use of free sliding have been published. Among them, I am interested in the development of PUs crosslinked by PRXs. Murakami, *et al.* have reported the synthesis of three PUs crosslinked by PRXs consisting of half-methylated CyDs (MeCyD) and PEGs as well as their thermal and physical properties. However, in the report, the PU-PRXs synthesized from three types of PRXs in which the filling ratio of MeCyDs and the length of PEG are different were used despite that the filling ratio would have affected the thermal and physical properties of PUs. Therefore, discussion in detail for the thermal and physical properties requires comparison among the PUs crosslinked by PRXs with similar filling ratios of MeCyD and the same length of PEG. In addition, the influence of the isocyanate index ($\text{NCO index} = \frac{[\text{NCO}]_{\text{total}}}{[\text{OH}]_{\text{total}}}$) for PUs crosslinked by PRXs consisting of MeCyD and PEGs on the thermal and physical properties has not yet been reported. Furthermore, the PU-PRXs have one structural issue. That is the formation of multiple crosslinks from one CyD molecule in PRX. The sliding effect of PRX may be inhibited because of the multiple crosslinks that function as a chemical crosslink. To solve this issue I have considered replacing one of 18 hydroxyl groups of CyD with an amino group whose reactivity with an isocyanate is much higher than that of

a hydroxy group.

The dissertation consists of five chapters.

In Chapter 1, the introduction and aim of this dissertation research were described.

In Chapter 2, the design and synthesis of PRXs were described. In the synthesis of PRXs with MeCyD, I designed and synthesized eight PRXs: PRX4000(43), PRX4000(63), PRX4000(60), PRX6000(37), PRX6000(50), PRX6000(59), PRX20000(44), PRX20000(52). The names were abbreviated as PRX $a(b)$, where a is derived from PEG's name and b indicates the filling ratio of MeCyD. It was found that i) the filling ratios of MeCyD were controlled by adjusting the concentrations of CyD used in the synthesis of the corresponding pseudo-polyrotaxanes, ii) the half-methylation of PRXs enhances their solubility in DMF used for the synthesis of PUs. Monoamino-CyD (amCyD) was synthesized according to the literature. In the synthesis of PRXs with amCyD, the nucleophilic substitution reaction with a phenoxide, which is usually used for the PRX synthesis, cannot be used because of the high nucleophilicity of the amino group. Therefore, I developed a new way that a click reaction is used and successfully synthesized PRX4000(74)NH₂.

In Chapter 3, the synthesis and characterization of PU-PRXs with MeCyD were described. I synthesized eight PU-PRXs with MeCyD: PU-PRX4000(43)1.5, PU-PRX4000(63)1.5, PU-PRX4000(60)1.0, PU-PRX6000(37)1.5, PU-PRX6000(50)1.5, PU-PRX6000(59)1.0, PU-PRX20000(44)1.5, and PU-PRX20000(52)1.5, where the numbers at the end of the names are the NCO indexes for the PU synthesis. Influence of the filling ratios of MeCyD and lengths of PRXs as well as the NCO indexes on the structure, thermal and physical properties were estimated by gel fraction test, attenuated total reflection Fourier transform infrared (ATR-FT-IR) spectroscopy, differential scanning calorimetry (DSC), dynamic viscoelastic test, and tensile test. It was found that i) the glass transitions are affected by the NCO indexes whereas the filling ratios of MeCyD and lengths of PRX influence the behaviors of the reorganized crystallization in the soft segment, ii) the PU-PRXs with the higher filling ratios of MeCyD show some types of relaxations after their glass transitions, iii) the elongations are affected by the filling ratios of MeCyD, and NCO indexes.

In Chapter 4, the synthesis and characterization of PU-PRXs with amCyD were described. I synthesized two PU-PRXs with amCyD: PU-PRX4000(74)NH₂1.5 and PU-PRX4000(74)NH₂1.0. The thermal and physical properties were estimated by the same measurements in Chapter 3. It was found that i) the degree of swelling of PU-PRX4000(74)NH₂1.5 is much larger than that of PU-PRX4000(63)1.5, ii) PU-PRX4000(74)NH₂1.5 shows some types of relaxations after its glass transition similar to PU-PRX4000(63)1.5, iii) PU-PRX4000(74)NH₂1.5 shows the best elongation among all the PU-PRXs. These results suggest that the number of crosslinks in PU-PRX4000(74)NH₂1.5 decreased successfully compared to that of PU-PRX4000(63)1.5.

In Chapter 5, I summarized the results of PU-PRXs and state the usefulness and future outlook.