Synthesis and Characterization of Flexible and Strong Polyurethane using PPG-βCD-Polyrotaxane as a Chain Extender

JiHyun Lee[1], SuMin Kwak[1], Md Hasan Turabee[1], KyungMan Choi[2] and Ildoo Chung[1]*

[1]Department of Polymer Science and Engineering, Pusan National University, Korea

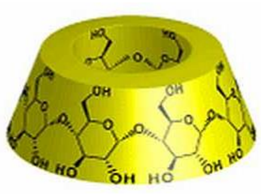
[2]Korea Institute of Footwear and Leather Technology, Busan, Korea

Abstract

Highly stretchable polymer have getting much attention because of their unique properties. In this study, a highly stretchable polymer was synthesized by crosslinking polyurethane with pre-synthesized polyrotaxane from polypropylene glycol (PPG) with low covered cyclodextrin (CD) which acts as both chain extender and crosslinker. Polyrotaxane was used to synthesized by threading beta cyclodextrin (β-CD) along the axis of PPG-diamine polymer backbone followed end capped with 2,4,6-trinitrobenzene sulfonic acid (TNBS). The synthesized polyurethane and polyrotaxane were characterized by ^{1}HNMR and FTIR spectroscopies. Coverage of polyrotaxane was adjusted by mole ratio of PPG and β-CD. DSC and TGA were used to characterize thermal properties of polyurethane. Tensile test was also conducted to measure elongation and tensile strength.

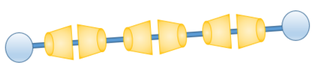
Introduction

Cyclodextrin (CD)



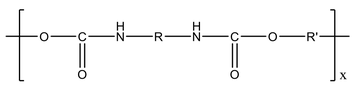
- ►Cyclic oligosaccharides consisting of six to eight glucose units
- ►The formation of non-covalent inclusion complexes with PEG or PPG exhibits great chemical stability
- ► Hydrophobic central cavity and hydrophilic outer surface

Polyrotaxane (PR)



- ►Multiple rings threaded onto a molecular axle
- ►Molecular axle prevented by two bulky end groups
- ►Multiple rings can move freely

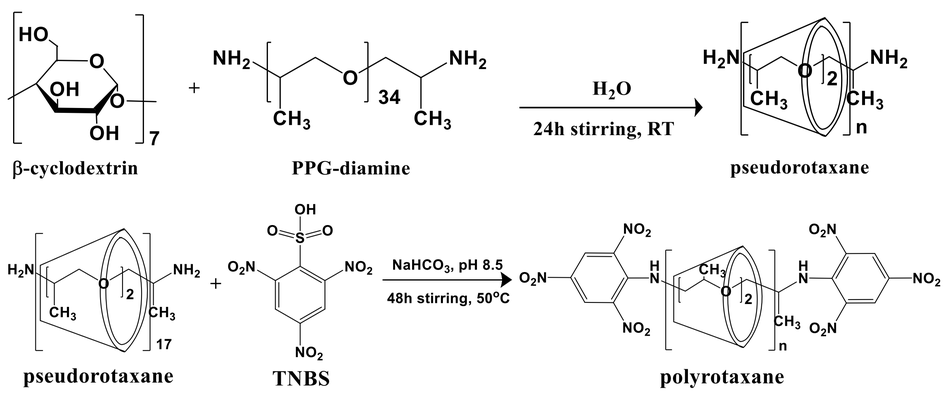
Polyurethane (PU)



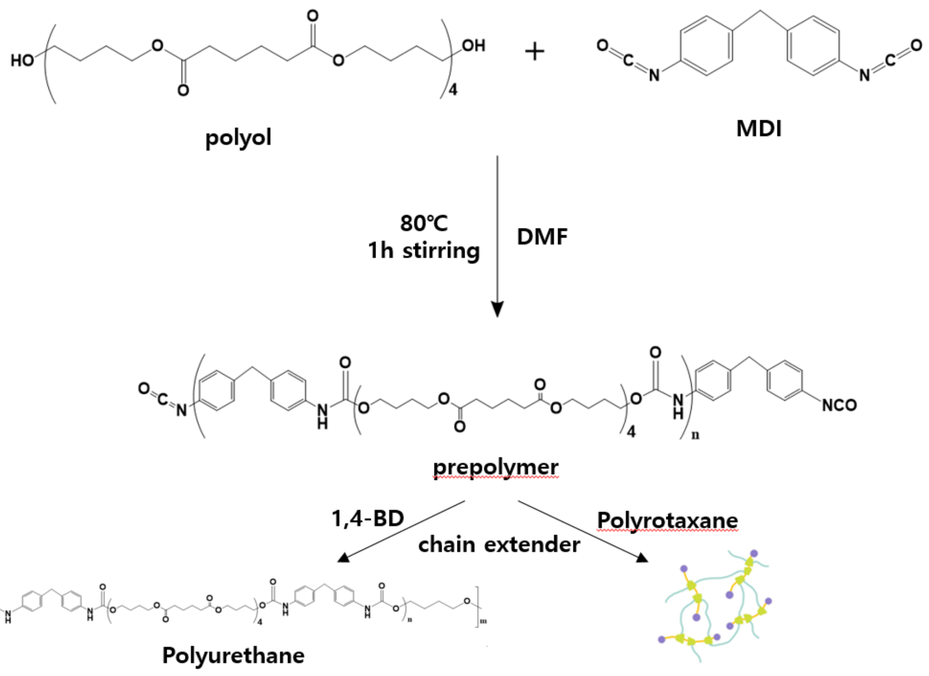
- ►It is mainly made using polyol and diisocyanate
- ►Thermoplastic polymer with elasticity close to the rubber and durability and toughness similar to metals

Experiment

Synthesis of CDPR



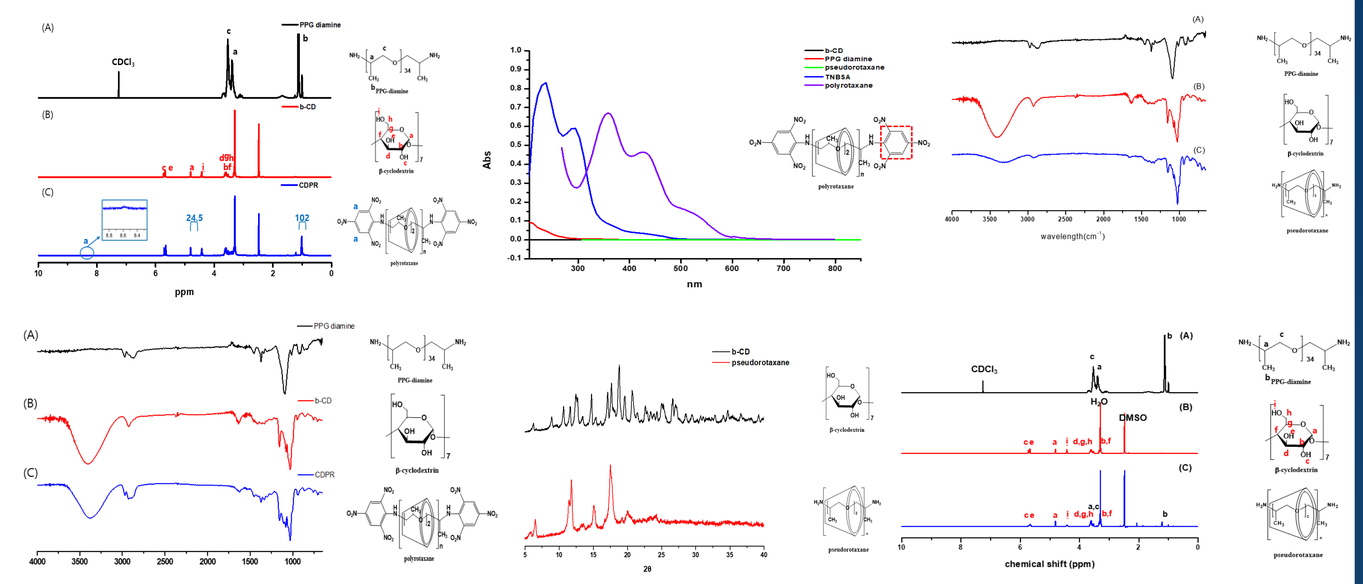
Synthesis of PU

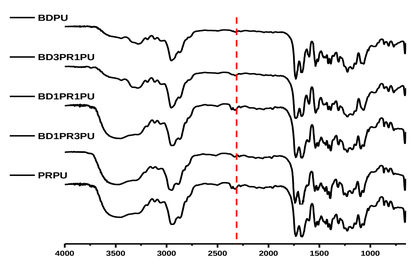


	polyol	MDI	1,4-BD	CDPR	DMF
BDPU	10 g	3.0 g	0.18 g	-	25 g
BD3PR1PU	10 g	3.0 g	0.13 g	0.08 g	25 g
BD1PR1PU	10 g	3.0 g	0.1 g	0.16 g	25 g
BD1PR3PU	10 g	3.0 g	0.04 g	0.25 g	25 g
PRPU	10 g	3.0 g	-	0.33 g	25 g

Results

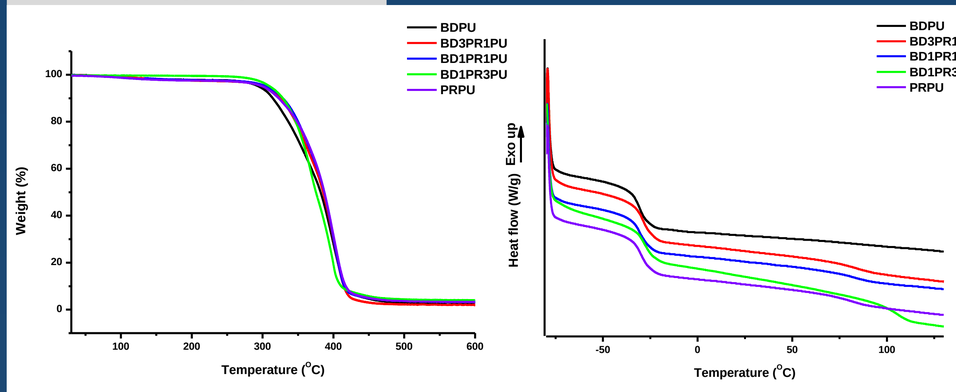
Structure analysis





- ● XRD analysis shows that pseudorotaxane was synthesized.
- ● The structure of the synthesized polyrotaxane was analyzed by NMR, FT-IR, and UV-VIS. The number of threaded cyclodextrin was confirmed by comparing integral.
- ● The benzene structure present in TNBS at the end group was confirmed through UV-VIS analysis.
- ● FT-IR analysis was confimed that the peak of diisocyanate of MDI disappeared after PU was synthesized.

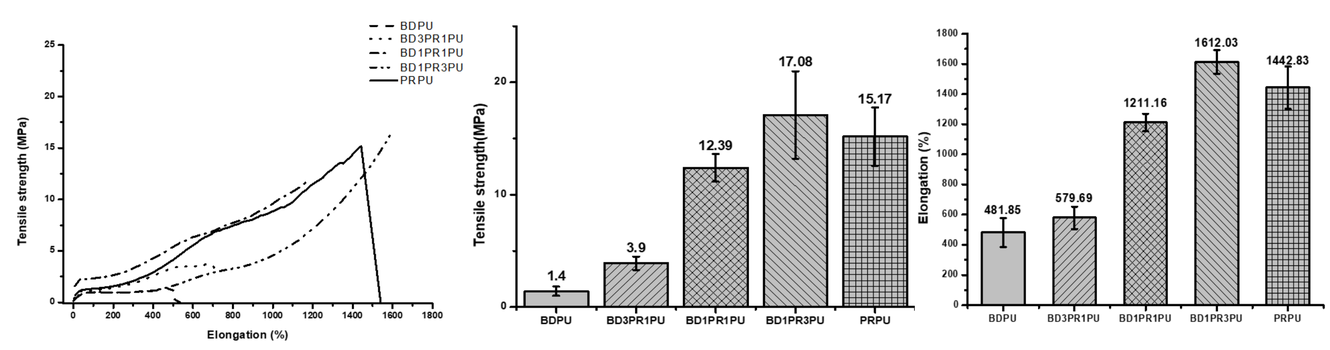
thermal properties



	Degradation temperature (℃)	Tg (℃)
BDPU	325	-30.53
BD3PR1PU	334	-28.30
BD1PR1PU	338	-29.75
BD1PR3PU	336	-27.57
PRPU	340	-29.33

- ● The thermal properties of five types of PUs were confirmed by TGA and DSC.
- ● The degradation temperature of PU was higher when polyrotaxane was included than that of PU containing only 1,4-BD.
- ● This shows that the thermal stability increases due to the hydrogen bonding of polyrotaxane, resulting in an increase in the degradation temperature.
- ● As a result of DSC analysis, Tg was around -30 ℃, and there was no significant difference because of the flexibility of cyclodextrins.

mechanical property



- ● Tensile strength and elongation of five types of PUs were confirmed by UTM.
- ● The tensile strength of PU containing only 1,4-BD was 1.4 MPa, and as the content of polyrotaxane increased, the tensile strength also increased at the same time. In particular, when the ratio of 1,4-BD and polyrotaxane was 1:3, a value of 17.08 MPa was shown.
- ● The elongation of PU containing only 1,4-BD was 481 %, and as the content of polyrotaxane increased, the elongation also increased at the same time. In particular, when the ratio of 1,4-BD and polyrotaxane was 1:3, a value of 1612 % was shown.
- ● Polyrotaxane-based polyurethane can increase both tensile strength and elongation.

Conclusion

Structure of CDPR was analyzed by NMR and FT-IR spectroscopies. The number of β-CD in polyrotaxane was 4. It was confirmed by NMR integral. And CDPR was characterized by UV-Vis for end group analysis of benzene group at 350 nm. The crystal structure of CDPR was analyzed as 6.5, 11.8, 15, 17.5 by XRD analysis. Thermal properties were measured through TGA and DSC analysis. Degradation temperature was over 330 ℃ and Tg was over -30 ℃. Mechanical property was also confirmed by UTM. When polyrotaxane was used as a chain extender for the synthesis of polyurethane, the tensile strength and elongation increased.

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