

## IONIC CROSSLINKING OF POLYURETHANE COPOLYMERS BY THE GRAFTED PENDANT GROUPS

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**Abstract:** In this investigation, the PUs grafted with a dimethylamino or a carboxyl pendant group were ionically crosslinked by neutralization to increase their molecular interaction and the impact on tensile strength and shape memory is examined. The maximum tensile stress was improved by controlling the ratio of A and C-type PU. Shape memory properties are high and reproducible, although grafted with the pendant groups.

### 1. Introduction

Polyurethane (PU) has undergone an extensive study and can be functionalized by the grafted pendant groups. Actually, polyethyleneglycol (PEG) has been grafted to polyurethane to improve the biocompatibility in biomedical applications, and low temperature shape recovery was improved by the grafted pendant group. The carbamate unit in PU was frequently employed as the grafting point due to advantages such as ample linking sites, high reactivity, and mild coupling conditions. Shape memory PU with propionic acid side group was already reported for the control of mechanical strength. Meanwhile, the neutralization pairing between dimethylamino and carboxyl head groups was applied for the vesicle formation from single chain surfactants. In this investigation, the PUs grafted with a dimethylamino or a carboxyl pendant group were ionically crosslinked by neutralization to increase their molecular interaction and the impact on tensile strength and shape memory is examined.

### 2. Experimental

Synthesis of PU was followed according to the literature, except that a volume of 3-dimethylaminopropanol or 3-hydroxypivalic acid in 20 ml DMF was added into the linear PU reaction mixture, and the mixture was stirred at 50 °C under nitrogen for another 2 hrs. The final product was consecutively washed with deionized water and ethanol to remove any remaining reagent, and dried in an oven (60 °C) for a week. The PU pairing was carried out by dissolving and stirring a specific amount of A- and C-type PUs in DMF for a day, and the solution was casted for the preparation of specimen. An FT-IR spectrometer (JASCO 300E) equipped with an ATR was used to measure the IR spectrum. A differential scanning calorimeter (DSC-2010, TA instrument) was used to collect calorimetry data for both heating and cooling scans at a rate of 10 °C/min between -50 and 250 °C. The absolute viscosity in DMF was measured using a vibrating viscometer (AND SV-10) at 25 °C.

### 3. Results and Discussion

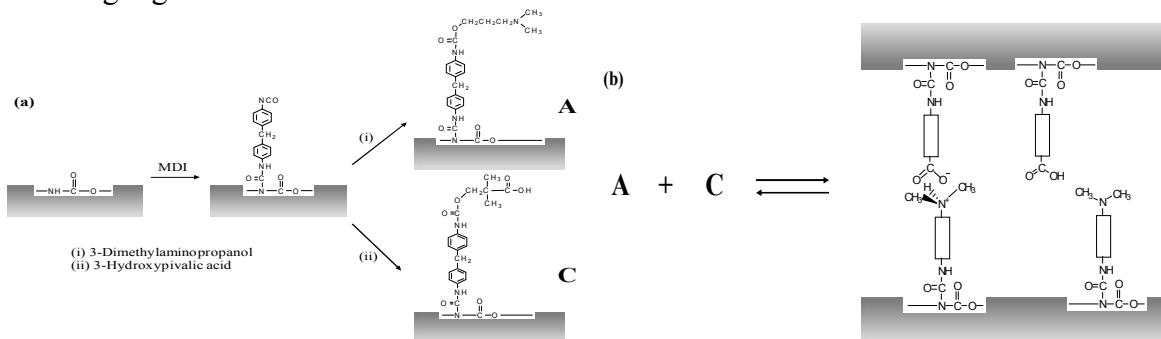
The PU was synthesized based on previous methods, wherein MDI and PTMG functioned as hard and soft segments, respectively, and BD was used as a chain extender. The specific mole ratios are summarized in Table 1. The second MDI was used to graft the 3-

dimethylaminopropanol as a basic pendant group or 3-hydroxypivalic acid as an acidic pendant group.

**Table 1: Composition of the PU**

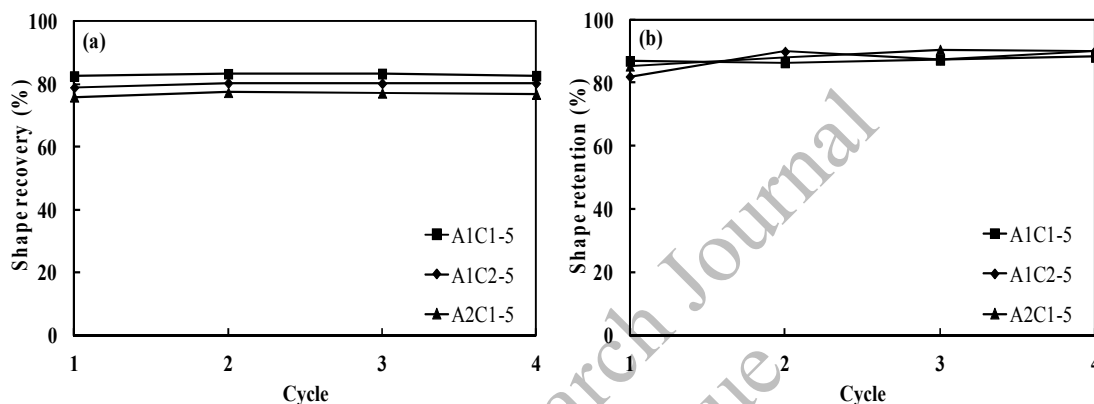
Sample code	Composition (mmol)				
	MDI-1	PTMG	BD	MDI-2	Pendant group
A-1	50	20	30	-	-
A-2	50	20	30	5	5
A-3	50	20	30	10	10
A-4	50	20	30	15	15
A-5	50	20	30	25	25
C-1	50	20	30	-	-
C-2	50	20	30	5	5
C-3	50	20	30	10	10
C-4	50	20	30	15	15
C-5	50	20	30	25	25

The average maximum tensile stress of the linear PU (9 MPa) increased after ionic crosslinking for sample 2 series: the maximum stress went up to 36.5 MPa for A1C1-2, 55.5 MPa for A1C2-2, and 44.4 MPa for A2C1-2. But the maximum stress gradually decreased as the sample number or pendant group content increased, which originated from the fact that the repulsion between pendant groups reduced the molecular interactions and the tensile strength. Specifically, the tensile strength was dependent on A/C pairing ratio, based on the results that A1C2 series showed a superior strength to A1C1 and A2C1 series: the extra dipole-dipole interaction and hydrogen bonding, due to excess C content, between pendant carboxyl and PU for A1C2 series was responsible for the higher tensile strength. The excess dimethylamino group of A2C1 series also improved the tensile strength through hydrogen bonding with PU compared to A1C1 series. Therefore, the excess C or A content in A1C2 and A2C1 series provided an extra tensile strength in addition to the ionic crosslinking. The tensile strain at break of the linear PU (1921%) gradually decreased as the sample number increased: 1278 % for A1C1-5, 1128 % for A1C2-5, and 1612 % for A2C1-5 were observed. The overall tensile properties were that maximum tensile stress could be raised by ionic crosslinking and A/C pairing ratio while maintaining high strain at break.



**Figure 1: (a) PU grafting with dimethylamino group (A) or carboxyl group (C), and (b) ionic crosslinking equilibrium between A and C (the box designates MDI unit)**

Shape memory tests were repeated under cyclic stretch-release conditions between -25 and 45 °C, following the same shape memory test conditions of previous PUs. In Figure 2(a), the shape recovery of the selected PUs remained above 80 % and did not significantly decrease after four cyclic tests. For example, the shape recovery of A1C1-5 remained same from 83 % in the first test to 83 % in the fourth test. Shape retention also maintained around 80 % for the four test cycles. For example, the shape retention of A1C1-5 (87%) in the first cycle slightly increased to 88 % in the fourth cycle (Figure 2(b)). Shape recovery and shape retention of a linear PU without ionic crosslinking were 87 % and 50 %, respectively, suggesting that ionic crosslinking significantly improved shape retention while maintaining a high shape recovery.



**Figure 2:** (a) Shape recovery and (b) shape retention of ionically crosslinked PUs.

#### 4. Conclusion

PU was grafted with a basic dimethylamino group or an acidic carboxyl group. Neutralization of the acidic and basic pendant groups provided an ionic crosslinking of PUs. Characterization such as IR, DSC, viscosity, and acid-base titration supported the grafting and neutralization of the pendant groups. The maximum tensile stress was improved by controlling the ratio of A and C-type PUs. Shape memory properties are high and reproducible, although grafted with the pendant groups. Therefore, it was demonstrated that the ionic crosslinking was useful in the minor control of molecular interactions.

#### 5. Acknowledgments

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