

The Lateral Grafting of Phenyl Group to Polyurethane Copolymer and its Impact on Molecular Interactions

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Polyurethane (PU) has been known for shape memory, ease of synthesis, and versatile applications,¹⁻³ and the cross-linking improved the tensile and shape memory properties.⁴⁻⁶ The grafting of functional groups to polymers has been extensively researched for the development of new functional polymers without harming their basic structure.⁷ Actually, the pendant naphthalene kept PU flexible at low temperature by hindering the molecular interactions between PU chains.⁸ PU was made water-compatible by incorporating a pendant carboxylate-ammonium salt group.⁹ The previous pendant groups were all attached to the PU through a diol-containing pendant group. Here, allophanate bonding was employed as a method for grafting a functional group to PU due to the advantages of having more available linking sites, higher reactivity, and simple reaction conditions.¹⁰ The pendant group can change the molecular interaction between PU chains, and the impact of this on the tensile and shape memory properties is very intriguing. The rigid aromatic ring as a pendant group may reduce molecular interactions and contribute to low temperature flexibility. In this investigation, the impact of the grafted phenyl group on the tensile properties and low temperature flexibility is examined.

Results and Discussion

The PU was synthesized using previously reported methods.⁴⁻⁶ The phenyl group was grafted to the PU chain via an allophanate bonding, and the repulsion between the grafted phenyls was intended to disrupt the molecular interactions between the PU chains and allow the PU to be flexible enough to move at low temperature. The PU grafting with diisocyanate has already been well researched and can be carried out under very mild reaction conditions.¹⁰ In this experiment, the usage of a catalyst such as dibutyl tin laurate (DBTL) or triethylamine was not necessary because the grafting reaction was fast enough to finish without catalysis. The structure of the phenyl-grafted PU is shown in Figure 1(a). Phenylisocyanate was selected as the pendant group because the phenyl was rigid enough to exert the molecular repulsion and the monoisocyanate structure could obviate the possibility of crosslinking observed in diisocyanate grafting (Figure 1(b)). The content of phenyliso-

cyanate was gradually raised while the hard and soft segment contents were fixed in order to investigate the effect of phenyl grafting (Table 1).

The IR spectra of the selected ones (P-0, P-3, and P-5) are compared in Figure 2(a). Intermolecular attractions, such as hydrogen bonding and dipole-dipole interactions, between the hard segments of the PU can be analyzed from the IR spectra. The bonded C=O stretching vibration appears from 1699 to 1706 cm⁻¹, slightly lower than for free carbonyl groups (1731 to 1733 cm⁻¹).^{11,12} As the phenyl content increased, the bonded carbonyl peak slightly decreased relative to the free carbonyl, suggesting that the molecular interactions were interrupted by the grafted phenyl. The thermal behavior was investigated by DSC from -50 to 250 °C (Figures 2(b)). The glass transition temperature (T_g) of the soft segment in the PU was low (under -60 °C) and difficult to detect by DSC; instead, the melting temperature (T_m) of the soft segment in the PU was determined. The T_m increased with the increase of phenyl content; specifically, the T_m was 15.0 °C for P-0, 20.9 °C for P-3, and 17.7 °C for P-5. The enthalpy change (ΔH) for the phase transition, corresponding to the area of each peak, also increased with the phenyl content. The increase in T_m and enthalpy change with an increase in phenyl content is due to the restricted chain movement by the grafted phenyl. The viscosity increased from 2.07 cP for P-0 to 3.07 cP for P-1 and then decreased to 2.48 cP for P-3 and 2.27 cP for P-5. The grafted phenyl was responsible for the initial increase in viscosity due to the intermingling and dragging on each other. However, PU chains were pulled apart by the phenyls, and the viscosity began to decrease once more phenyls were attached to the PU chains. Therefore, the viscosity result suggests that the phenyl was coupled to the PU chains as designed and can reduce the extent of molecular interaction between the PU chains.

The tensile stress and strain were compared in the stress-strain curves in Figure 3(a). Especially, the maximum stress initially increased and then gradually decreased with the increasing phenyl content (Figure 3(b)). For example, the average maximum stress decreased from 9.7 MPa for P-0 to 39.3 MPa for P-1 and 11.8 MPa for P-5. The average strain at break also initially increased and then decreased with an

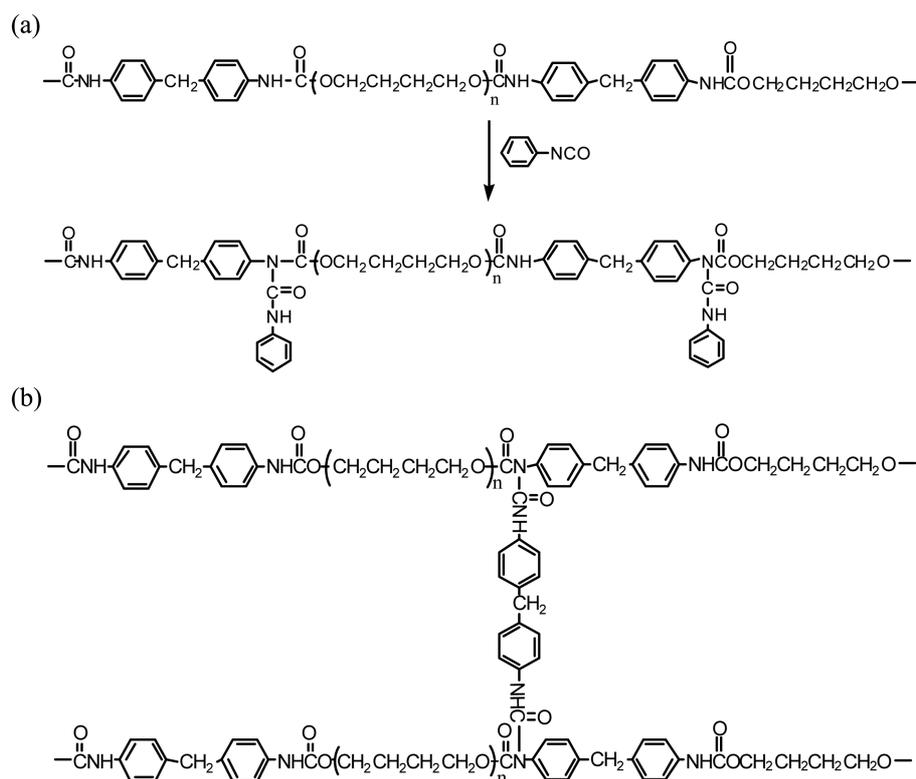


Figure 1. (a) Grafting of phenyl group to PU chain, and (b) crosslinked PU chains.

Table 1. Composition of the PU

Sample code	Composition (mmole)			
	MDI	PTMG	BD	PI ^a
P-0	50	20	30	-
P-1	50	20	30	2.5
P-2	50	20	30	5
P-3	50	20	30	10
P-4	50	20	30	15
P-5	50	20	30	20

^aPI stands for phenylisocyanate.

increase in phenyl content. For example, the strain at break changed from 1798% for P-0 to 2342% for P-1 and 1607% for P-5. The initial increase in stress and strain seems to originate from the friction between PU chains in tensile direction by the grafted phenyl and the repulsion between PU chains was responsible for the decreased stress and strain as more phenyls were grafted. Therefore, tensile stresses and strains could be controlled relative to linear PU by the grafting of phenyl group.

Shape memory tests were repeated under cyclic stretch-release conditions between -25 and 45 °C. The previously known T_m of PU, with the same soft segment, was used as a reference for comparison. Shape recovery was above 80% and reproducible over four test cycles, and improved as more phenyl was grafted. For example, the shape recovery increased from 80% for P-0 to 85% for P-1 and 88% for P-5. The shape recovery tests demonstrated that the PU grafted with phenyl maintained better shape recovery relative to

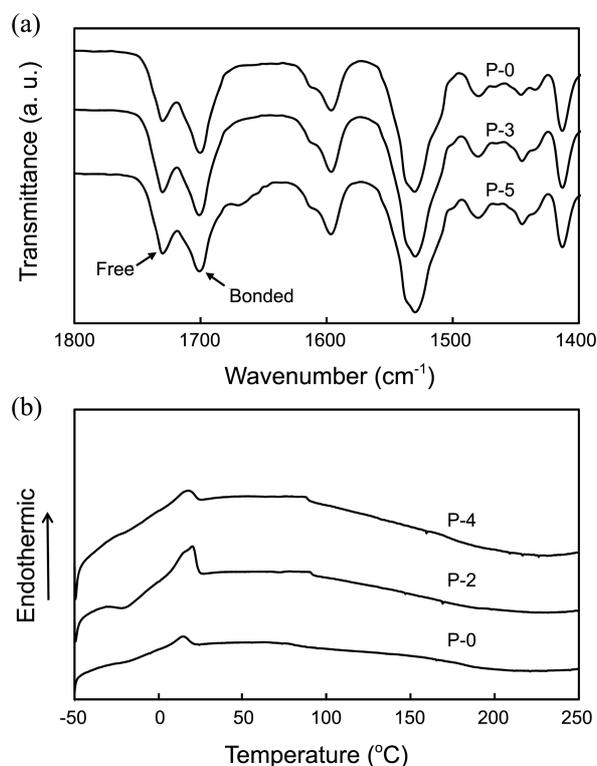


Figure 2. (a) DSC thermograms, and (b) IR spectra of P series.

linear PU (P-0) and reliability under the test conditions. In contrast, the shape retention decreased with the increase of the phenyl content. For example, the shape retention of P-0 (96%) decreased to 93% for P-2 and 88% for P-5. Similar

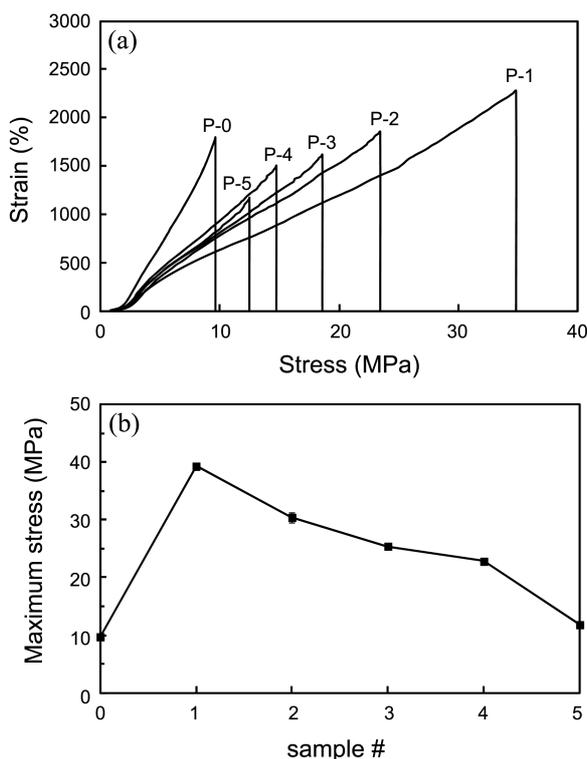


Figure 3. Profiles of (a) stress-strain curves, and (b) maximum stress.

to the results for the shape recovery, the shape retention remained unchanged after cyclic testing. Representative samples (P-0, P-2, and P-4) were selected to compare their shape recovery at 0 °C. The twisted spiral specimens were bound and stored in a temperature-controlled chamber for at least 3 hours before testing and were allowed to return to their original shape. The resulting pictures are shown in Figure 4. All of the samples with the grafted phenyl (P-2 and P-4) instantly recovered their original linear shape at 0 °C; however, the one without the phenyl (P-0) failed to recover its linear shape at the same temperature. The molecular interactions formed in linear PU, hydrogen bonding and dipole-dipole interaction, are significantly reduced after the attachment of phenyl. This resulted in both rotational and vibrational freedom for the PU when recovering its original shape at the freezing temperature, allowing for the instant recovery relative to the linear sample. This experiment clearly demonstrated the importance of the grafted phenyl to shape recovery, which was due to the reduced interaction between the PU chains. Due to the low temperature flexibility, PU with the grafted phenyl could have potential applications to elastomers working in freezing conditions.

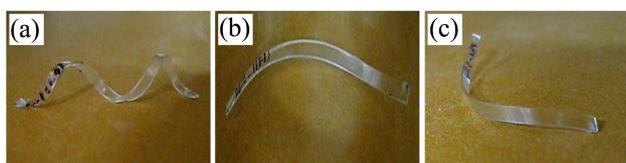


Figure 4. Low temperature (0 °C) shape recovery test of (a) P-0, (b) P-2, and (c) P-4.

Experimental

Materials. Poly(tetramethyleneglycol) (PTMG, $M_n=2000$ g/mol, Aldrich), phenylisocyanate (Aldrich), and 4,4'-diphenylmethanediisocyanate (MDI, Junsei) were dried overnight under high vacuum (0.1 Torr) before use. 1,4-Butanediol (BD) was obtained from Duksan Chemical and dried under high vacuum overnight. *N,N*-Dimethylformamide (DMF) was distilled over CaH_2 under nitrogen before use.

Synthesis. Synthesis of PU was followed according to the literature,^{4,6} except that a volume of phenylisocyanate in 100 mL DMF was added into the linear PU reaction mixture and the mixture was stirred at 50 °C under nitrogen for 2 hrs. The final PU product was dried in an oven (60 °C) for a week to completely remove any remaining DMF.

Mechanical and Shape Memory Analysis. The specimen for the mechanical and shape memory tests was prepared by pouring a solution of PU and DMF (10 g of PU in 100 mL of DMF) into a Petri dish (12 cm × 1 cm) and then drying it at 60 °C for 60 hrs to fabricate a thin film. The specimen was made from the thin film, and the tensile strength was measured according to the standard ASTM D638 using a universal test machine (UTM) equipped with a temperature-controlled chamber (Lloyd Instrument, Model LR50K) with a gauge length of 25 mm, crosshead speed of 10 mm/min, and a load cell of 2.5 kN. The UTM was also used to measure the stress and strain at various temperatures to investigate the effects on shape memory. This shape memory test was carried out according to the method outlined in the literature.^{4,6}

General Analysis. An FT-IR spectrometer (JASCO 300E) equipped with an ATR accessory was used to measure the IR spectrum using the following scan parameters: 4 cm^{-1} resolution, 25 scans, and 2 mm/s scan speed. 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/minute between -50 and 250 °C. After melting at 250 °C for 5 minutes and cooling quickly to -50 °C, a 20 mg specimen was warmed to 250 °C at 10 °C/minute. The second heating scan was selected for comparison. The absolute viscosity of the SMPU dissolved in DMF was measured using a vibrating viscometer (AND SV-10) at 25 °C and was determined from an average of five tests at five different concentrations (m/v of 0.25, 0.5, 1, 2, and 4%).

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