Controlling Molecular Interactions between Polyurethane Copolymers by Grafting Isopropyl Functional Groups

Yong-Chan Chung¹, Jae Won Choi, Hye Lim Lee¹, and Byoung Chul Chun†
Department of Nano Engineering, Inje University, Gimhae 621-749, Korea
¹Department of Chemistry, The University of Suwon, Hwasung 445-743, Korea
(Received June 12, 2013/Accepted August 6, 2013)

Abstract: Grafted isopropyl groups were used to control the molecular interactions between polyurethane (PU) copolymers, and their effect on the tensile properties of PU was investigated. The grafted isopropyl groups were selected to interrupt the molecular interactions and disturb the close contact between PU chains through its branched structure, and thus improve the low-temperature recovery while maintaining the high tensile properties and the shape recovery at ambient temperature. The grafted isopropyl groups made a difference to the phase separation of the hard and soft segments in the PU structure, as determined by IR and DSC. The crosslink density and viscosity experienced an unusual increase with the increase in isopropyl content owing to crosslinking by the grafting reagent. The shape recovery and retention remained high even with the grafted isopropyl groups. Finally, the effect of the isopropyl groups on low-temperature recovery was compared with that of the linear PU, and the reason for the flexibility is discussed.

Keywords: isopropyl, low-temperature recovery, grafting, polyurethane

1. Introduction

Grafting of a side group to polymer has been applied to impart a special function to the polymer [1,2]. Among the polymers, polyurethane (PU) has been investigated due to its excellent elasticity, impact and scratch resistance, and versatile applications in coating, adhesive, seal, synthetic fibers, bedding, molding, insulation foam, electronics, and automotive parts [3-6]. Functional polymers can be also developed by compounding a functional material and polymer. For example, an electroactive functional polymer composite containing carbon nanotubes [7], electromagnetic fillers [8], or Ni chains [9] has been reported, demonstrating a quick shape recovery upon the application of an electric current or electromagnetic field. But a more advanced and practical method than compounding would be to graft polymers with functional groups.

There are ample examples of the polymers with the grafted functional side groups exhibiting thermal response, low-temperature shape recovery, ion-sensing, and electro-luminescence. For example, the side groups of poly(acrylate) polymers are known to affect the thermal and mechanical properties of the polymers by hindering molecular interactions between polymer chains [10,11]. Tertiary butyl side group decreases the transition temperature of the poly(acrylate) polymer, and gas permeation through the polymer membrane is significantly increased due to the fact that the dense polymer chain packing is inhibited by the tertiary butyl side groups [12]. Isopropyl group is adopted as a side group in poly(N-isopropyl acrylamide) (PNIPAA) that shows a reversible swelling-shrinking behavior around 32 °C and the resulting polymer is utilized as a temperature-sensitive hydrogel and polymeric membrane [13,14]. The PNIPAA membrane is suggested for pervaporation technology that separates liquid mixtures through selective permeation. The PNIPAA is also used for the controlled release system due to the thermal and pH sensitive characteristics [15]. In addition, the isopropyl side group is used for the gas permeation control of poly(acetylene) membrane [16]. Considering the diverse applications of isopropyl as a side group, it is worth to test the branched structure of isopropyl as a functional side group and to determine its impact on molecular interaction. As a method for grafting a functional group to PU, aliphannate bonding has been successfully employed due to advantages such as more available linking sites, higher reactivity, and simple reaction conditions [17]. In this investigation, the impact of isopropyl side group on tensile properties and shape recovery of PU is examined, and the reason for the better low temperature recovery is discussed.
2. Experimental

2.1. Materials
Poly(tetramethylene glycol) (PTMG, $M_n = 2000$ g/mol, Aldrich, USA) and 4,4'-diphenylmethanediisocyanate (MDI, Junsei Chemical, Japan) were dried overnight under high vacuum (0.1 torr) before use. Isopropanol and 1,4-butanediol (BD) were obtained from Duksan Chemical (Korea), and BD was dried under high vacuum overnight. N,N-dimethylformamide (DMF, Duksan Chemical) was distilled over CaH$_2$ before use.

2.2. Synthesis of Polyurethane
A mixture of MDI-1 and PTMG was stirred at 50 °C for 3 hours in a 500 ml four-neck flat-bottomed flask equipped with a condenser, mechanical stirrer, and nitrogen blanket to prepare a prepolymer. MDI-2 and BD dissolved in 20 ml of DMF was sequentially added to the flask and allowed to react for another hour under the same conditions. Subsequently, a volume of MDI-3 was added to the above reaction mixture, and the reaction was allowed to proceed for 40 minutes. Finally, a volume of isopropanol equivalent to the number of moles of the MDI-3 was added with an additional 100 ml of DMF, and the mixture was stirred under the same conditions for 2 hours. The final reaction mixture was precipitated in distilled water, cut to pieces, and sequentially washed in distilled water until clearness and ethanol. The solvent in PU product was removed by suction filtration on a filter paper, and the filtered PU product was completely dried in an oven at 60 °C for a week. The resulting PU structures are shown in Figure 1, and the specific mole ratios of the reaction mixture are summarized in Table 1.

2.3. Crosslink Density
A specimen (20×20×1 mm) with a known weight ($m_1$) was swollen in 50 ml of toluene in a closed-cap bottle for 24 hours, and the swollen weight of the specimen ($m_2$) was measured after quickly removing the adsorbed toluene on the polymer surface with a tissue. The swollen specimen was dried at room temperature for a week, and the dry weight of the specimen was measured ($m_3$). The solvent volume ($V_s$) in a swollen specimen, averaged from five swelling experiments, was calculated from the weight difference between the swollen ($m_2$) and dry states ($m_3$) and the solvent density (0.8699 g/cm$^3$). The polymer volume ($V_p$) in the dry state was calculated by dividing the polymer dry weight ($m_1$) by the polymer density. The volume fraction of the polymer in the swollen state ($v_1$) was calculated by the equation, $V_p/(V_s + V_p)$. The derivation of the cross-link density is detailed in the results and discussion section.

2.4. Mechanical and Shape Memory Analysis
The specimen for the mechanical and shape memory test was prepared by pouring a solution of PU and DMF (10 g of PU in 100 ml of DMF) into a Petri dish (12×1 cm) and then drying it at 60 °C for 60 hour to fabricate a thin film. The specimen was made from the thin film according to the specifications of ASTM D638. The tensile strength was measured according to ASTM D638 by a universal test machine (UTM) equipped with a temperature-controlled chamber (Lloyd Instrument, Model LR10K) with a gauge length of 25 mm, crosshead speed of 10 mm/minute, 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 shape memory effect. The shape memory test was carried.

<table>
<thead>
<tr>
<th>Sample code</th>
<th>MDI-1 (mmole)</th>
<th>PTMG (mmole)</th>
<th>MDI-2 (mmole)</th>
<th>BD (mmole)</th>
<th>MDI-3 (mmole)</th>
<th>Isopropanol (mmole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 1-1</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>1 1-2</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>1 1-3</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>1 1-4</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>1 1-5</td>
<td>20</td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>2 1-1</td>
<td>17.5</td>
<td>17.5</td>
<td>32.5</td>
<td>32.5</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>2 1-2</td>
<td>17.5</td>
<td>17.5</td>
<td>32.5</td>
<td>32.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>2 1-3</td>
<td>17.5</td>
<td>17.5</td>
<td>32.5</td>
<td>32.5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>2 1-4</td>
<td>17.5</td>
<td>17.5</td>
<td>32.5</td>
<td>32.5</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>2 1-5</td>
<td>17.5</td>
<td>17.5</td>
<td>32.5</td>
<td>32.5</td>
<td>15</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 1. (a) PU with a pendant isopropyl group and (b) PU crosslinked by MDI-3.

Table 1. Composition of the PU
out following a previously described method [6,17].

2.5. General Analysis
A differential scanning calorimeter (DSC-2010, TA Instrument) was used for the heating and cooling scan at a rate of 10 °C/minute between −50 and 250 °C. An FT-IR spectrometer (JASCO 300E, JASCO) that was equipped with an ATR was used to measure the IR spectrum using the following scan parameters: 4 cm⁻¹ resolution, 25 scans, and 2 mm/second scan speed. Low temperature recovery test was carried out in a cold chamber (Jisco J-RHC2) and was recorded by a video camera (SONY HDR series). The absolute viscosity (averaged over five experiments) was obtained using a vibrating viscometer (AND SV-10) for PU samples dissolved in DMF at five different concentrations (0.25, 0.50, 1.0, 2.0, and 4.0% (w/w)) at 25 °C.

3. Results and Discussion

3.1. Synthesis
The PU was synthesized based on previous methods [17], wherein MDI and PTMG function as hard and soft segments, respectively, and BD was used as a chain extender. MDI was divided into MDI-1 and MDI-2, where MDI-1 reacted first with PTMG and then MDI-2 and BD was used for chain extension of the oligomer (MDI-1 and PTMG). The reason for the separation of MDI-1 and MDI-2 was to prevent a premature cross-linking by an allophanate bonding if MDI-1 and MDI-2 was added together. The isopropyl group was linked to the PU chain through MDI-3 and was intended to reduce the molecular interactions between PU chains and free the PU from binding in order to be flexible enough to move under subzero temperature conditions. Isopropyl was selected as the pendant group because the branched and rigid structure was required for disrupting molecular interactions. Therefore, the isopropyl group was designed to endow the PU with flexibility and quick shape recovery at subzero temperatures. The structure of the PU with the grafted isopropyl group is shown in Figure 1(a). Because some of the MDI-3 could be used for cross-linking another PU chains as shown in Figure 1(b), the cross-link density is worth to be determined. The unexpected cross-linking could improve the tensile strength, which will be shown in the tensile property section. The cross-link density was determined from a polymer swelling experiment to determine whether the degree of cross-linking was dependent on the MDI-3 content. The interaction parameter, χ, between toluene and the polymer was determined from the following expression [18]:

\[ \chi = (\delta_2 - \delta_1)^2 V_1 / RT \]  

\( \delta_1 \) and \( \delta_2 \): solubility parameter of solvent and polymer  
\( V_1 \): molar volume of solvent  
\( R \): gas constant  
\( T \): absolute temperature

3.2. IR Analysis
The IR spectra of the selected I1 (I1-1, I1-3, and I1-5) and I2 (I2-1, I2-3, and I2-5) series are compared in Figure 3. The new urea C=O stretch peak at 1650 cm⁻¹ appears for both I1 and I2 series as the isopropyl content increases, which is due to the formation of the isopropyl group.

Table 2. Crosslink density of the PU as determined by swelling experiments

<table>
<thead>
<tr>
<th>Sample code</th>
<th>( \rho ) (g/cm³)</th>
<th>( V_1 ) (cm³)</th>
<th>( V_2 ) (cm³)</th>
<th>( 10^n ) (mole/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11-1</td>
<td>1.11</td>
<td>0.123</td>
<td>0.299</td>
<td>0.652</td>
</tr>
<tr>
<td>11-2</td>
<td>1.11</td>
<td>0.144</td>
<td>0.346</td>
<td>0.917</td>
</tr>
<tr>
<td>11-3</td>
<td>1.02</td>
<td>0.134</td>
<td>0.384</td>
<td>1.18</td>
</tr>
<tr>
<td>11-4</td>
<td>1.12</td>
<td>0.128</td>
<td>0.390</td>
<td>1.22</td>
</tr>
<tr>
<td>11-5</td>
<td>1.05</td>
<td>0.130</td>
<td>0.385</td>
<td>1.19</td>
</tr>
<tr>
<td>12-1</td>
<td>1.02</td>
<td>0.323</td>
<td>0.346</td>
<td>0.97</td>
</tr>
<tr>
<td>12-2</td>
<td>1.05</td>
<td>0.323</td>
<td>0.374</td>
<td>1.10</td>
</tr>
<tr>
<td>12-3</td>
<td>1.05</td>
<td>0.397</td>
<td>0.420</td>
<td>1.48</td>
</tr>
<tr>
<td>12-4</td>
<td>1.01</td>
<td>0.364</td>
<td>0.432</td>
<td>1.59</td>
</tr>
<tr>
<td>12-5</td>
<td>1.04</td>
<td>0.472</td>
<td>0.403</td>
<td>1.33</td>
</tr>
</tbody>
</table>

\( \rho \): density, \( V_1 \): polymer volume, \( V_2 \): volume fraction of polymer, and \( n \): crosslink density.

Figure 2. Crosslink density of the I1 and I2 series.

The solubility parameters of toluene (\( \delta_3 \)) and PU (\( \delta_2 \)) were 18.2 and 20.5 (MPa)⁻¹, respectively [19,20]. The degree of cross-linking was calculated from the Flory-Rehner equation (2):

\[ -\ln(1 - v_2) + v_2 + \chi v_2^2 = V_n [v_2 - 1/2v_2] \]  

\( v_2 \): volume fraction of polymer in the swollen mass  
\( \chi \): interaction parameter  
\( V_n \): polymer volume  
\( n \): crosslink density

The crosslink density was found to increase with the isopropyl content (Table 2 and Figure 2), which was not directly due to the isopropyl group but to the cross-linking effect by the MDI-3 that was used to cross-link the PU chains instead of linking isopropyl group.
to the allophanate bonding by MDI-3 and which supports the idea that the lateral linking by MDI-3 is made as designed. In addition, a slight increase in C-H bending peak at 1510 cm\(^{-1}\) is observed as the isopropyl content increases, which is due to the laterally linked isopropyl group and agrees with the above result. Intermolecular attraction, such as hydrogen bonding and dipole-dipole interaction, between hard segments can be analyzed from the IR spectra, where the bonded C=O stretching vibration appears at 1699 to 1706 cm\(^{-1}\) and is slightly lower than that of the free carbonyl group (1731 to 1733 cm\(^{-1}\)) [21,22]. The carbonyl peak shift is used to analyze the phase separation of the hard and soft segments and can be quantified by comparing the degree of phase separation (DPS) that is calculated using the equation (DPS=A\(_{1700}\)/A\(_{1725}\)+A\(_{1700}\)), where A\(_{1700}\) and A\(_{1725}\) represent the absorbance at 1700 cm\(^{-1}\) and 1725 cm\(^{-1}\), respectively. The DPS of the I1 series decreases from 0.597 for I1-1 to 0.591 for I1-3 and 0.550 for I1-5, and that of I2 series changes from 0.626 for I2-1 to 0.608 for I2-3 and 0.622 for I2-5. In line with the DPS results, the bonded carbonyl peak of the I1 series decreases compared to the free carbonyl in Figure 3(a), and the decrease in the bonded carbonyl peak of the I2 series is not apparent in Figure 3(b). The I1 series is more affected by the isopropyl group than the I2 series because the rigid I2 series, due to its lower soft segment content, is less affected by the bulky isopropyl group than the I1 series. It is determined from the IR spectra that the isopropyl group is linked to the PU chains in the I1 and I2 series and the extent of molecular interaction is more affected by the isopropyl group for the I1 series.

### 3.3. Thermal Analysis

The effects of the isopropyl group and hard segment content on soft segment melting are investigated from the DSC data for the selected samples of the I1 and I2 series in Figure 4. Because the T\(_m\) of the soft segment is important as shape recovery temperature, the soft segment T\(_m\) is investigated by DSC. The soft segment T\(_m\) of the linear PUs (I1-1 and I2-1) is observed at approximately 15 °C, but the melting peak is significantly reduced or disappears as the isopropyl content increases (I1-3, I1-5, I2-3, and I2-5). The disappearance of the melting peak by the grafted isopropyl group may have resulted from the fact that the isopropyl group disrupts the molecular interactions between the PU chains and that the enthalpy change for soft segment melting is minimized compared to that of the linear PU. In addition, the partial cross-linking induced by the MDI-3, as shown in Figure 1(b), restricts soft melting; thus, the soft segment melting

---

**Figure 3.** IR spectra of the (a) I1 and (b) I2 series.

**Figure 4.** DSC thermograms of the (a) I1 and (b) I2 series.
3.4. Viscosity

The viscosity of the I1 and I2 series is investigated at five different concentrations (m/v, 0.25, 0.5, 1, 2, and 4%) in Figure 5. The viscosity of the I1 and I2 series increases up to the third sample (I1-3 and I2-3) and then decreases with further increase in the isopropyl content. The branched isopropyl group is responsible for the viscosity increase up to the third sample by intermingling and dragging each other. However, PU chains are pulled apart by the repulsion of isopropyl groups, and the viscosity decreases if isopropyl groups are highly grafted to PU chains. Such trends continue for the five different concentrations and for both the I1 and I2 series. Therefore, the viscosity result suggests that the isopropyl groups are coupled to the PU chains as designed.
3.5. Tensile Property

The tensile properties of PU, depending on the isopropyl and hard segment contents, are shown in Figure 6. The breaking stress substantially increases with the increase of isopropyl content for both the I1 and I2 series. For example, the breaking stress of the I1 series increases from only 17 MPa for I1-1, to 42 MPa for I1-2, and 59 MPa for I1-5, and that of I2 series increases from 28 MPa for I2-1, to 38 MPa for I2-2, and 45 MPa for I2-5. As already mentioned in the cross-link density section, the lateral cross-linking induced by the MDI-3, as the isopropyl content increases, is responsible for the significant increase in the breaking stress at high isopropyl content. The strain at break remains similar at approximately 2000%, although the isopropyl content is raised for both the I1 and I2 series. For example, the strain at break of the I1 series changes from 1805% for I1-1 to 2257% for I1-3 and 2128% for I1-5. In the I2 series, I2-1 changes from 2045% to 1975% for I2-3 and 2537% for I2-5. It is interesting that the tensile strain is not significantly reduced although tensile stress increases because the two measures have an inverse relationship. The breaking stresses of the previously investigated glycerol and pentaerythritol cross-linked PUs are only 12 MPa and 17 MPa, respectively, with strains at break of 1100% and 1200%, respectively. Compared to these two cross-linked PUs, the PU with the grafted isopropyl group demonstrates better breaking stress and strain at break, although a cross-linking agent is not used. Therefore, the tensile properties of PU are not weakened, although the branched isopropyl group is laterally attached to PU chains.

3.6. Shape Memory Property

The shape memory test was repeated under cyclic stretch-release conditions at a temperature range (between −25 and 45 °C) based on soft segment T_m. Because the shape memory properties around the room temperature were to be compared with the previous PUs, the shape memory test was conducted around the soft segment T_m. Because the linear PU does show a clear soft segment melting peak at approximately 15 °C in Figure 4, it is selected as the reference temperature for shape memory test although the melting peak disappears as the isopropyl content increases. Hard segments retain the distorted shape below T_m and recover the original shape above T_m. In contrast, soft segments absorb the applied tensile stress by unfolding the entangled chains. However, permanent deformation of the hard segment domain by repetitive stress is known to limit shape recovery. In Figure 7(a), the shape memory tests of the I1 and I2 series show that shape recovery remains high although isopropyl content is raised. For example, the shape recovery of I1-1 changes from 88% to 89% for I1-3 and 90% for I1-5. And the shape recovery of I2-1 changes from 92% to 89% for I2-3 and 83% for I2-5. Shape recovery tests demonstrate that the PU with isopropyl groups maintains high shape recovery under the test conditions. Unexpectedly, shape retention also remains high although isopropyl group is attached in Figure 7(b). For example, the shape retention of I1-1 (98%) changes to 93% for I1-3 and 93% for I1-5, and that of I2-1 (94%) changes to 93% for I2-3 and 92% for I2-5. The high shape retention is related to the reduced molecular interactions by isopropyl group because the extended shape is better preserved at −25 °C when the restoring force originating from molecular interaction is reduced. As shown in Figure 7, a significant difference is not observed between I1 and I2 series, suggesting that the hard segment content does not play an important role.

Representative samples, differing in hard segment and isopropyl content, from the I1 and I2 series (I1-1, I1-5, and I2-3) were selected to compare their shape recovery at freezing temperature. The circular samples were bound and stored in a temperature-controlled chamber (−30 °C) for 3 hours before testing and were allowed to return to their linear shape while increasing the surrounding temperature. The resulting pictures are shown in Figure 8. All of the samples does not fully recover their original linear shape up

![Figure 7](image-url)
to ~10 °C, but the full recovery temperature is dependent on the sample structure and the isopropyl content: −5 °C for I1-5, 0 °C for I2-3, and 5 °C for I1-1. Therefore, the full recovery temperature could be lowered if the isopropyl content was raised. The laterally protruded isopropyl group, as depicted in Figure 9, is responsible for the disruption of molecular interaction between PU chains and the low temperature flexibility. This low temperature recovery experiment demonstrates the importance of isopropyl content in low temperature recovery. Considering the improvement in the low temperature recovery by adopting a branched isopropyl group, there are still a lot of rooms for the modification of PU with the grafted functional groups for special effect such as photoluminescence, electroluminescence, antistatic, and antiseptic property.

4. Conclusion

The PU grafted with the isopropyl group was characterized and tested with respect to tensile properties, shape memory, and low temperature recovery. The breaking tensile stress significantly increases with the increase of isopropyl content. Similarly, shape recovery and shape retention tests also show excellent results. The lateral linking of the isopropyl groups is responsible for the interesting tensile and shape memory results. The shape recovery test performed at low temperature demonstrates that the isopropyl group plays an important role in recovering the original shape at subzero temperatures.

Acknowledgements: This study was supported by the R&D Center for Valuable Recycling (Global-Top Environmental Technology Development Program) funded by the Ministry of Environment (Project No.: GT-11-C-01-290-0).

References

13. W. Lequieu and F. E. Du Preez, “Segmented Polymer Networks Based on Poly(N-isopropyl acrylamide) and...
Poly(tetrahydrofuran) as Polymer Membranes with Thermo Responsive Permeability", Polymer, 2004, 45, 749-757.


