The Effect of the Diphenylamino Side Group on the Reduction of the Molecular Interaction between Polyurethane Copolymer Chains

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ABSTRACT: Polyurethane (PU) with a diphenylamino side group is tested for low temperature flexibility at -30°C and compared with a linear PU without the diphenylamino side group. The PU is composed of 4,4'-methylenebis(phenylisocyanate) (MDI), poly(tetramethyleneglycol) (PTMG), 1,4-butanediol (BD), and the diphenylamino group that is grafted to PU chains by a second MDI. The mechanical and shape memory properties of these two types of PU, which differ in the PTMG and the diphenylamino group content, are compared. In the best case, a 306% increase in the maximum stress compared with the linear polymer is attained with a little decrease in the strain. Shape recovery at 45°C increases to 94% and remains $\sim$90% after four cyclic tests. Low temperature flexibility can be improved by increasing the diphenylamino content. The PU with a diphenylamino side group demonstrates the low temperature flexibility at -30°C, whereas the linear PU must be warmed to room temperature to attain the same degree of flexibility. The exceptional low temperature flexibility is analyzed and is discussed together with the experimental data. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

The molecular interactions between polyurethane (PU) chains play a key role in its exceptional characteristics, such as excellent and reproducible shape recovery, control over the glass transition temperature (T_g) and melting temperature (T_m), and high tensile strength.[1–3] The molecular interactions can be controlled if a pendant side group with a different bulkiness or ionic charge is attached and intervenes in the molecular interaction.[4,5] Meanwhile, polymer grafting technology has been extensively used to attach pendant functional groups to the polymer chain and to crosslink other chains.[6,7] The grafting technology has also been used to develop functional PU with magnetic properties, metal ion sensing, low temperature flexibility, temperature or pH-sensing, or electric conductivity.[8,9] In our previous research, crosslinking of PU with agents such as glycerol, pentaerythritol, and dextrin has already been investigated to improve the tensile strength and shape memory effect.[10,11] Alternatively, flexible crosslinking by polyethyleneglycol (PEG) was devised to achieve both high mechanical strength and strain.[12,13] This crosslinking methodology represented the PU grafting method that we employ in this work. When the above methods are combined, the molecular interactions between PUs can be controlled if a proper functional group is attached to PU by the previous grafting technology. As a method for grafting PU, allophanate bonding was employed in this work due to certain advantages such as more available linking sites, higher reactivity, and ease of reaction conditions.[14]

The diphenylamino group was employed as a pendant side group to hinder interchain interactions and to improve solubility in an organic solvent during the synthesis of poly(amide-imide) due to its bulkiness and rigid structure.[15] The diphenylamino group is also used as an electron donating substituent in fluorescent charge-transfer dyes to control the wavelength shift[16] or as a bulky and hole-transporting side group in an organic light emitter.[17] Therefore, the diphenylamino group has been chosen as a bulky and rigid moiety in the design of special performance polymer and organic dyes. It will be of value to evaluate diphenylamino as a side group of PU and to determine its contribution to shape recovery under freezing conditions. Because polymers lose flexibility and become brittle at subzero temperature, low temperature flexibility is necessary for the products such as survival suits, tent, flexible hose, weather balloon, and outdoor sports wear. In this

Table I. Composition of the PU

Sample code	Composition (mmole)				
	MDI-1	PTMG	BD	MDI-2	Diphenylamine
P1-1	50	20	30	–	–
P1-2	50	20	30	2.5	1.25
P1-3	50	20	30	5.0	2.5
P1-4	50	20	30	7.5	3.75
P1-5	50	20	30	10	5.0
P2-1	50	17.5	32.5	–	–
P2-2	50	17.5	32.5	2.5	1.25
P2-3	50	17.5	32.5	5.0	2.5
P2-4	50	17.5	32.5	7.5	3.75
P2-5	50	17.5	32.5	10	5.0

investigation, the impact of the diphenylamino group linked to PU by allophanate linking is investigated with respect to the mechanical and shape recovery properties of PU. The reason for the extraordinary low temperature flexibility is discussed as well.

EXPERIMENTAL

Materials

Poly(tetramethyleneglycol) (PTMG; M_n = 2000 g/mol; Sigma-Aldrich, USA), 4,4′-diphenylmethanediisocyanate (MDI; Junsei Chemical, Japan), and 1,4-butanediol (BD; Junsei Chemical, Japan) were dried overnight under high vacuum. Diphenylamine was obtained from Sigma-Aldrich (USA). N, N-Dimethylformamide (DMF; Duksan Chemical, Korea) was distilled over CaH$_2$ before use.

Synthesis of Polyurethane

To prepare the prepolymer, a mixture of MDI and PTMG, as specified in Table I, was stirred at 50°C for 3 h in a 500-mL four-neck flat-bottomed flask with a condenser, mechanical stirrer, and nitrogen blanket. 1,4-Butanediol, dissolved in 20 mL of DMF, was added to the flask as a chain extender, and allowed to react for another hour under the same conditions. In this step, the viscosity increase of the reaction mixture generally reduced the revolution speed of the mechanical stirrer. Subsequently, a second volume of MDI for allophanate bonding in 20 mL of DMF was added to the above reaction mixture, and the reaction progressed for 40 min at 50°C. Finally, an equivalent amount of diphenylamine in 100 mL of DMF was slowly added with a pressure-equalized addition funnel over 30 min, and the mixture was stirred under the same conditions for 2 h. The final reaction mixture was precipitated in distilled water, and sequentially washed with distilled water until clearness, ethanol, and chloroform to remove any remaining reactants. The remaining solvent on PU was removed by suction filtration over a filter paper, and the filtered PU was completely dried in an oven at 60°C for a week. The specific mole ratios of the reaction mixture are summarized in Table I.

Crosslink Density

A specimen (20 × 20 × 1 mm^3) with a known weight (m_1) was swollen in 50 mL of toluene in a closed cap bottle for 24 h, 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) of the swollen specimen, averaged from five swelling experiments, was calculated from the weight difference between the swollen polymer (m_2) and the dry polymer (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 swollen polymer (v_1) was calculated using the equation, $V_p/(V_s + V_p)$. The derivation of the crosslink density is described in the results and discussion sections.

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 at 60°C for 60 h to fabricate a thin film. The specimen was made from the thin film according to the ASTM D638 specification. The tensile strength was measured according to 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 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 out following a previously described method.[13,14]

General Analysis

A differential scanning calorimeter (DSC-2010, TA instrument) was used to detect soft segment melting. A specimen (5 mg), after equilibrating at 40°C for 5 min and cooling to −50°C at −10°C/min, was warmed to 250°C at 10°C/min for heating scan, and was cooled at −10°C/min for cooling scan after 5-min interval. A second heating scan to 250°C at 10°C/min, after a 5-min interval at −50°C, was selected for a comparison of the transition temperature range. An FTIR spectrometer (JASCO 300E), 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/s scan speed. A diode array UV-V is
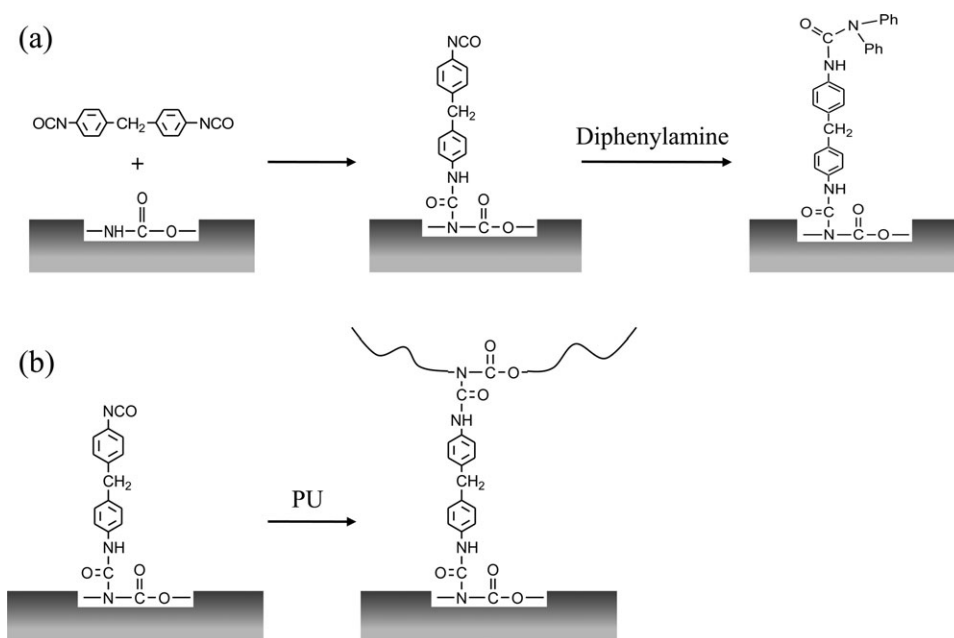
Figure 1. (a) Grafting of a diphenylamino side group to PU and (b) crosslinking of two PUs.

spectrometer (HP 8453) was used for scanning the PU solution in DMF in the range of 200–800 nm at 25°C. The absolute viscosity of PU dissolved in DMF was measured with a vibrating viscometer (AND SV-10) at 25°C and was determined from an average of five tests at five different concentrations (m/v, 0.25, 0.5, 1, 2, and 4 wt %). Low temperature flexibility test was carried out in a cold chamber (Jisco J-RHC2) and was recorded by a video camera (SONY HDR series). As for the determination of diphenylamino group loading, a PU solution (1 g dissolved in 20 mL of DMF) was diluted with 10 mL of isopropanol and titrated by a 0.1M HCl solution (50/50, water/isopropanol) using a drop of phenolphthalein indicator in ethanol. The blank titration value for the PU without diphenylamino group (P1-1 and P2-1) was subtracted from the titration result to get the net value. The diphenylamino content of the PU (mmole/g) was calculated from the average of five titrations. ^{1}H-NMR (CF₃COOD) spectrum of P1-5 was taken by a Varian-Unity Inova 500 NB spectrometer (500 MHz): 1.90 ppm (C**H₂**CH₂CH₂CH₂O)$_n$, 2.15 ppm CH₂C**H₂**CH₂CH₂O, 3.88 ppm (CH₂CH₂C**H₂**CH₂O)$_n$, 4.10 ppm CH₂CH₂CH₂C**H₂**O, 4.48 ppm (PhC**H₂**Ph), 7.14–7.50 ppm (MDI aromatic and diphenyl), and 8.4 ppm (N**H**C=O). The NMR spectrum of P1-5 agreed with the proposed structure and that of P2-5 also showed the similar shape as the aforementioned one.

RESULTS AND DISCUSSION

Synthesis
The PU was synthesized based on previous methods,[13,14] in which MDI and PTMG were the hard and soft segments, respectively, and BD was used as a chain extender. In this investigation, the diphenylamino group was linked as a side group via allophanate bonding to improve low temperature flexibility under extremely low temperature conditions due to the molecular repulsion between the rigid diphenylamino groups. The PU

grafting with diisocyanate, an allophanate bonding, has already been well researched and can be carried out under very mild reaction conditions.[14,18–22] In this experiment, the use of a catalyst such as dibutyl tin laurate (DBTL) or triethylamine was not necessary because the grafting reaction by MDI-2 was irreversible and fast enough to finish without catalysis in 40 min. If the MDI-2 reaction time was extended, more MDI-2 was involved in the crosslinking of PUs and the grafting could not proceed due to the aggregation of the crosslinked PUs. Therefore, the protruded diphenylamino group was expected to disrupt and reduce the hydrogen bonding and dipole–dipole interactions between PU chains and to improve the rotational and motional freedom of PU at subzero temperatures. The unreacted reagents after the synthesis could be removed by thorough washing in different solvents (water, ethanol, and chloroform). The grafting steps of the diphenylamino group to PU are shown in Figure 1(a). Quantitative analysis of the weakly basic diphenylamino group was accomplished by a strong acid (HCl) titration, and the diphenylamino group content determined by titration agreed well with the theoretical expectation for the entire PUs; this result suggests that the diphenylamino group was almost quantitatively attached to the PU chains for both P1 and P2 series (Figure 2).

In Table I, two equivalents of MDI-2 compared with diphenylamine was used to completely graft diphenylamino group to PU, and the excess MDI-2 could crosslink the PU chains as shown in Figure 1(b). To check the crosslinking effect by some of MDI-2, the crosslink density was calculated from a polymer swelling experiment to determine whether the degree of crosslinking was increased by MDI-2. The crosslink density was determined by the following method. The interaction parameter, χ, between toluene and the polymer was found from the following expression[21]:
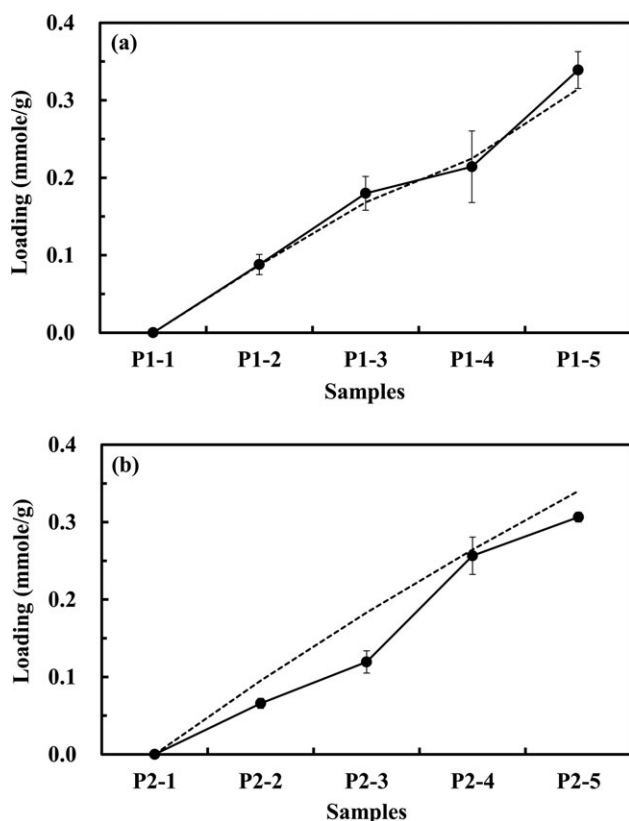
Figure 2. Determination of diphenylamino loading of the (a) P1 and (b) P2 series by titration (the dashed line shows the theoretical loading).

$$\chi = (\delta_2 - \delta_1)^2 V_1 / RT \quad (1)$$

where δ_1 and δ_2 = solubility parameter of solvent and polymer; V_1 = molar volume of solvent; R = gas constant; and T = absolute temperature

The solubility parameters of toluene (δ_1) and PU (δ_2) were 18.2 and 20.5 MPa$^{1/2}$, respectively.[24,25] The degree of crosslinking was calculated from the Flory–Rehner eq. (2):

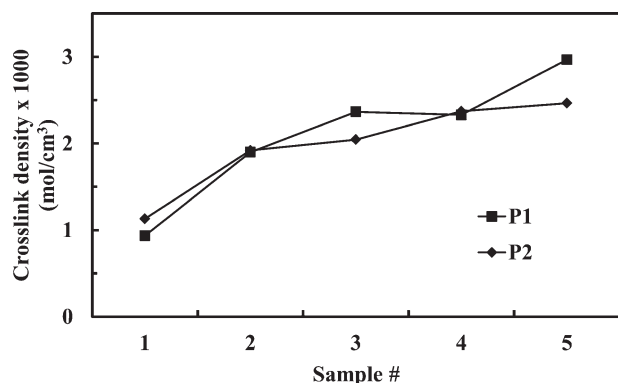$$-[\ln(1 - v_2) + v_2 + \chi v_2^2] = V_1 n [v_2^{1/3} - 1/2v_2] \quad (2)$$

Figure 3. Crosslink density profiles of the P1 and P2 series.

Table II. Crosslink Density of the PU from the Swelling Experiment

Sample code	$^a\rho$ (g/cm^3)	^bV_p (cm^3)	$^cV_2$	$^d10^3n$ (mole/cm^3)
P1-1	1.111	0.4673	0.3487	0.9333
P1-2	1.098	0.2002	0.4618	1.898
P1-3	1.052	0.1963	0.5002	2.364
P1-4	1.111	0.2130	0.4975	2.329
P1-5	1.020	0.2417	0.5412	2.966
P2-1	1.030	0.3498	0.3772	1.129
P2-2	1.111	0.1890	0.4638	1.921
P2-3	1.098	0.1911	0.4746	2.044
P2-4	1.063	0.1441	0.5008	2.372
P2-5	1.020	0.2221	0.5076	2.464

$^a\rho$ is density.
^bV_p is polymer volume.
$^cV_2$ is volume fraction of polymer.
^dn is crosslink density.

where v_2 = volume fraction of polymer in the swollen mass; χ = interaction parameter; and n = crosslink density.

The crosslink density increased with the increase of sample number (Figure 3 and Table II), which was not related to the attached diphenylamino group but was due to the crosslinking effect of MDI-2, as explained in the literature.[26] The crosslinking effect is advantageous, as demonstrated in a later section, in improving the tensile strength of PU—if PU is lightly crosslinked by MDI-2 and has good solubility in DMF for casting.

IR, UV, and Thermal Analysis

IR spectra of selected P1 series (P1-1 and P1-5) and P2 series (P2-1 and P2-5) are compared in Figure 4(a). The effect of grafting the diphenylamino group can be observed by the new C—H bending peak at ~1500 cm^{-1} and the new urea C=O peak at ~1640 cm^{-1}. These peaks originate from the grafting of diphenylamino group and appear as the diphenylamino content increases. Intermolecular attraction between hard segments, such as hydrogen bonding and dipole–dipole interactions, can be deduced from the IR spectra, where the bonded C=O stretching vibration appeared at ~1700 cm^{-1}, which is slightly lower than the free carbonyl group that appears at approximately 1725 cm^{-1}.[27,28] As the diphenylamino content increased, the bonded carbonyl peak of the P1 and the P2 series decreased compared with that of the free carbonyl; this results suggests that the molecular interaction between PUs was interrupted by the diphenylamino group. The carbonyl peak change can be quantified by comparing the degree of phase separation (DPS) that implies the phase separation of hard and soft segments and can be 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.[12] The DPS of the P1 series decreased from P1-1 (0.587) to P1-5 (0.547), and that of the P2 series also showed a similar trend from P2-1(0.607) to P2-5 (0.577). Therefore, the diphenylamino side group in the P1 and the P2 series reduced the attraction between hard segments because the diphenylamino group containing the rigid
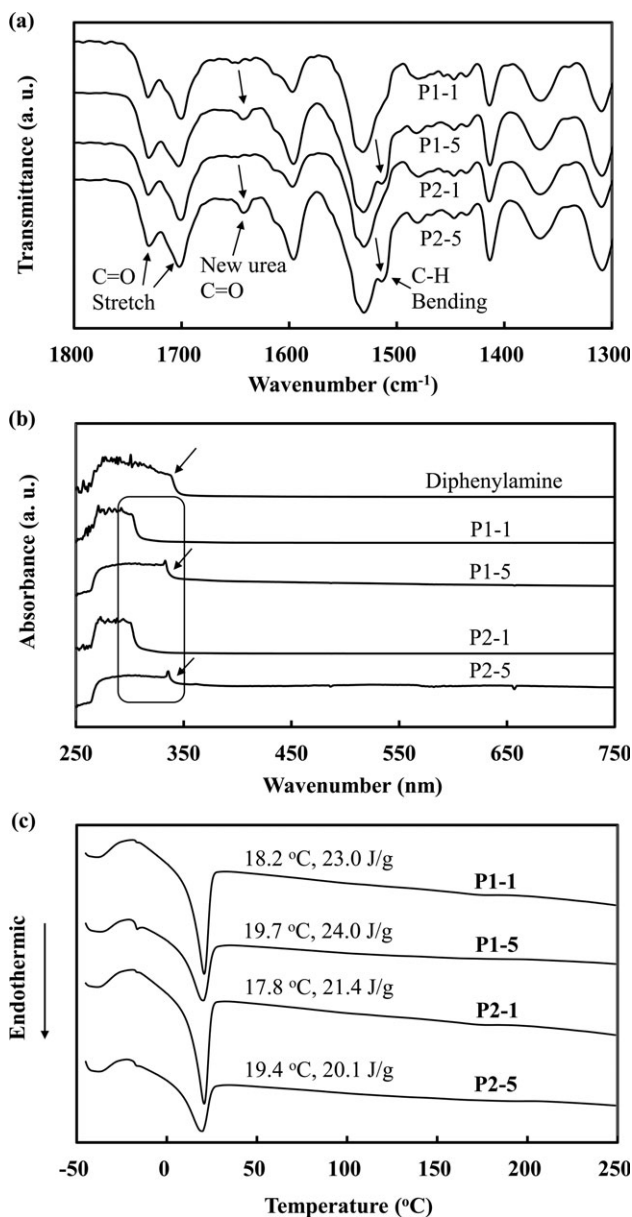
Figure 4. (a) IR spectra, (b) UV-VIS spectra, and (c) DSC profiles of the P1 and P2 series.

In Figure 4(c), the effects of diphenylamino group and the hard segment content on soft segment melting were evaluated using DSC data for the selected P1 and P2 series (P1-1, P1-5, P2-1, and P2-5). Because the T_g of the soft segment (PTMG) was too low to detect, the soft segment T_m was investigated by DSC. The soft segment T_m and transition enthalpy (ΔH) of the P1 series slightly increased from 18.2°C and 23.0 J/g for P1-1 to 19.7°C and 24.0 J/g for P1-5 due to the restricted rotation of the soft segment by the rigid diphenylamino group attached to PU chains. The T_m and ΔH of the P2-5 also showed a similar trend as those of the P1-5. Therefore, the soft segment melting was slightly hindered by the attached diphenylamino group; this result is in accordance with the IR spectra, where the molecular interaction between carbonyl groups was reduced by the attached diphenylamino group. The soft segment melting temperature from the DSC results is important for determining the reference temperature for the shape memory test, and the thermal analysis result showed that the soft segment melting was affected by the attached diphenylamino group.

Viscosity

The viscosity of the P1 and the P2 series was investigated at five different concentrations (m/v, 0.25, 0.5, 1, 2, and 4%), as shown in Figure 5. The viscosity difference in the P1 and the P2 series, if compared at 4%, initially increased and then decreased following an increase in the diphenylamino
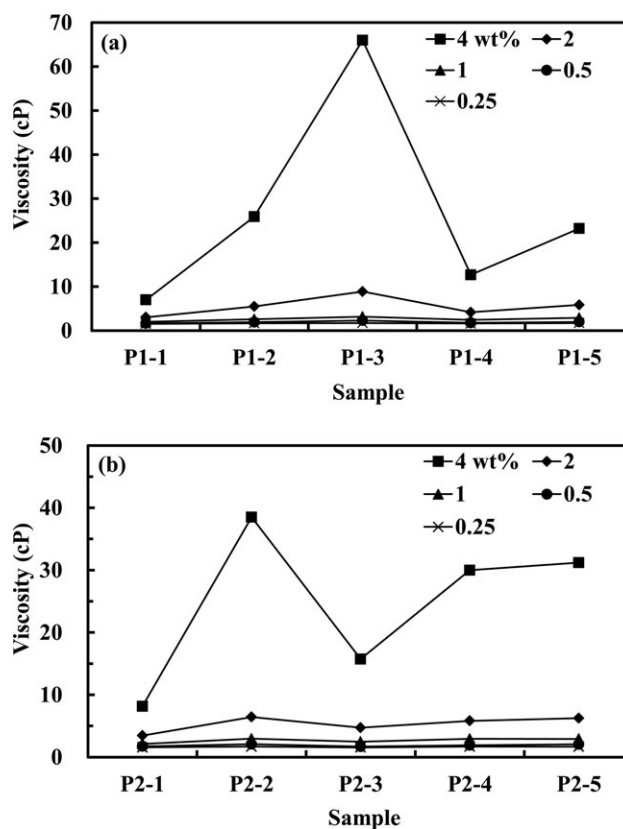
phenyl ring and the branched structure is suited for minimizing the impact of hydrogen bonding and dipole−dipole interactions between hard segments.

The UV-VIS spectra of the P1 and the P2 series were compared with that of diphenylamine in Figure 4(b), in which the absorption band of the linear P1-1 and P2-1 originated from the aromatic absorption of MDI unit in PU. The UV-VIS spectra of P1-5 and P2-5 were different from those of P1-1 and P2-1, in that the new absorption band between 305 and 330 nm appeared after the diphenylamino side group was attached. The new absorption band corresponds to the diphenylamino group. The UV-VIS spectra clearly demonstrated the presence of the diphenylamino side group in the P1-5 and the P2-5.

Figure 5. Viscosity vs. concentration profiles of the (a) P1 and (b) P2 series.
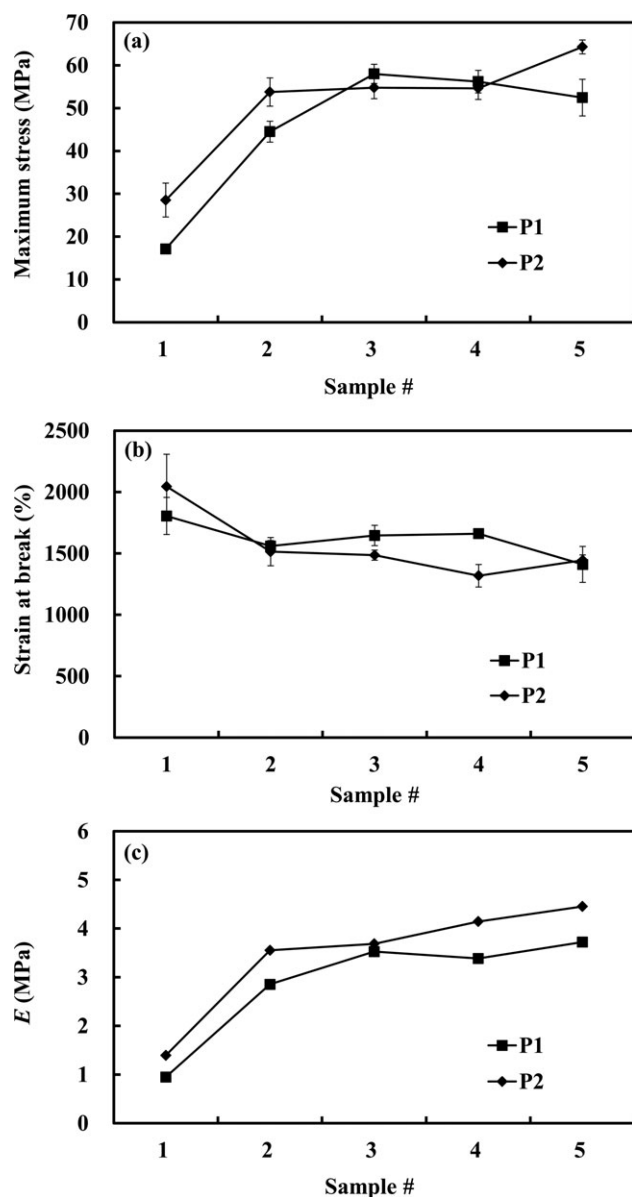
Figure 6. Profiles of (a) maximum stress, (b) strain at break, and (c) elastic modulus (*E*) of the P1 and P2 series.

group content. The rigid and branched structure of the diphenylamino group was responsible for the initial viscosity increase by intermingling and dragging. However, PU chains were pulled apart by the repulsion of diphenylamino groups, and the viscosity decreased if diphenylamino groups were highly attached to PU chains. Such trends continued for both the P1 and the P2 series. Therefore, the viscosity difference suggests that the diphenylamino groups are coupled to the PU chains as designed and can control the entanglement of PU chains; these effects result in better flow at high concentrations.

Tensile Property

The tensile properties of PU, as a function of the diphenylamino and hard segment content, are shown in Figure 6.
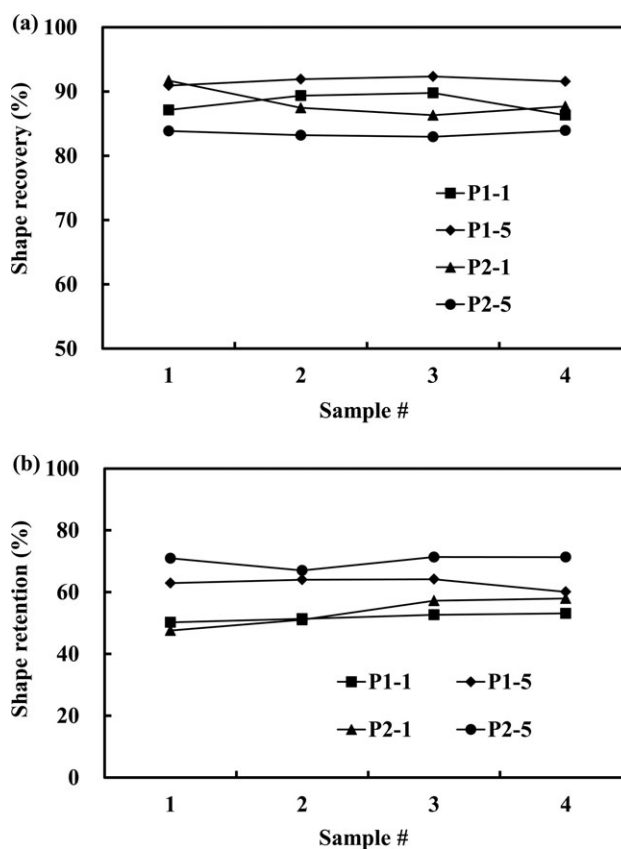

Figure 7. (a) Shape recovery and (b) shape retention profiles of the P1 and P2 series.

Maximum stress gradually increased with increasing diphenylamino content for both the P1 and the P2 series. For example, the maximum stress of the P1 series increased from only 17 MPa for P1-1 to 58 MPa for P1-3 and 53 MPa for P1-5, and the P2 series changed from 28 MPa for P2-1 to 55 MPa for P2-3 and 64 MPa for P2-5. The crosslinking by the excess MDI-2 was responsible for the increase in the maximum stress with the

Table III. Shape Memory Properties

Sample code	Shape memory (%)[a]	
	Recovery	Retention
P1-1	87	50
P1-2	94	55
P1-3	89	48
P1-4	87	57
P1-5	91	62
P2-1	92	48
P2-2	89	70
P2-3	95	59
P2-4	87	62
P2-5	84	70

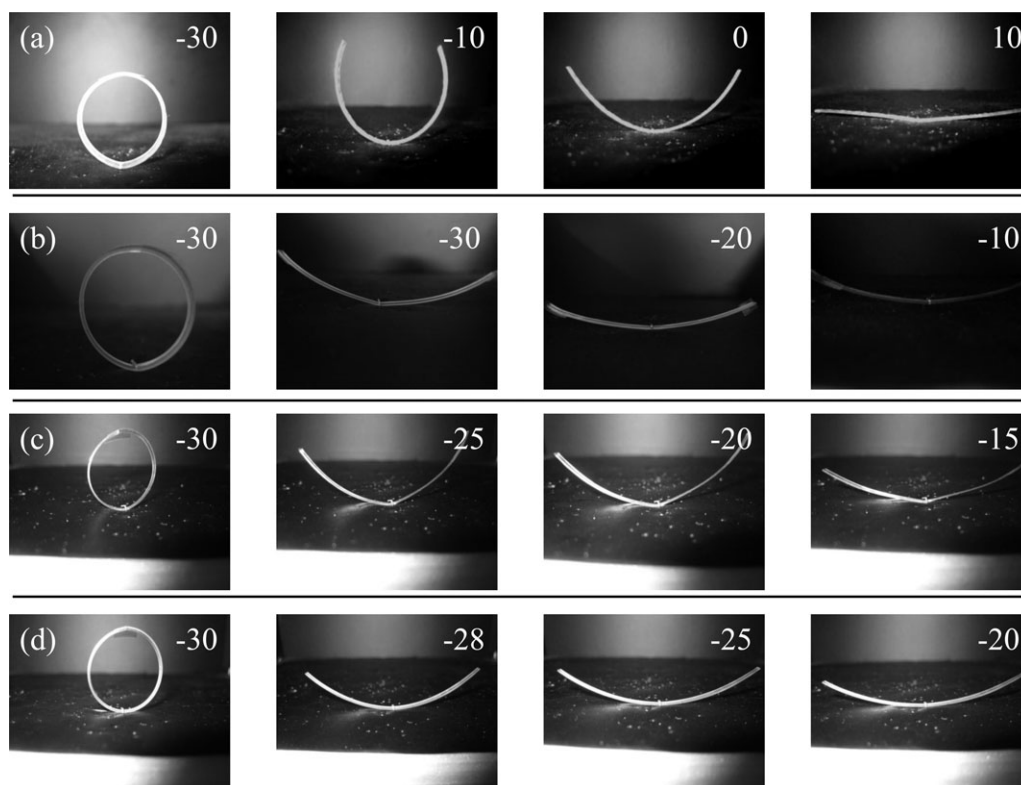[a]First cycle shape memory results.

Figure 8. Low temperature flexibility of (a) P2-1 (control), (b) P1-5, (c) P2-3, and (d) P2-5, where the number designates the surrounding temperature.

increase in the sample number. The strain at the break slightly decreased with an increase in the sample number for both the P1 and the P2 series. For example, the strain at the break of the P1 series changed from 1805% for P1-1 to 1410% for P1-5. In the P2 series, P2-1 decreased from 2045% to 1444% for P2-5. The crosslinking by the MDI-2 could bind the PU chains and decreased the tensile strain with the increase of sample number, because the MDI-2 content increased with the increase of sample number. The tensile strain results are uncommon in the crosslinked structure, considering the high maximum tensile stress. The elastic modulus from the stress and strain results increased for both P1 and P2 series with the increase of sample number as shown in Figure 6(c), in which the elastic modulus increase was also due to the crosslinking by the MDI-2. The maximum stress and strain at the break results are significantly improved compared with the previous crosslinked PUs.[16,17] Therefore, the tensile properties of the PU maintained a high stress and strain, even though the diphenylamino side group was attached.

Shape Memory and Low Temperature Flexibility

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. A hard segment works to retain a distorted shape below T_m and to recover the original shape above T_m. In contrast, the soft segment absorbs the applied tensile stress by

unfolding the entangled chains, but permanent deformation in the hard segment domain by repetitive stress is known to limit shape recovery. In Figure 7(a), the cyclic shape memory tests of the selected P1 and the P2 series demonstrated that shape recovery was reproducible after four test cycles. Shape recovery of P1 and P2 series was ∼90% and remained almost same after four cyclic tests. For example, shape recovery of P1-5 changed from 90% in the first test to 92% in the fourth test, and shape recovery of P2-5 was slightly increased from 83% in the first test to 84% in the fourth test. The shape recovery test demonstrated that PU with a diphenylamino side group maintained a high shape recovery and its reliability under the test conditions. Shape retention was also reproducible after the four test cycles
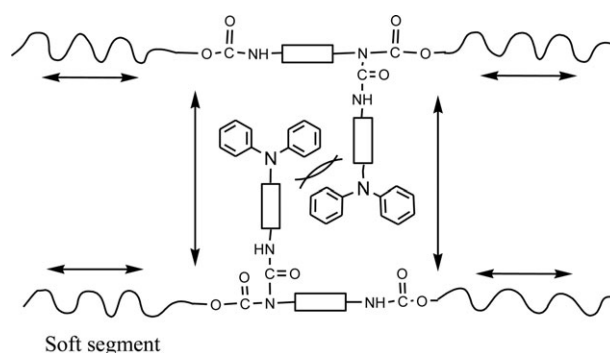

Figure 9. Schematic drawing of the repulsion between PU chains by the diphenylamino side group (the rectangle represents MDI).

and remained between 50 and 70% after the diphenylamino group was attached [Figure 7(b)]. For example, the shape retention of P1-1 (50%) increased to 62% for P1-5, and that of P2-1 (48%) also increased to 70% for P2-5. The shape retention was low compared with the shape recovery, because the diphenylamino side group reduced the molecular interaction between PU chains and resulted in the high shape recovery of PU chains even at −25°C (the shape retention test temperature). The high shape recovery and the reduced shape retention were obtained compared with the previous PUs after the diphenylamino group was attached. After the four test cycles, the PU specimen remained flexible and did not show any apparent damage from the repetitive tests. The shape recovery and retention of the P1 and the P2 series are compared in Table III, where a significant difference in the shape recovery and retention results between the P1 and the P2 series are not observed; this result suggests that the hard segment content does not play an important role in the shape memory effect.

Representative samples (P2-1 (control), P1-5, P2-3, and P2-5) were selected to compare their low temperature flexibility. The circular samples were bound and stored in a temperature-controlled chamber for 3 h and were allowed to restore their original linear shape while the surrounding temperature was increased. The resulting pictures are shown in Figure 8. The samples with the diphenylamino side group (P1-5, P2-3, and P2-5) instantly opened even at −30°C, but the linear sample (P2-1) had to be heated above 0°C to open in a similar fashion as the PUs with the diphenylamino side group. The low temperature flexibility test was stopped if the PU did not move at all. The stopping temperature for each PU (10°C for P2-1, −20°C for P1-5, −15°C for P2-3, and −20°C for P2-5) suggests that the low temperature flexibility depends on the diphenylamino group content. The repulsion by the rigid and bulky diphenylamino side groups and the reduced molecular interaction between PU chains were responsible for the decrease in the stopping temperature and the better flexibility under freezing conditions (Figure 9). The structural advantage of diphenylamino group is clear, considering the fact that the low temperature flexibility appears only at 0°C if a flexible n-butyl group is grafted to the PU.[29] Although tertiary butyl or isopropyl group was tested as a side group to poly(acrylate) polymers to affect the thermal and mechanical properties,[30] the application of diphenylamino side group to the low temperature flexibility is new to PU and is mechanistically different from the commercial PU with low temperature flexibility. The subzero temperature flexibility experiment clearly demonstrated that the diphenylamino group plays a decisive role in low temperature recovery. The PU with the diphenylamino side group, due to its excellent flexibility at very low temperatures, has potential applications in items used at cold temperatures such as for seals, gaskets, textiles, tubing, machinery parts, and packaging.

CONCLUSIONS

PU with a diphenylamino side group was synthesized by an allophanate grafting method and characterized and tested for tensile properties, shape memory, and low temperature flexibility. The maximum stress improved, and the strain at break slightly decreased with the increase in the MDI-2 content. The shape recovery and shape retention tests also showed excellent and reproducible results. Low temperature flexibility at subzero temperatures was dependent on the diphenylamino group content. Therefore, low temperature tests demonstrated that the diphenylamino side group played an important role in maintaining the flexibility at low temperatures.

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