

Blocking of Soft Segments with Different Chain Lengths and Its Impact on the Shape Memory Property of Polyurethane Copolymer

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ABSTRACT: The arrangements, whether block or random type, of the soft segments of polyurethane block copolymers prepared with MDI and two kinds of poly(tetramethylene glycol) (PTMG; MW of 1000 or 2000) in various ratios were compared for possible effects on the physical properties of the copolymers. A long soft segment, PTMG-2000, was superior in all mechanical properties (strain, stress, and modulus) because a long chain length could provide more motional freedom than a short one (PTMG-1000) could and therefore was helpful in forming strong interchain attractions among hard segments. Inclusion of more PTMG-2000 led to a lower T_g and a peak shift in infrared spectra. The

arrangement of two soft segments in a block-type copolymer, a key finding in this study, was controlled by separately synthesizing two prepolymers, each with a different chain length, and connecting two prepolymers in a second step. Random-type copolymers prepared for purposes of comparison were allowed to react with two PTMGs in one step. Two types of copolymers were compared, and the reason for the differences in the shape memory property are discussed. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 1435–1441, 2007

Key words: polyurethane block copolymer; shape memory

INTRODUCTION

Material that can be restored to its original shape after distortion by an external stimulus such as heating, electrical current, or photo energy is called a shape memory material. This designation covers a wide range of materials (metal, ceramic, and polymer). In particular, the unique properties and potential applications of shape memory polymers (SMPs) in medical, electrical, and fabric fields have drawn broad attention, and polyurethane is one of the intensively researched SMP candidates.^{1–3} Polyurethane SMP, composed of hard and soft segments, forms hard and soft domains because of the incompatible nature of each segment.⁴ Hard segments binding each other through such interactions as hydrogen bonding, dipole–dipole interaction, and van der Waals forces work as physical crosslinking points and contribute to restoring the original shape after distortion.⁵ Flexi-

ble soft segments absorb external stress during elongation or compression and decide the phase-transition temperature. Accomplishment of shape retention and recovery by the harmonic motion of hard and soft segments result in reversible shape conversion around the phase-transition temperature. The shape memory properties of some polyurethanes have already been reported: (1) SMP with poly(ethylene adipate) as the soft segment was analyzed at thermodynamic and mechanical points,⁶ and (2) polyurethane SMP with a different modulus around the T_g was studied.⁷ But problems such as permanent deformation of the hard segment and rigidity of the soft segment after repetitive shape recovery cycles still remain to be solved. Higher shape recovery ratio, better shape recovery speed, and a narrow transition temperature range compared to those of a shape memory metal are required for use as a mechanical actuator.⁸ In this study, the arrangement and composition of two poly(tetramethylene glycol)s (PTMGs) with different chain lengths as the soft segment were varied, and the resultant mechanical and shape memory properties were investigated with the help of analytical instruments [infrared, X-ray diffraction (XRD), gel permeation chromatography, differential scanning calorimetry (DSC), and universal testing machine].

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EXPERIMENTAL

Materials and synthesis

Poly(tetramethylene glycol) (PTMG) from either Aldrich Chemical, Milwaukee, WI (MW = 1000 g/mol) or Cheil Chemical, Kumi, Korea (MW = 2000 g/mol), and 4,4'-methylene bis(phenyl isocyanate) (MDI) from TCI were dried under high vacuum (0.1 torr) overnight before use. 1,4-Butanediol (BD) was dried over 4-Å molecular sieve for moisture control. In a four-necked, flat-bottomed flask, a mixture of MDI and PTMG, according to the recipe in Table I, was allowed to react in bulk conditions under nitrogen at 50°C for 1 h to form the prepolymer, followed by chain extension with BD at 70°C for 1 h to obtain the final polyurethane product after drying at 70°C for 24 h. For the synthesis of the block-type copolymer, two reactors were used: prepolymers prepared by the above method from each reactor containing MDI plus PTMG with different chain lengths (PTMG-1000 or PTMG-2000) were linked with BD. Every reactant was mixed in a reactor for the synthesis of random-type copolymers. Hard-segment content was controlled to 35 wt % for both types of copolymer. To prepare specimens for the mechanical test, polyurethane copolymer dissolved in *N,N*-dimethylformamide (DMF) was cast into a 1-mm-thick sheet after drying at 70°C for 60 h.

Molecular weight and viscosity

A gel permeation chromatographer (Waters 600E) equipped with a μ -styragel column and a reflective index detector (RI 2000) was used to measure the molecular weight of the 0.4 wt % copolymer solution, eluting with THF (HPLC grade). Viscosity was determined by a Vibro viscometer (AND SV-10).

IR spectroscopy

IR spectra were scanned by a Fourier transform infrared (FTIR) spectrophotometer (Bomem MB series 104)

for sheet-type specimens prepared by dissolving in chloroform and subsequent slow drying at room temperature for 12 h.

DSC

A differential scanning calorimeter (TA 2010) was employed to detect the glass-transition temperature (T_g) from the second heating scan from -100°C up to 150°C at a heating rate of $10^\circ\text{C}/\text{min}$ with a 1-min interval between heating and cooling scans.

X-ray diffraction analysis

X-ray diffraction patterns were scanned under conditions of $2\theta = 10^\circ\text{--}30^\circ$ and $5^\circ/\text{min}$ by a wide-angle X-ray diffractometer (WAXD; Rigaku Rint 2000, Cu $K\alpha$ /40 kV/30 mA).

Mechanical and shape memory properties

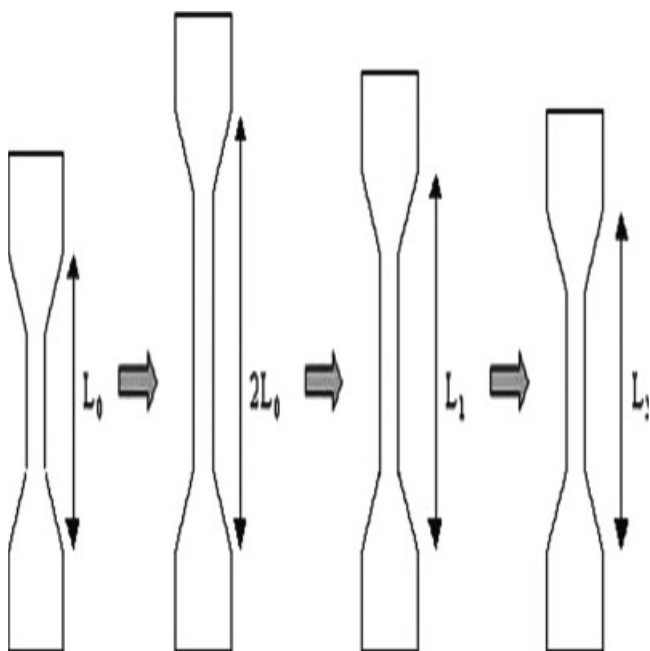
The tensile properties were analyzed by a universal testing machine (Lloyd LR 50K) equipped with a temperature-controlled chamber using dumbbell-type specimens prepared according to ASTM D-638. The experimental conditions were gauge length = 25 mm, crosshead speed = 10 mm/min, and load cell = 2.5 kN. Shape memory tests were carried out following these procedures: L_1 , for shape retention, was the length after drawing the specimen 100% at $T_g + 20^\circ\text{C}$ for 5 min and letting it shrink at $T_g - 20^\circ\text{C}$ for 30 min; L_2 , for shape recovery, was measured after incubating the specimen at $T_g + 20^\circ\text{C}$ for 10 min and cooling at $T_g - 20^\circ\text{C}$ (Scheme I). Measurement was repeated three times, and the shape retention and shape recovery rates could be calculated from L_1 and L_2 by the following equations:

$$\text{Shape retention rate (\%)} = (L_1 - L_0)/L_0 \times 100$$

$$\text{Shape recovery rate (\%)} = (2L_0 - L_2)/L_0 \times 100$$

TABLE I
Composition of Polyurethane Block Copolymer

Sample Code ^a	Mole ratio of soft segments ^b	Reactant (mol)				
		MDI 1	PTMG-1000	MDI 2	PTMG-2000	BD ^c
B1000	10 : 0	5.00	3.00	—	—	2.00
B8020	8 : 2	4.56	2.40	1.14	0.60	2.70
B6535	6.5 : 3.5	4.03	1.95	2.17	1.05	3.20
B5050	5 : 5	3.4	1.50	3.40	1.50	3.80
B3565	3.5 : 6.5	2.52	1.05	4.90	1.95	4.42
B2080	2 : 8	1.60	0.60	6.40	2.40	5.00
B0100	0 : 10	—	—	8.50	3.00	5.50
R3565	3.5 : 6.5	7.42	1.05	—	1.95	4.42
R2080	2 : 8	8.00	0.60	—	2.40	5.00



Scheme 1 Test specimen for shape retention and shape recovery rate (where L_0 = initial specimen length, $2L_0$ = length of L_0 strained 100% above T_g and below T_m , L_1 = deformed length below T_g after load removal, L_2 = final specimen length above T_g and below T_m).

RESULTS AND DISCUSSION

Synthesis

Polyurethane prepared from a combination of MDI, PTMG, and BD according to Table I was designed in two ways, block type or random type. For the block type, one mixture of MDI and PTMG-1000 for short soft segments and another mixture of MDI and PTMG-2000 for long soft segments were allowed to react to form prepolymer in separate reactors, and the prepolymers were mixed in a reactor, followed by chain extension with BD. Therefore, a short soft-segment block and long soft-segment block were connected in a polyurethane copolymer chain. In contrast, for random type, all the reactants were put in a reactor, and polymerization went on without any restriction. The molecular weight of the copolymers ranged around 9000 g/mol. Dependence of mechanical and shape memory properties on the arrangement of soft segment, block and random type, was very intriguing to understanding the shape memory mechanism of the polyurethane material (Table II, Scheme 2).

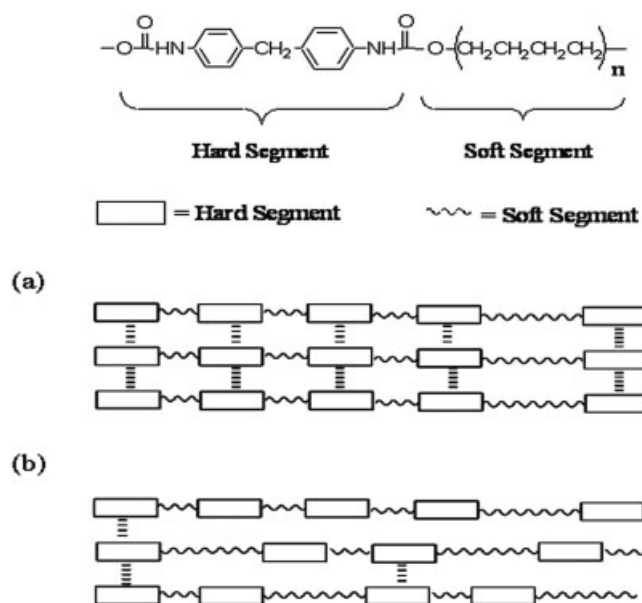
IR analysis

Shape memory polyurethane is known to be phase-separated by hard- and soft-segment domains, with the soft segment responsible for phase transition.^{9,10} As the composition of PTMG-2000 (long soft segment) increased, a shift of the carbonyl group stretching

TABLE II
Molecular Weight and Viscosity
of Polyurethane Block Copolymer

Sample Code	Mn (g/□)	Mw (g/□)	PDI	Viscosity (cP)
B1000	8046	9627	1.20	0.57
B8020	6636	8960	1.35	0.56
B6535	7005	9148	1.31	0.58
B5050	6895	9170	1.33	0.53
B3565	7896	9713	1.23	0.54
B2080	7203	9315	1.29	0.56
B0010	7172	9240	1.29	0.55
R3565	7203	8947	1.24	0.54
R2080	7108	8930	1.26	0.53

peak from 1730 cm^{-1} to 1700 cm^{-1} was observed in the IR spectra (Fig. 1). Strong interchain attraction among hard segments by dipole-dipole interaction and/or hydrogen bonding with an increase in PTMG-2000 content reduced the electron density of carbonyl bonding and made it more stretchable than with an increase in PTMG-1000, resulting in the appearance of a carbonyl stretch peak at lower energy or a lower wave number. Overall, IR spectra supported that the long and flexible soft segment of PTMG-2000 provided more motional and conformational freedom than did the short PTMG-1000 so that the hard segments could better adjust themselves to interact with each other, and clear phase separation between the hard and soft segments occurred. Differences in the arrangement of the soft segments, block or random type, did not seem to affect the general shape of the IR spectra, when compared with the same composition of PTMG-1000 and PTMG-2000 (Fig. 2).



Scheme 2 Stylized view of polyurethane copolymers: (a) block type, (b) random type.

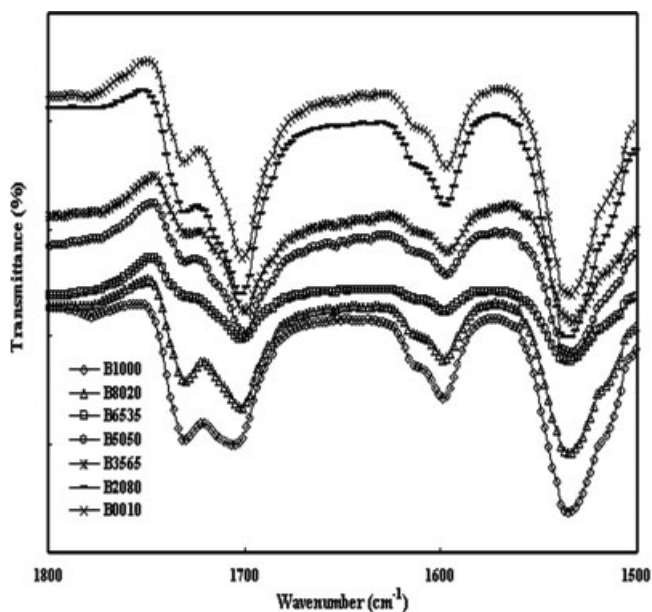


Figure 1 Infrared spectra of block-type polyurethane copolymers.

X-ray diffraction

Strong diffraction peak was observed at $2\theta = 19.5^\circ$ (0.45-nm line) for various soft-segment combinations of polyurethanes.¹¹⁻¹⁴ As more PTMG-2000 was included, the peak intensity increased compared with the blunt shape of those with a high percentage of PTMG-1000 (Fig. 3). Similar to the reasoning explaining the IR results, the long soft segment, because of

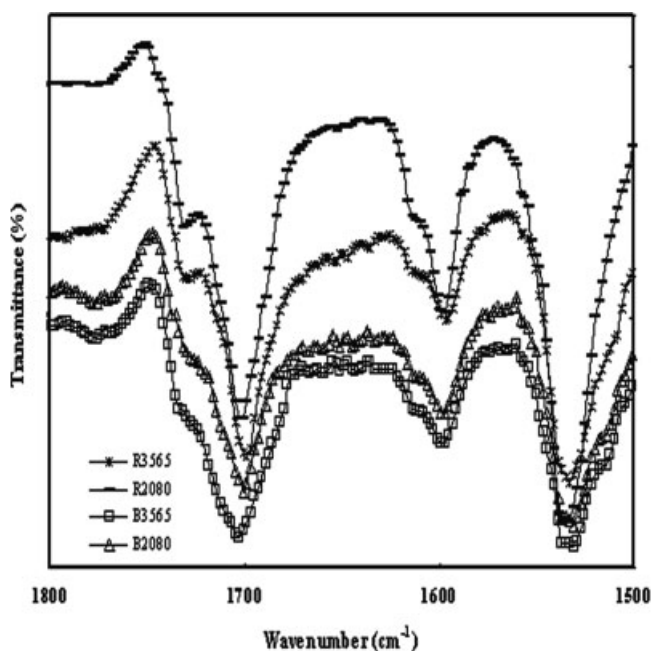


Figure 2 Infrared spectra of block- and random-type polyurethane copolymers.

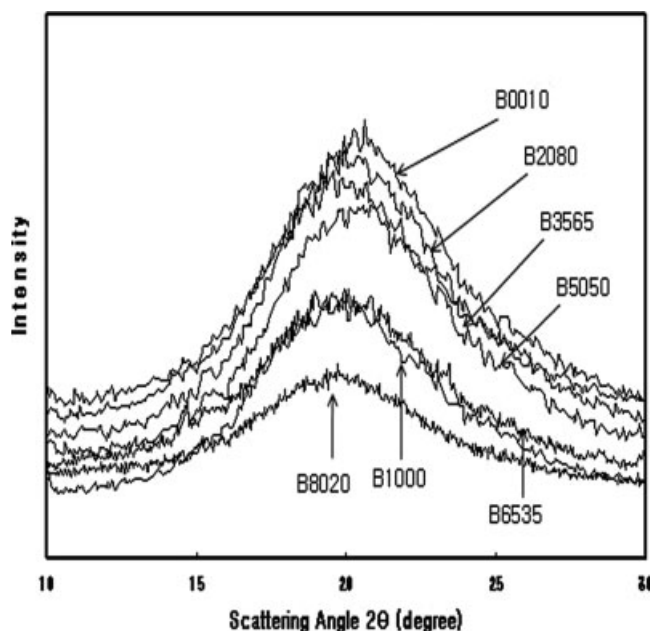


Figure 3 X-ray diffraction spectra of block-type polyurethane copolymers.

its longer chain length, was advantageous over the short one in adjusting hard segment orientation when interacting with other hard segments. Therefore, a higher percentage of PTMG 2000 enlarged the hard domain area together with the increase in diffraction peak intensity. The dependence of diffraction peaks on the arrangement of soft segments, block or random type, was also examined with the same combinations of 35 : 65 or 20 : 80 wt % (PTMG 1000/PTMG 2000). The block type showed relatively higher peak intensity than the random type for both combinations, suggesting that the ordered structure of block type was able to form better interaction among the hard segments, finally resulting in a large hard-domain area (Fig. 4).

Thermal analysis

As more PTMG 2000 was included instead of PTMG 1000, the glass-transition temperature decreased (Fig. 5). Because the transition originated from the rotational movement of soft segments, long and flexible soft segments could start the transition at a lower temperature than could short soft segments. Combining the above results, polyurethane became rich in the hard-domain area (X-ray diffraction result) and flexible with the increased PTMG-2000 content. Differences in the arrangement of soft segments with the same composition did not show any apparent change in the glass-transition temperature: the soft segments were independent of each other because the interaction among soft segments, unlike hard segments, was very weak, and consequently the

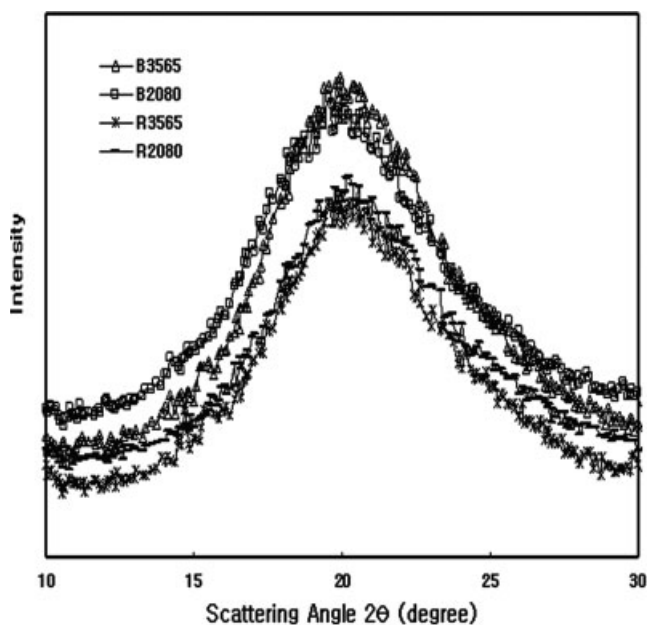


Figure 4 X-ray diffraction spectra of block- and random-type polyurethane copolymers.

blocking of soft segments did not make much of a difference in the glass-transition temperature compared with the random type.

Mechanical property

Overall, the mechanical properties (stress, strain, and modulus) improved with an increase in PTMG-2000

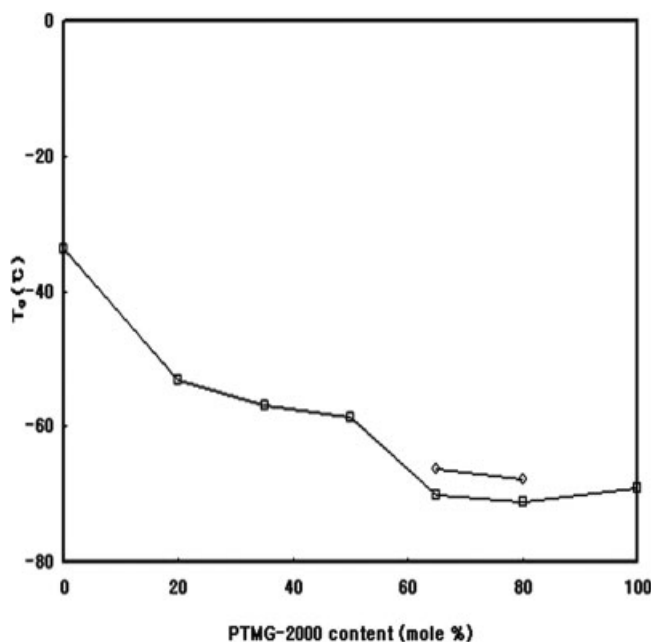


Figure 5 Glass-transition temperature of the copolymers as a function of PTMG 2000 content: (a) block type (\square), (b) random type (\circ).

content (Fig. 6). A especially significant difference occurred with a PTMG-2000 content higher than 50 mol%. The chain length of PTMG-2000 being relatively longer than that of PTMG-1000 gave the soft segments better impact-absorbing ability, so that the one with high PTMG-2000 content could stretch longer and stand greater external stress. When the block- and random-type copolymers of the same composition were compared, the random-type copolymer unexpectedly showed better mechanical properties than the block-type copolymer. The concentration of short soft segments (PTMG-1000) in the same region in the block-type copolymer weakened the soft-segment spot because the long soft segments (PTMG-2000) could better withstand external stress, as shown by the mechanical property results, thus compensating for the weakness of the soft segments not aligned close to the short one as in the random-type copolymer. The mechanical properties were more dependent on the long soft-segment content than on the arrangement of two different types of soft segments (Table III).

Shape memory effect

Ideal shape memory polymer works perfectly with the condition that through interchain attractions (hydrogen bonding and/or dipole-dipole interaction), the hard domain retains the original shape and the soft domain reversibly repeats stretching and shrinkage cycle.¹⁵⁻¹⁷ In reality, shape memory polymer slowly lost its shape recovery ability with repetitive shape memory tests because the dynamic na-

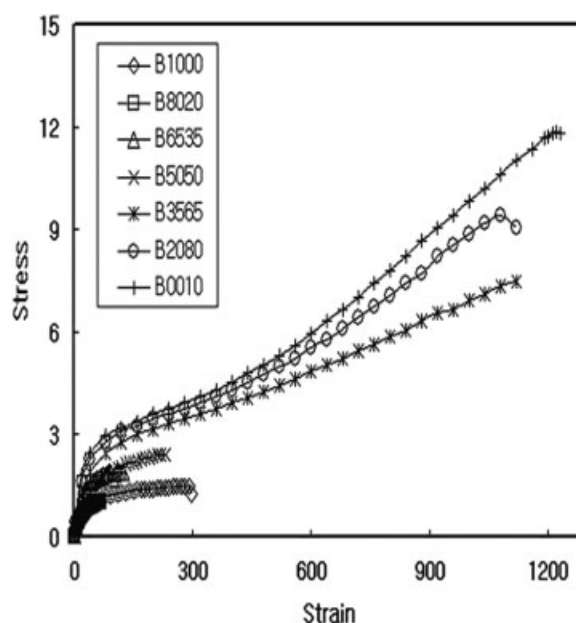


Figure 6 Stress-strain curve of block-type polyurethane copolymer.

TABLE III
Mechanical Properties of Polyurethane Block Copolymer

Sample code	Maximum stress (MPa)	Strain at break (%)	Tensile modulus (MPa)
B1000	1.42	277.4	4.35
B8020	1.02	73.0	5.57
B6535	1.94	119.0	6.01
B5050	2.26	217.6	7.21
B3565	8.25	1161.2	11.07
B2080	9.05	1105.0	12.48
B0010	11.21	1267.7	16.49
R3565	9.78	1361.0	11.35
R2080	11.51	1262.0	14.23

ture of copolymer chains does not allow the hard segment to have a constant shape, a key factor in attaining high shape recovery ratio, over the temperature ranges tested. In this investigation, every effort was made to improve the shape recovery ratio by employing two soft segments with different chain lengths or blocking of two soft segments. Shape retention of more than 80% was maintained for both block- or random-type copolymers with every combination of two soft segments and became even better after the third cycle (Fig. 7). Shape retention results were better with the employment of two soft segments instead of one (compare 35 : 65 with 0 : 10 in Fig. 7), and not much difference in overall shape retention result was found between block- and random-type copolymers with the same composition.

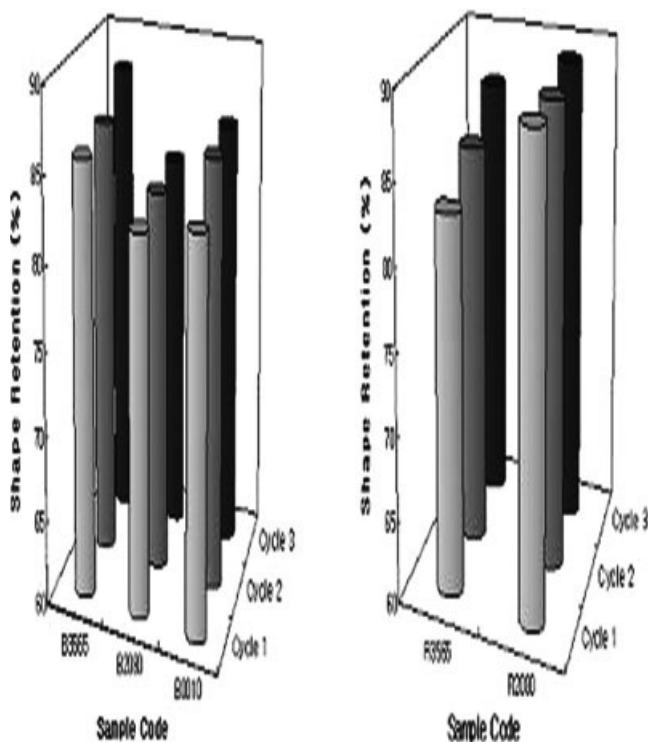


Figure 7 Shape retention profile of polyurethane copolymers: (a) block type, (b) random type.

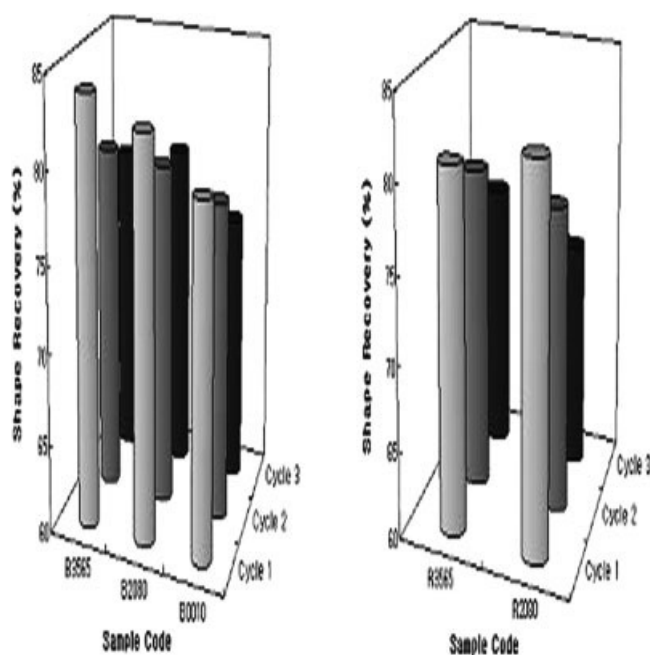


Figure 8 Shape recovery profile of polyurethane copolymers: (a) block type, (b) random type.

The shape recovery ratio worsened after the third cycle for both the block- and random-type copolymers, and better similar to the shape retention results, shape recovery results were better with a combination of two soft segments than employing a single soft segment (compare 35 : 65 with 0 : 10 in Fig. 8). That the best shape recovery ratio was obtained with a 35 : 65 block-type copolymer warranted the search for highly reliable shape recovery polymer by controlling soft segment composition and arrangement.

CONCLUSIONS

The structural, thermal, mechanical, and shape memory properties and soft-segment arrangement (block or random type) of polyurethane copolymers prepared from various combinations of MDI and two different polyols were compared. Employment of more PTMG-2000 resulted in a peak shift of the carbonyl group in IR spectra, increased peak intensity in XRD analysis, and better mechanical properties. Interestingly, a block-type soft-segment arrangement showed inferior mechanical properties to a random-type arrangement. Better shape retention and a higher rate of recovery were obtained by applying a two-soft-segment strategy and a block-type arrangement. Preliminary shape recovery results obtained from the soft-segment combination and the control of soft-segment arrangement were quite encouraging, and room for structural modification of the high shape recovery remains.

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