

Synthesis of Thermoplastic Polyurethane and Its Physical and Shape Memory Properties

Huei-Hsiung Wang, Uen-En Yuen

Department of Fiber and Composite Materials, Feng Chia University, Taichung, Taiwan, Republic of China 40710

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ABSTRACT: In this article, thermoplastic polyurethane (PU) with a shape memory property was synthesized. First, the PU prepolymer was prepared by reacting poly(tetramethylene glycol) with 4,4'-diphenylmethane diisocyanate, then extended with various extenders such as linear aliphatic 1,4-butanediol, benzoyl-type 4,4-bis(4-hydroxyhexoxy)-isopropylane and naphthalate-type bis(2-phenoxyethanol)-sulfone or naphthoxy diethanol. The experimental results showed that the tensile strength, elongation at break, and initial modulus at 300% of these copolymer films were in the range of 31–64 Mpa, 42%–614%, and 8.26–11.5 MPa, respectively. Thermal analysis showed that the glass-transi-

tion temperature of these copolymers was in the range of -73°C to -50°C for the soft segment ($T_{g,s}$) and 70°C – 106°C for the hard segment ($T_{g,h}$) and that the melting point was in the range of 14.6°C – 24.2°C for the soft segment and 198°C – 206°C for the hard segment. The extender with a benzoyl or naphthalate group was better able to promote its shape memory property than was the regular polyurethane. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 607–615, 2006

Key words: polyurethanes; thermoplastics; structure–property relations

INTRODUCTION

Polyurethane (PU) is a thermoplastic polymeric material composed of repeating hard and soft segments; therefore, it possesses good mechanical properties, such as medium tensile strength and high elongation. It is used widely in synthetic leather, fiber, and adhesive.^{1,2} It began to be developed as a shape memory material in the 1960s. Scientists have found that the shape memory alloy (SMA), like the nickel–titanium alloy, will start to restore its former shape after the temperature increases. Therefore, tubes of different sizes of SMA metal can be perfectly jointed after having one side enlarged, connected, and finally thermally heat treated.^{3–5}

For the polymeric materials, the polyurethane-like SMA alloy possesses shape memory properties because it is in different states prior to and after the vitreous state transition point. High-molecular-weight material with shape memory generally falls into three categories: temperature-controlled shape memory, solvent-controlled shape memory, and electric-field-controlled shape memory.^{6–8} In this article we are mainly concerned with polymer material with temperature-controlled memory.

The first temperature-controlled shape memory of high polymers found was polynorbornene (PN), which “memorizes” its shape through the entanglement and twisting of the high-molecular-weight polymer chains. The vitreous state of transition temperature of the polynorbornene was nearly in the range of 35°C – 45°C , and it could be used in medical applications.^{9–12}

Shape memory material of polyurethane consists of two states, a frozen (or fixed) state and a reversible state (or the state that changes from soft phase to hard phase and vice versa). The frozen state of polyurethane is the vitreous or the crystal state, and the reversible state corresponds to the transition between the vitreous state and the rubber state at T_g or the crystal molten state at T_m .^{13–16}

The purpose of this study was to attempt to change the soft and hard chains of polyurethane structures and to improve the physical and chemical properties and shape memory property of the polyurethane. In addition to applications in biomedicine and functional materials, shape memory material can also be used in the textile industry, for example, in the manufacture of brassieres, the linings or collar of suits, where shape memory function is needed.

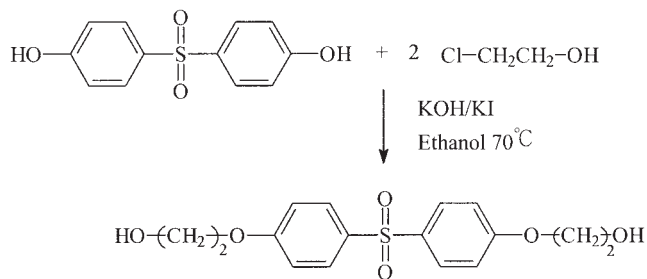
Correspondence to: H.-H. Wang.

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EXPERIMENTAL

Materials

Poly(tetramethylene glycol) (PTMG) with molecular weights of 2000 and 1000, from the Hodotani Co.



Scheme 1

(Tokyo, Japan), and 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (1,4-BD), and *N,N'*-dimethyl formamide (DMF), all from Merck Co. (Darmstadt, Germany), were used without further purification. Chain extenders of different types were used: linear aliphatic-type 1,4-butanediol (from Merck Co., Darmstadt, Germany), benzoyl-type 4,4-bis(4-hydroxyhexoxy)-isopropylane (BPE; from Chu Long Chemical Co. Ltd., Taichung, Taiwan), and naphthalate-type bis(4,4-hydroxyphenyl) sulfone or 1,5-dihydroxynaphthalene (from Lancaster Co., Morecambe, UK). In addition, the reagent of 2-chloroethanol was used to modify the chain extender (from Lancaster Co., Morecambe, UK). They were all used without further purification.

Preparation of the chain-extending agents

Preparation of bis(2-phenoxyethanol)-sulfone

To prepare the bis(2-phenoxyethanol)-sulfone (BES), 10 g (or 0.04 mol) of bis(4,4'-hydroxyphenyl) sulfone, 8.96 g (or 0.16 mol) of potassium hydroxide, and 2 g of potassium iodide were added to 175 mL of ethanol (concentration of 95%) in a four-necked reactor. The reactor was flushed with nitrogen to prevent a side reaction, and the mixture was agitated at the reflux temperature until the added compounds were dissolved completely.

Then 17.44 g (or 0.16 mol) of 4-chloro-1-hexanol was added to the reactor, and the reaction was maintained at 70°C for 24 h. After that, the solution was put in a rotary condenser and evaporated to totally remove the ethanol. The remnant was put in water and filtered and washed twice. The filtered cake was finally dried, and BES was obtained. The reaction scheme is depicted in Scheme 1.

Preparation of naphthoxy diethanol

To prepare the naphthoxy diethanol (ND), 8 g (or 0.05 mol) of 1,5-dihydroxynaphthalene, 11.03 g (or 0.20 mol) of potassium hydroxide, and 2.5 g of potassium iodide were added to 200 mL of ethanol in a four-necked reactor. The reactor was flushed with nitrogen,

and the solution was agitated at the reflux temperature until the added compounds were dissolved completely.

Then 21.8 g (or 0.16 mol) of 4-chloro-1-hexanol was added to the reactor, and the reaction was maintained at 70°C for 24 h. After that, the solution was put into a rotary condenser and evaporated to totally remove the ethanol. The remnant was put into water and filtered and washed twice. Finally, the cake was dried and ND was obtained. The reaction scheme is depicted in Scheme 2.

Preparation of thermoplastic polyurethane

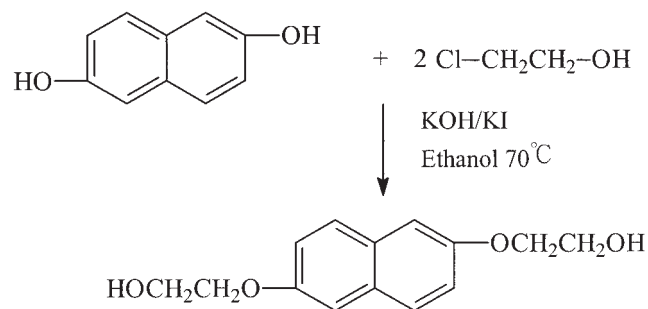
A two-stage melting polymerization process was employed to synthesize the thermally moldable polyurethane. Before the reaction, PTMG was first added into a four-necked reactor and heated to a temperature of 105°C–110°C at a pressure of 3–4 mm Hg for 1.5–2 h in order to remove the moisture. Then the MDI (based on NCO/OH = 1.05) was added so the prepolymerization reaction would proceed at 90°C for 1.5–2 h, and then chain extender of different types was added. The solution was agitated for 1–3 min and then poured into a preheated flat mold in a vacuum oven where it remained at 100°C for 20 h. Finally, the samples were removed from the vacuum oven, and the reaction was complete. The reaction scheme is depicted in Scheme 3.

Proportions and compositions of the copolymer and the contents of the soft- and hard-chain segments

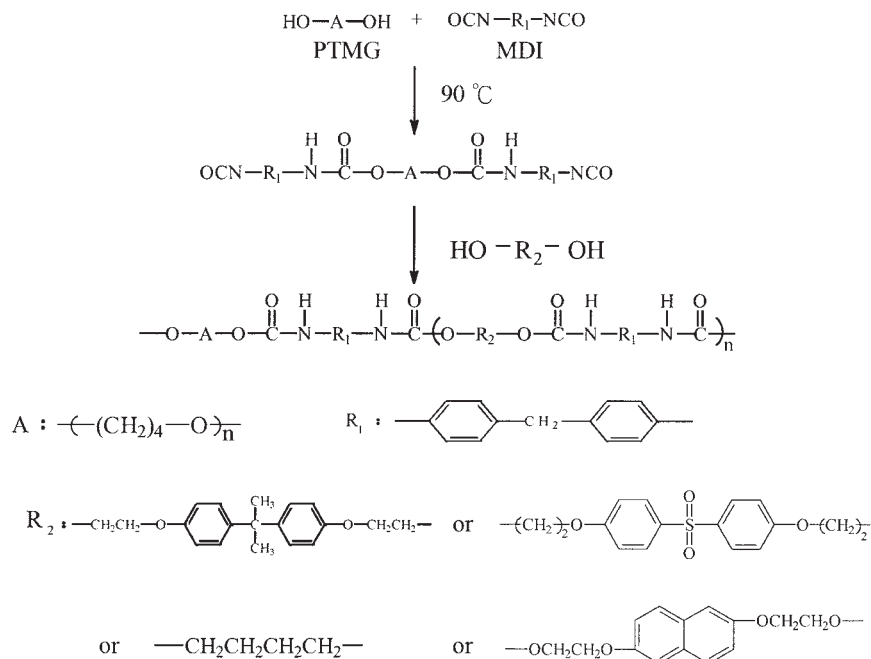
The codes of all the PU polymer films are shown in Table I. The proportions and compositions of the copolymer and the contents of the soft- and hard-chain segments are also listed.

Measurements

Infrared spectra of PU with different chain extenders were obtained with a Hitachi Model 260-50 Type (Hi-



Scheme 2



Scheme 3

tachi, Tokyo, Japan) over a range of 700–500 cm^{-1} . Intrinsic viscosity was determined by a Cannon-type viscometer (Rheotec Co., Radeburg, Germany) in a

water bath at a constant temperature of 25°C. Inherent viscosity (η_{inh}) was calculated as $\eta_{\text{inh}} = [\ln(t/t_0)]/C$, where t_0 is the flowing time of pure solvent, t is the

TABLE I
Polyurethane Polymer Codes and Compositions

Code	Composition	Ratio	Hard content segment (wt %)	Soft content segment (wt %)
P1S	PTMG1000/MDI/1,4-BD	1:6:5	66.10	33.90
P1SA1	PTMG1000/MDI/1,4-BD/BPE	1:6:3.5:1.5	69.60	30.40
P1SA2	PTMG1000/MDI/1,4-BD/BPE	1:6:1.5:3.5	73.26	26.74
P1A	PTMG1000/MDI/BPE	1:6:5	75.49	24.51
P2S	PTMG2000/MDI/1,4-BD	1:6:5	49.37	50.63
P2SA1	PTMG2000/MDI/1,4-BD/BPE	1:6:3.5:1.5	53.37	46.63
P2SA2	PTMG2000/MDI/1,4-BD/BPE	1:6:1.5:3.5	57.81	42.19
P2A	PTMG2000/MDI/BPE	1:6:5	60.63	39.37
P1SB1	PTMG1000/MDI/1,4-BD/BES	1:6:3.5:1.5	69.90	20.10
P1SB2	PTMG1000/MDI/1,4-BD/BES	1:6:1.5:3.5	73.81	26.19
P1B	PTMG1000/MDI/BES	1:6:5	76.13	23.87
P2SB1	PTMG2000/MDI/1,4-BD/BES	1:6:3.5:1.5	53.72	46.28
P2SB2	PTMG2000/MDI/1,4-BD/BES	1:6:1.5:3.5	58.49	41.51
P2B	PTMG2000/MDI/BES	1:6:5	61.46	39.54
P1SC1	PTMG1000/MDI/1,4-BD/ND	1:6:3.5:1.5	68.62	31.38
P1SC2	PTMG1000/MDI/1,4-BD/ND	1:6:1.5:3.5	71.45	28.55
P1C	PTMG1000/MDI/ND	1:6:5	73.26	26.74
P2SC1	PTMG2000/MDI/1,4-BD/ND	1:6:3.5:1.5	52.23	47.77
P2SC2	PTMG2000/MDI/1,4-BD/ND	1:6:1.5:3.5	55.59	44.41
P2C	PTMG2000/MDI/DNA	1:6:5	57.80	42.20

- Hard-segment content = $\frac{\text{MDI} + 1,4\text{BD/BPE/BES/ND (weight)}}{\text{PTMG} + \text{MDI} + 1,4\text{BD/BPE/BES/ND (weight)}}$
- Soft-segment content (wt %) = 100% hard-segment content (wt %).
- SA: using 1,4-BD and BPE as chain extender.
- SB: using 1,4-BD and BES as chain extender.
- SC: using 1,4-BD and ND as chain extender.

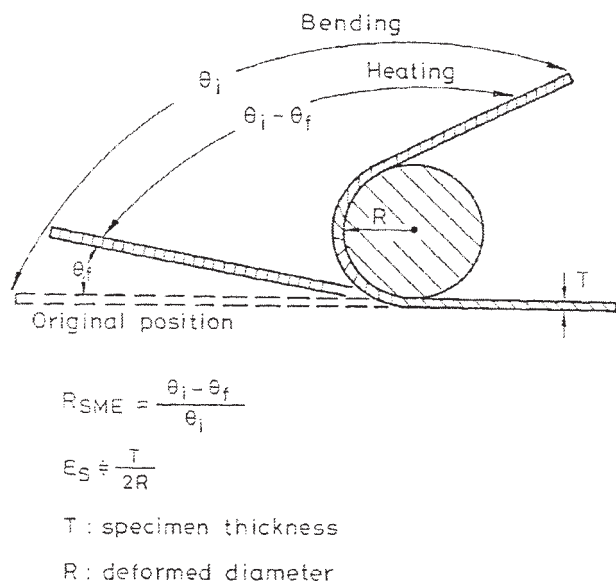


Figure 1 Bending test of shape memory experiment.

flowing time of the polymer solution, and C is a constant (g/dL).

The mechanical properties were measured using an Instron Mode 1122 testing instrument (Instron Corporation, Canton, MA) at a cramp rate of 20 mm/min; a paper extension rate of 10 mm/min with a specimen 50 mm in length, 10 mm in width, and a thickness of 0.1–0.2 mm; and a full load of 20 kg.

Differential scanning calorimetry (DSC) was performed by a Du Pont 2200 (Wilmington, DE) at a heating rate of 20°C/min under a nitrogen atmosphere in order to obtain the glass-transition temperature (T_g) and the melting point.

To evaluate the shape recovery properties, a self-made test apparatus, shown in Figure 1, was used to bend the test sample to 90° at 90°C and to quench it at –45°C to freeze the deformed shape. Then the temperature was increased at 3°C/min to record the relationship between the ratio of recovery and the temperature.

RESULTS AND DISCUSSION

Characteristics of polyurethane with different extenders

4,4'-Diphenylmethane diisocyanate and four kinds of chain extenders (BD, BPE, BES, and ND) were used to prepare three series of polyurethanes (SA, SB, and SC series). Twenty copolymers were synthesized from one type of MDI, two types of PTMG (PTMG1000 and PTMG2000) and four types of chain extenders with different molar ratios. The inherent viscosity values of all the polyurethanes are listed in Table II. As can be seen, the inherent viscosity of the PTMG2000 series

was higher than that of the PTMG1000 series. In addition, with an increased content of benzoyl or naphthalate structure, viscosity increased. This might have been a result of the more molecular polarity of the aromatic structure in the main chain. Viscosity rose along with hard-segment content.

As can be seen in Figures 2–4, the characteristic absorption peak of 3300 cm^{-1} demonstrated a >NH stretching vibration, and the –CH= stretching vibration of benzyl was observed at 3030 cm^{-1} . The characteristic absorption of >C=O was observed at 1735 cm^{-1} , the >C=O of the urea group at 1640 cm^{-1} , the aromatic –NH at 1600 cm^{-1} , the C–O at 1230 cm^{-1} , and the C–O–C of PTMG at 1110 cm^{-1} . Moreover, with BES (SB series) as a chain extender, the absorption peak of –SO₂– appeared at 1160–1140 cm^{-1} ; with BPE as the extender, the absorption peak of –C(CH₃)– appeared at 1375–1385 cm^{-1} . These absorption peaks suggest the successful synthesis of polyurethane polymer.

Thermal properties of polyurethanes

Typical thermal properties of all types of PU polymers, measured by DSC, are shown in Figure 5 and listed in Table III. As shown in Table III, the glass-transition temperature of the P1 series (PTMG = 1000), which had a greater hard-segment content, was higher than that of the P2 series (PTMG = 2000). Furthermore, the glass-transition temperature was higher with benzoyl or naphthalate structure because of steric hindrance of the chain rotation. Also, al-

TABLE II
Inherent Viscosity of All Polymers

Code	Hard-segment content (wt %)	Soft-segment content (wt %)	Inherent viscosity (η_{inh})
P1S	66.10	33.90	0.72
P1SA1	69.60	30.40	0.84
P1SA2	73.26	26.74	0.98
P1A	75.49	24.51	1.15
P2S	49.37	50.63	0.83
P2SA1	53.37	46.63	1.01
P2SA2	57.81	42.19	1.28
P2A	60.63	39.37	1.41
P1SB1	69.90	20.10	0.82
P1SB2	73.81	26.19	0.97
P1B	76.13	23.87	1.08
P2SB1	53.72	46.28	0.93
P2SB2	58.49	41.51	1.24
P2B	61.46	39.54	1.36
P1SC1	68.62	31.38	0.76
P1SC2	71.45	28.55	0.89
P1C	73.26	26.74	1.03
P2SC1	52.23	47.77	0.91
P2SC2	55.59	44.41	1.04
P2C	57.80	42.20	1.15

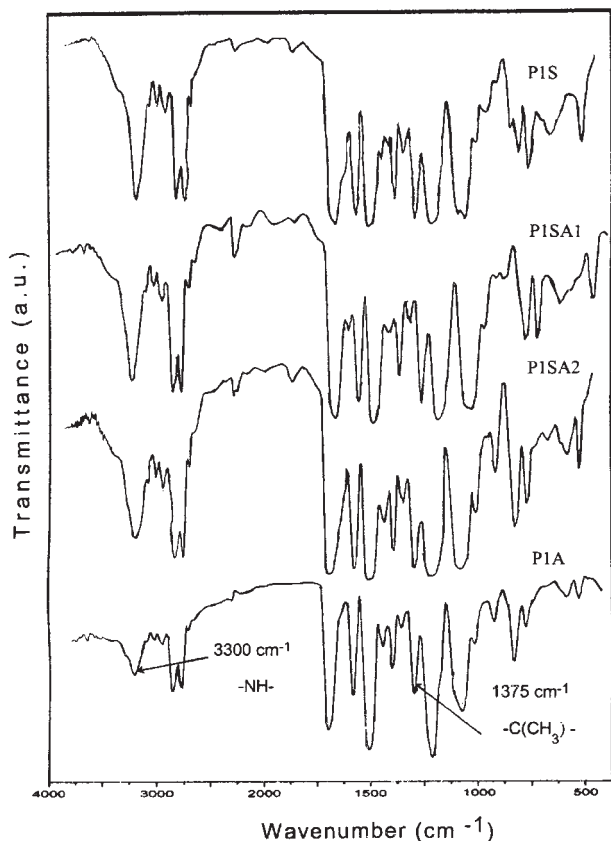


Figure 2 FTIR spectra of P1A series.

though both the PBE and BES chain extenders had a benzoyl structure, the BES, which had a $-(SO_2)-$ structure, was considered stiffer than the $-C(CH_3)-$ of the BPE, resulting in higher T_g s. Moreover, an increased soft-segment length would decrease steric hindrance, and the separation of T_g^s and T_g^h increased in the P₂ series, promoting phase separation.

As shown in Table III, in the hard-segment region, the P1 series show a higher glass-transition temperature than did the P2 series. It increased with a higher content of the hard segment. In the same series, the T_g^h varied with different hard-segment contents. It increased with an increased amount of biphenyl in the extender. In addition, because the benzoyl or naphthalate group was in the main chain, heat resistance was increased. The value of $T_g^h - T_g^s$ (ΔT_g) can be used as a measure of phase separation in PU. As can be seen in Table III, the T_g^h of the copolymer increased with the addition of more BES, BPE, or ND. For the melting point, it was found that there was no T_m^h except for the P1-S in P1 series. This was attributed to the presence of benzoyl or naphthalate extender, which increased the steric hindrance. The structure was not compact enough to form crystalline. Nevertheless, with the P1-S it was easy to form H-bonding and for it to be folded into the crystalline because it only had an aliphatic structure. There was the same

tendency in P2 series. Moreover, the P1 series did not show a T_m^s , a melting point in the soft segment. This was a result of the polyglycol in the P1 series, whose molecular weight was only 1000. It was too short to fold into the crystalline; the chain was also especially affected by the hard segment. Nevertheless the P2 series always showed the crystalline structure of T_m^s . It was in the range of 14.6°C–24.2°C and increased with an increasing amount of hard segments.

Mechanical properties

The mechanical properties of all copolymers are listed in Table IV. Their chain lengths and soft- or hard-segment contents demonstrate a great effect on the mechanical properties. As the molecular weight of polyol is greater (such as PTMG = 2000), the breaking elongation of the polymer increased. Meanwhile, as the aromatic extender of BPE, BES, or ND was introduced into the PU, tensile strength was also enhanced, but elongation decreased. The P1-S in the P1 series showed greater elongation, but not exceeding 300%. The P2 series also did not exceed 600%. This is believed to have occurred because a domain structure with many more crosslinked points formed when there was a higher hard-segment content. The domain

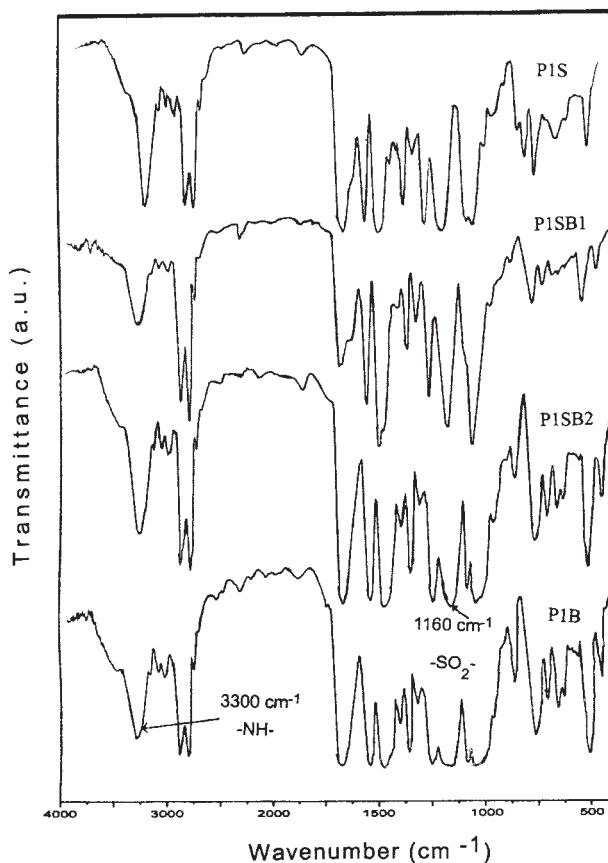


Figure 3 FTIR spectra of P1B series.

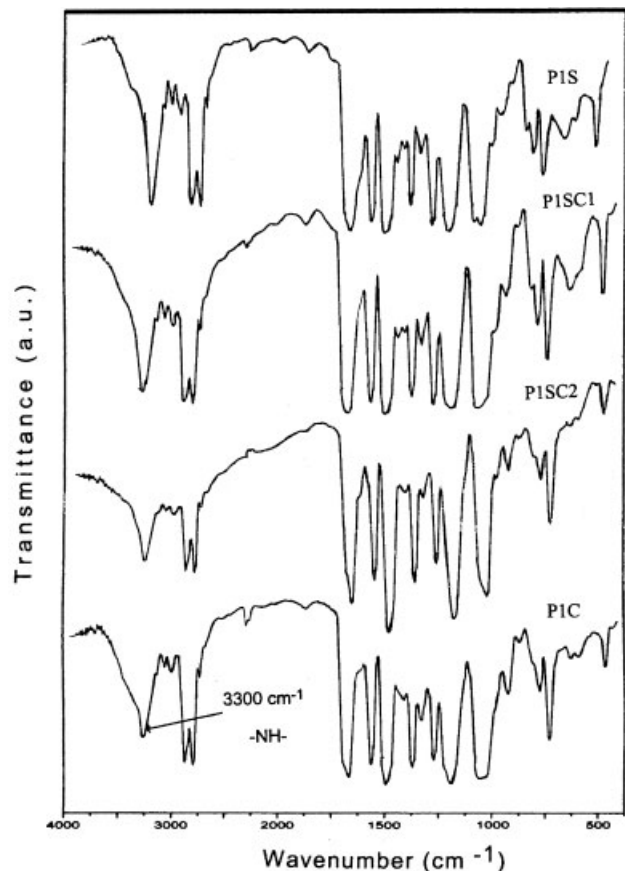


Figure 4 FTIR spectra of P1C series.

was aligned together in an orderly manner to produce higher strength. In the beginning of the extension, the soft segment generated induced crystallization. Because a high hard-segment content (50%–80%) was used in the experiment, after the appearance of induced crystalline in the soft chain, the physical crosslinks would prohibit more extension of the soft segment, and then the polymer film would break up.

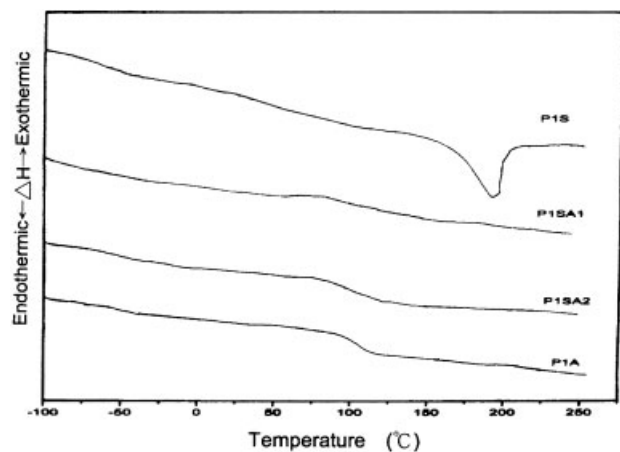


Figure 5 DSC diagram of polymer P1A series.

TABLE III
Glass-Transition Temperatures and Melting Points
of Polymers

Code	T_g of soft segment (T_{gs})	T_m of soft segment (T_{ms})	T_g of hard segment (h)	T_m of hard segment (T_{mh})	$T_{gh} - T_{gs}$
P1S	-61.1	—	83.6	206	145
P1SA1	-58.3	—	88.3	—	147
P1SA2	-55.2	—	92.7	—	148
P1A	-53.5	—	95.3	—	149
P2S	-73.3	14.6	70.7	198	144
P2SA1	-66.1	19.7	79.6	—	146
P-SA2	-64.9	22.3	82.9	—	148
P2A	-64.2	23.8	85.4	—	150
P1SB1	-52.3	—	106	—	158
P1SB2	-51.6	—	108	—	160
P1B	-51.1	—	111	—	162
P2SB1	-64.2	20.6	98.2	—	162
P2SB2	-63.6	23.1	102	—	165
P2B	-61.9	24.2	103	—	165
P1SC1	-52.6	—	110	—	163
P1SC2	-51.3	—	114	—	165
P1C	-50.2	—	116	—	166
P2SC1	-63.8	21.2	104	—	168
P2SC2	-62.9	22.6	106	—	169
P2C	-62.4	23.5	107	—	169

Nevertheless, in the softer chains of the P2 series, the hard segment start to slip over into the hard-segment domain. The soft segment was finally able to sustain the maximum stress. Induced crystalline can reinforce the soft chain; thus, more elongation resulted.

TABLE IV
Mechanical Properties of All Polymers

Code	Breaking strength (MPa)	Breaking elongation (%)	$M_{300\%}$	$M_{600\%}$
P1S	31.2	198	—	—
P1SA1	36.8	142	—	—
P1SA2	43.2	97	—	—
P1A	48.2	52	—	—
P2S	34.89	614	8.26	5.51
P2SA1	40.6	403	9.16	—
P2SA2	42.3	254	—	—
P2A	46.1	208	—	—
P1SB1	39.6	132	—	—
P1SB2	52.5	63	—	—
P1B	64.3	42	—	—
P2SB1	42.7	348	11.5	—
P2SB2	53.1	201	—	—
P2B	56.2	143	—	—
P1SC1	37.6	152	—	—
P1SC2	42.3	75	—	—
P1C	56.1	47	—	—
P2SC1	41.4	327	10.3	—
P2SC2	48.2	203	—	—
P2C	50	112	—	—

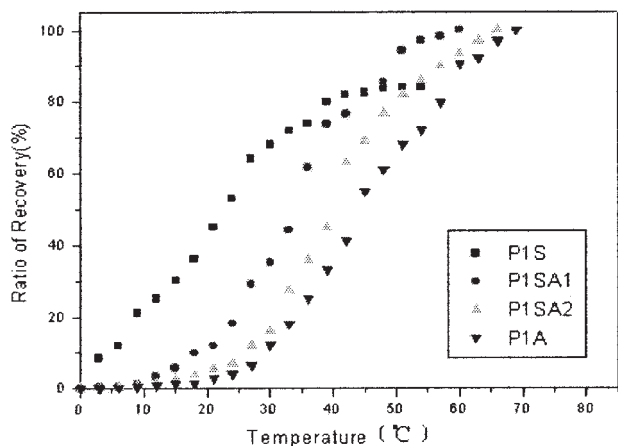


Figure 6 Relationship between ratio of recovery and temperature in P1A series.

A comparison of the different chemical structure of the extenders to their mechanical properties demonstrated that the BES exhibited the best strength but that its elongation was low. This was probably related to the polarity of the extender structure. The $-(SO_2)-$ group in the BES was a polar group, whereas its $-C(CH_3)-$ was a nonpolar group. The interaction of $-(SO_2)-$ with ester groups in the main chain would enhance the mechanical properties. The behavior of BES showed the greatest strength, but BPE showed better elongation. The strength and elongation of the ND series fell in between the other two series. It is believed that was because the naphthalate group had better structural stability than the benzoyl group, giving the former increased strength but poor solubility. The formation of film was considered difficult; thus, poorer behavior of mechanical properties resulted.

Shape recovery properties

A shape recovery material has a recovery and a fixed state. The phase-transition temperature in the recovery state is required to be higher than the operation temperature in order to freeze the material in the operation environment. Moreover, the characteristic temperature of the fixed state has to be higher than both the transition temperature of the recovery state and the operation temperature to stabilize the structure in the operation condition.

The measurement of a shape recovery property is expressed by its recovery ratio versus its operation temperature. The recovery ratio is defined as the ratio of recovery angle to its original deformation angle under a constantly increasing rate of temperature of $3^\circ C/min$. Figures 6–9 shows that all the PUs, except for P1S and P2S in the P1 and P2 series, demonstrated 100% recovery. This is explained by the two phases in structure, that is, the soft and hard domains in the PU.

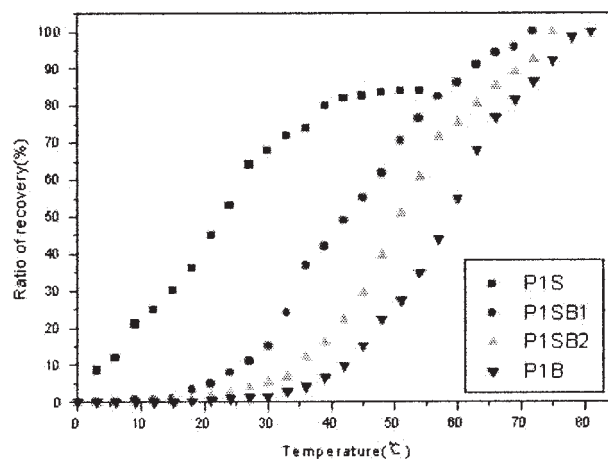


Figure 7 Relationship between ratio of recovery and temperature in P1B series.

The hard segment can contribute to the ratio of recovery, that is, the elastic restoration force for recovery as it is deformed. The soft chain can provide the elongation. After the presence of the benzoyl group in the main chain, the benzoyl structure is included in the hard segment region to make it stiffer in the structure. It exhibits a better shape recovery property than that of a linear structure with 1,4-BD as chain extender. In addition, the P1 series (PTMG = 1000) possesses a shorter chain length in the soft segment. The glass-transition temperature of the soft segment (T_{gs}) was high, but it required a higher temperature to start the recoverable deformation. Moreover, as seen in Figures 9–11, PU with the addition of a benzoyl or naphthalate structure produced a better shape recovery property than that of PU only extended with 1,4-BD. It is believed that the aromatic structure contributed better potential to the shape recovery property; thus, it required a higher temperature to start the restoration. In

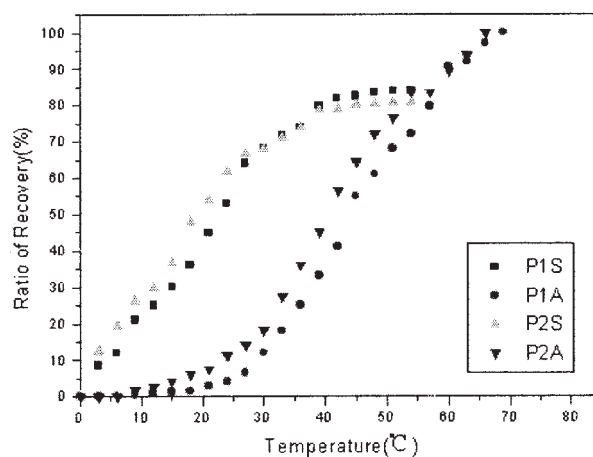


Figure 8 Relationship between ratio of recovery and temperature in PIC series.

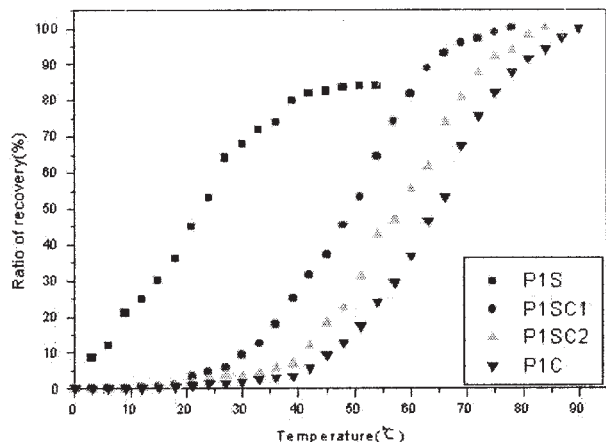


Figure 9 Relationship between recovery ratio and temperature with BPE as chain extender.

addition, the P2 series contained a greater amount of soft segment, and the glass-transition temperatures of the soft and hard segments were lower than those in the P1 series. Restoration began at a lower temperature because the molecules could move at lower temperatures.

In addition, from the recovery ratio–temperature curve, a tangent line can be drawn at the point in the dominant recovery ratio region (10%–20%) to intercept with the x axis to obtain the initial recovery temperature, T_0 , and $T_{1/2}$ can also be obtained at the temperature of the half recovery ratio. As can be seen in Table V, after the addition of a benzoyl or naphthalate group, the initial and half recovery temperatures were higher than those of the 1,4-BD as extender. This indicates that the modified PU provided a stiffer molecular chain. It reinforced the elastic recovery force but required higher temperatures to start the recovery. The polymer with benzoyl or naphthalate group showed an increased recovery temperature as the

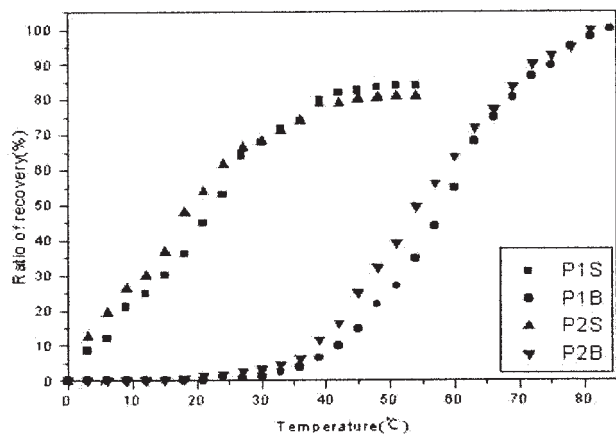


Figure 10 Relationship between recovery ratio and temperature with BES as chain extender.

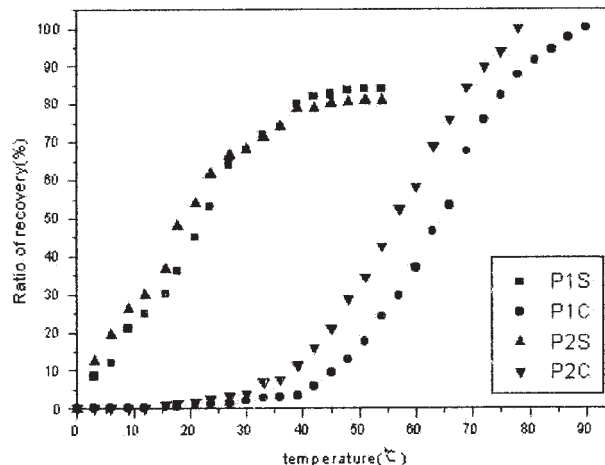


Figure 11 Relationship between recovery ratio and temperature with ND as chain extender.

hard-segment content increased. Moreover, those with a naphthalate group demonstrated an even higher recovery temperature than those with a benzoyl group.

CONCLUSIONS

In this study, we successfully synthesized thermoplastic PU with shape memory properties using different chain extenders such as benzoyl, naphthalate, and regular 1,4-BD. From thermal analysis, it was found that the glass-transition temperature in soft chain, $T_{g,s}$,

TABLE V
Initial Recovery and Half Recovery Temperatures of All Polymers

Code	Initial recovery temperature (T_0) (°C)	Half recovery temperature ($T_{1/2}$) (°C)
P1S	2.0	22.9
P1SA1	10.5	34.0
P1SA2	18.2	39.8
P1A	25.8	43.9
P2S	-2.5	19.2
P2SA1	8.0	30.0
P2SA2	11.7	35.3
P2A	14.4	40.3
P1SB1	26.8	43.5
P1SB2	31.6	51.0
P1B	38.4	58.6
P2SB1	16.1	36
P2SB2	24.7	47.1
P2B	33.8	53.4
P1SC1	27.2	49.8
P1SC2	35.1	58.2
P1C	41.3	64.6
P2SC1	17.8	46.5
P2SC2	24.6	48.8
P2C	32.4	56.3

was not related to the hard-segment content but decreased with increased length of the soft chain. The $T_{m,s}$ only appeared in P2 series with a longer chain length of the soft segment. In addition, the glass-transition temperature of the hard segment, $T_{g,h}$, increased with the presence of an aromatic structure in BES, BPE, or ND. For the mechanical properties, the tensile strength was enhanced with the hard segment; however, elongation decreased with an increased amount of hard segment. Nevertheless, because the PU with the naphthalate structure was difficult to dissolve, its mechanical properties were lower in extension. For the properties of shape memory, the introduction of a benzoyl or naphthalate structure into the main chain improved the shape memory property. However, the initial recovery temperature showed a tendency to increase as the glass-transition temperature of the hard segment increased. This indicates that the initial recovery temperature (T_0) and the half recovery temperature ($T_{1/2}$) increased as a benzoyl or naphthalate group was introduced into the main chain. Similarly, the initial recovery temperature was higher in the P1 series than in the P2 series because the P1 series had a higher hard-segment content. In contrast, a stiffer chain required a higher temperature to

start the restoration, especially those containing naphthalate groups in the main chain.

References

1. Oetel, G. Polyurethane Handbook. Hanser Publishers: Munich, Germany, 1985.
2. Hepbrun, C. Polyurethane Elastomers. Applied Science Publishers: London, 1982; p 9.
3. Funakuba, H. Shape Memory Alloys. Vol. 1. Gordon and Breach Science Publisher: New York, 1987; Chapter 3.
4. Chen, L. W. Chem Technol 1993, 2, 96.
5. Nakayama, K. Int Polym Sci Technol 1991, 18(3), 43.
6. Peterovic, Z. S.; Budinski-Simendic, J. Rubber Chem Technol 1980, 53, 1032.
7. Arshady, R.; George, M. R. Polym Commun 1990, 31, 448.
8. Matuszak, M. L.; Frisch, K. C. J Polym Sci Polym Chem Ed 1973, 11, 637.
9. Blackwell, J.; Naqarajan, M. R.; Hoitink, T. B. Polymer 1982, 23, 950.
10. Speckhard, T. A.; Copper, S. L. Rubber Chem Technol 1986, 59, 405.
11. Petrovic, Z. S. J Polym Sci Part B: Polym Phys 1989, 27, 545.
12. Abousahr, S.; Lwilkes, G. J Appl Sci 1984, 29, 2695.
13. Miller, J. A.; Lin, S. B.; Hwang, K. S.; Wu, K. S.; Gibson, P. E.; Cooper Stauart, L. Macromolecules 1985, 18, 32.
14. Wayman, C. M. MRS Bull 1993, 49.
15. Takeda, K.; Ayiyama, M.; Yamamizu, T. Angew Macromol Chem 1988, 157, 123.
16. Clough, S. B.; Schneider, N. S. J Macromol Sci Phys 1968, B2, 553.