Effect of Cationic Group Content on Shape Memory Effect in Segmented Polyurethane Cationomer

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ABSTRACT: To illustrate the importance of cationic groups within hard segments on shape memory effect in segmented polyurethane (PU) cationomers, the shape memory polyurethane (SMPU) cationomers composed of poly(ε-caprolactone) (PCL), 4,4′-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BDO), and N-methyldiethanolamine (NMDA) or N,N-bis(2-hydroxyethyl)isonicotinamide (BIN) were synthesized. The comparison of shape memory effect between NMDA series and BIN series was made. The relations between the structure and shape memory effect of the two series of cationomers with various ionic group contents were investigated. It is observed that the stress at 100% elongation is reduced for these two series of PU cationomers with increasing ionic group content. Especially for NMDA series, the stress reduction is more significant. The fixity ratio and recovery ratio of the NMDA series can be improved simultaneously by the insertion of cationic groups within hard segments, but not for the BIN series. Characterizations with DSC and DMA suggest that the crystallibility of soft segment in SMPU cationomers was enhanced by incorporation of ionic groups into hard segments, leading to a relative high degree of soft segment crystallization; compared with the corresponding nonionomers, incorporation of charged ionic groups within hard segments can enhance the cohesion force among hard segments particularly at high ionic group content. This methodology offers good control of the shape memory characteristic in thin films and is believed to be beneficial to the shape memory textile industries. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 103: 545–556, 2007

Key words: polyurethane; cationomer; shape memory effect; cyclic tensile test

INTRODUCTION

In recent decades, shape memory polymers have emerged as the key smart material developed widely in both academia and industry for their low cost, good processing ability, high shape recoverability, and larger range of shape recovery temperature compared with that of shape memory alloys.[1,2] Several polymer systems have been reported to possess shape memory properties, such as *trans*-polyisoprene (TPI), poly(styrene-*co*-butadiene) and polynorbornene, etc. The most readily available is segmented shape memory polyurethane (SMPU) which has aroused much attention since the Nagoya Research and Development Center of Mitsubishi Heavy Industry (MHI) developed a series of functional polymers.[3] Foremost among the reported microscopic structures on segmented SMPU systems, the two-phase heterogeneous structure is the well acceptable picture, consisting of a rigid fixed and a soft reversible phase. According to the mechanism of shape memory effect, the reversible phase having a melting or glass transition temperature of the soft segments as the transition temperature is used to hold the temporary deformation, whereas the fixed phase is referred to the hard segments covalently coupled to the soft segments. They inhibit plastic flow of the chains by having physical crosslinkage points between them that are responsible for memorizing the permanent shape.[4–8] In the linear segmented PU system, the strong intermolecular force among hard segments results from their possessing the hydrogen bonding and high polarity due to the presence of urethane and urea units. The shape memory effect (SME) of PU therefore is mainly influenced by the hard segment content and the moiety of its molecular structure.[7,9,10] In addition, it is reported that soft segment content, its molecular weight, conformation, and morphological structure play significant roles in affecting the SME.[8,11] Conducting research on SMPU, these parameters are paramount in controlling the shape memory property in general. This in turn provides a means to control the measurable shape recovery and shape fixity ratio in particular.

Recently, SME of segmented PU ionomers has been studied based on the influence of ionic groups on micro-phase separation. Kim and coworkers systematically studied the effect of soft segment content

and its length on the SME using cyclic tensile test, and the result was compared with dynamic mechanical and thermal analyses between PU ionomers and the corresponding nonionomers.[12] They also pointed out that the ionomer species augment the overall modulus of the polymer film via Coulombic forces resulting from the increased cohesion among hard segments and micro-phase separation. Jeong et al.[13] preliminarily investigated the shape memory properties of SMPU ionomers based on poly(ε-caprolactone) (PCL), 4,4'-diphenylmethane diisocyanate (MDI), 1,4-butanediol (BDO), dimethylolpropionic acid (DMPA), hexamethylene diisocyanate (HDI), and hexamethylene diamine (HAD) with DMPA content ranging from 1.5 to 4.5% using cyclic tensile test. Their result suggested that fatigue of the SME is reduced with the incorporation of ionic moieties into hard segments. It was then evident that ionic moieties on hard segments can influence the SME significantly. Adjusting the interconnectivity among hard segments can be potentially used to control in particular the shape memory recovery ratio or alter the modulus of the rubbery state in SMPU. In some cases, increasing the hard segment content provides an option to alter their interconnectivity at the expense of the crystallizable soft segment content, and thus lowering the shape fixity ratio.[4] In our previous report and Lin's study, chemically crosslinked hard segment structure has been systematically incorporated into PU so as to improve its mechanical and shape memory property.[14,15] However, the advantage of processing ability of this originally thermal plastic SMPU would be lost due to the formation of crosslinkage points. For polyurethane cationomer, Chen and Chan[16] have revealed that a dual effect of ionization exists in the polyurethane cationomer with NMDA as chain extender: (i) the improved cohesion through ionic interaction, (ii) the disruption of the order of hard domains by ion insertion. With respect to the dual effect of ionic groups within hard segments, in this article, ionomer moiety was used to act as a part of chain extender for hard segments, providing the Coulombic force to increase the cohesion among hard segments and then help recover deformation; meanwhile, the introduction of ionic groups into hard segments was expected to alter the packing

extent of hard domain or the micro phase separation, which possibly improves the crystallizability for soft segment. This provides an easy means to adjust the interconnectivity between the hard segment and the crystallizable soft segment in thermal plastic SMPU, providing a systematic step to improve the SME in segmented PU.

In the synthesis of PU samples, the extender with ammonium in backbone N-Methyldiethanolamine (NMDA) and the extender with pendant groups N,N-bis(2-hydroxyethyl)isonicotinamide (BIN) used partly in chain extender were respectively, introduced into the hard segments of PU. Then the PU nonionomer was synthesized and the corresponding PU cationomer was obtained by neutralization reaction of (N-Methyldiethanolamine) NMDA or BIN with stoichiometric acetic acid (HAc). The content of extender with ionic moiety was gradually increased from the minimum to the maximum allowable value. Knowing in advance that ionic moiety content and other parameters such as categories of hard segment, soft segment content, and its molecular weight can alter the molecular structure, only the first one is kept as the adjustable parameter while the latter three parameters are kept fixed. The role of ionic groups on SMPU films was then investigated by using dynamic mechanical analysis and thermal cyclic test. Meanwhile, the variation of shape memory effect induced by two categories of ionic extender was compared and studied. The conclusion, in turn, offers a novel approach to improve shape memory function in these molecular systems.

EXPERIMENTAL

Material preparation

The formulae of the PU samples are shown in Tables I and II. PCL diols (Daicel Chemical Industries) with molecular weight (M_n) 10,000 were dried and degassed at 80°C under 1–2 mmHg for 12 h prior to PU synthesis. Extra pure grade of MDI (Aldrich Chemical Company), NMDA (Advanced Technology and Industrial Company), and BIN (Aldrich) (Fig. 1) was used without further treatment. BDO (Acros Organics) was dried by molecular sieves. HAc (Ace-

TABLE I
Formulation of NMDA Series PU Ionomer

Sample code	PCL (wt %)	NMDA (wt %)	Moles of PCL	Moles of NMDA	Moles of BDO	Moles of MDI	Moles of HAc
75-0	75	0	1	0	9.07	10.07	0
NMDA75-2	75	2	1	2.24	6.64	9.88	2.24
NMDA75-4	75	4	1	4.48	4.21	9.69	4.48
NMDA75-8	75	7.46	1	8.35	0	9.35	8.35
NMDA75-4N	75	4	1	4.48	4.21	9.69	0
NMDA75-8N	75	7.46	1	8.35	0	9.35	0

TABLE II
Formulation of BIN Series PU Ionomer

Sample code	PCL (wt %)	BIN (wt %)	Moles of PCL	Moles of BIN	Moles of BDO	Moles of MDI	Moles of HAc
75-0	75	0	1	0	9.07	10.07	0
BIN75-4	75	4	1	2.54	5.63	9.16	2.54
BIN75-6	75	6	1	3.81	3.91	8.71	3.81
BIN75-8	75	8	1	5.07	2.19	8.27	5.07
BIN75-11	75	10.56	1	6.7	0	7.7	6.7
BIN75-6N	75	6	1	3.81	3.91	8.71	0
BIN75-11N	75	10.56	1	6.7	0	7.7	0

tic acid glacial, International Laboratory) was used to neutralize the cationic group with stoichiometric amount.

Prepolymer was synthesized by terminating a 10,000 g/mol molecular weight PCL with diisocyante MDI at 80°C for 2 h in a four-necked cylindrical vessel equipped with a mechanical stirrer. Then it was chain-extended with BDO and/or NMDA or BIN for the same period of time. Dimethylformamide (DMF) was used in the PU synthesis as solvent, which was dehydrated with 4 Å molecular sieves for 2 days prior to usage. The neutralization reaction was carried out at 40°C for 1 h by adding stoichiometric amount of HAc subsequently. Films were prepared by casting the solution with $\sim$ 15 wt % concentration in Teflon mold at 60°C for 24 h. It was further dried at 75°C under a vacuum of 1–2 mmHg for 1 day.

In this study, we fix the soft segment content and its length in PU cationomer so as to investigate the sole effect of ionic group content on the SME of PCL-10000 based SMPU. The series of PU copolymers cationomer are nomenclated by abbreviation of

ion chain extender and followed by 3 numbers. The first two numbers denote the soft segment content, the third number represents the ion extender weight content, and for some PU noncationomer, the alphabet "N" in the end indicating it is the sample without neutralization for the corresponding ionomers. As an example, the sample NMDA75-4 contains 75 wt % of soft segment, $\sim$ 4 wt % of NMDA and its nonionomer is NMDA75-4N. The sample 75-0 contains no NMDA or BIN but only MDI, BDO, and PCL-10000 components as the control sample in this study.

Differential scanning calorimetry

Melting temperature of PU samples is determined by a Perkin–Elmer Diamond DSC with nitrogen as purge gas. Indium and zinc standards were used for calibration. All samples ($\sim$ 5 mg) were heated to 240°C at 10°C/min beforehand to remove the thermal history and then cooled to −70°C at a cooling rate of 10°C/min. Subsequently, heating scan up to 240°C at 10°C/min was carried out.

Dynamic mechanical analysis

In this test, the PU films were prepared by casting in Teflon mold with an area of 5 × 25 mm^2. The film thickness is about 0.5 mm and the distance between two clamps is 15 mm in the initial testing status. Dynamic mechanical properties of the samples were determined by using a Perkin–Elmer DMA at frequency of 2 Hz. The heating rate is 2°C/min and temperature is scanned from −100 to 150°C.

Cyclic tensile test

Cyclic tensile test was performed using an INSTRON 4466 cyclic tester equipped with a temperature control chamber. The standardized film size for the test is 5 × 20 mm^2 and thickness is 0.5 mm. The film was heated initially to 70°C (T_{high}) in 600 s. After the sample was stretched to 100% elongation (ε_m) at T_{high} with a stretching rate of 10 mm/min, cool air is vented passively into the chamber to cool down the
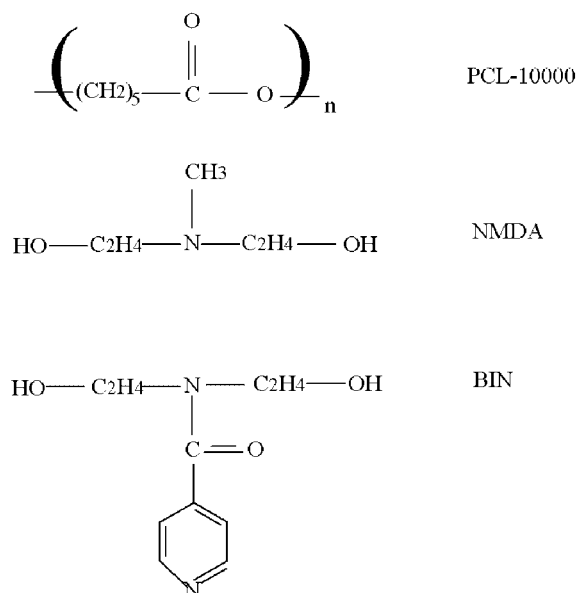

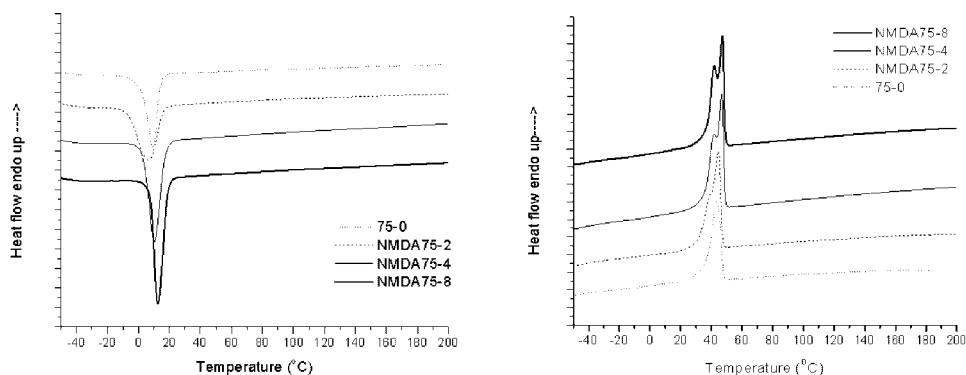
Figure 1 Schematic of PCL10000, NMDA, and BIN.

Figure 2 Cooling scan (left) and reheating scan (right) of NMDA series SMPU cationomer.

sample to 20°C (T_{low}) at ε_m in 900 s. The strain was released from ε_m to 0 and the recurrent heating and cooling process start subsequently. The complete thermal cycle for each sample will be repeated 4 or 5 times for assessing the shape memory effect. Detailed parameter definitions such as shape recovery ratio (R_r) or shape fixity ratio (R_f) used to characterize the SME is defined in literature.[4,17]

RESULTS AND DISCUSSION

Thermal properties

The thermograms of all the SMPU cationomers studied showed the exothermic crystallization peak of the soft segment in the cooling scan and the endothermic melting peak of the soft segment in the reheating (the second heating) scan as shown in Figures 2 and 3. All the crystallization and melting behavior of hard segment cannot be detected in this testing cycle. The thermal properties data have been shown in detail in Table III. In NMDA and BIN series of SMPU cationomers, it was observed that T_{cs} (crystallization temperature of soft segment) and ΔH_{cs} (the enthalpy of crystallization of soft segment) increased significantly with increasing ionic group content. Generally, the enthalpy of crystallization in cooling

scan can be used to investigate the crystallizability of specimen. Therefore, the resultant data of cooling scan suggests that the soft segment of SMPU cationomer with high ionic group content have relatively stronger crystallizability. Moreover, the value of T_{cs} and ΔH_{cs} of NMDA series are lower than that of BIN series, indicating that the crystallizability of soft segment in NMDA series is weaker than that in BIN series. Accordingly, it can be observed that, in the reheating scan, T_{ms} (the melting point of soft segment) and ΔH_{ms} (the melting enthalpy of soft segment) of these two series increased with increasing ionic group content within hard segment. The crystallinity of segmented PU ionomer samples was calculated from the enthalpy of 100% crystalline PCL, 32.4 cal/g, given by Crescenzi et al.[18] In that, it can be concluded that the crystallinity of soft segment in segmented PU is significantly raised with the existence of ionic groups within hard segment. The more ionic groups within hard segment, the higher the crystallinity of soft segment that can be achieved. According to the mechanism of shape memory effect proposed for segmented copolymers reported in previous studies,[4–6] the crystalline soft segment is responsible for the fixity of deformation. Therefore, it is expected that the higher crystallinity of soft segment might facilitate the temporary
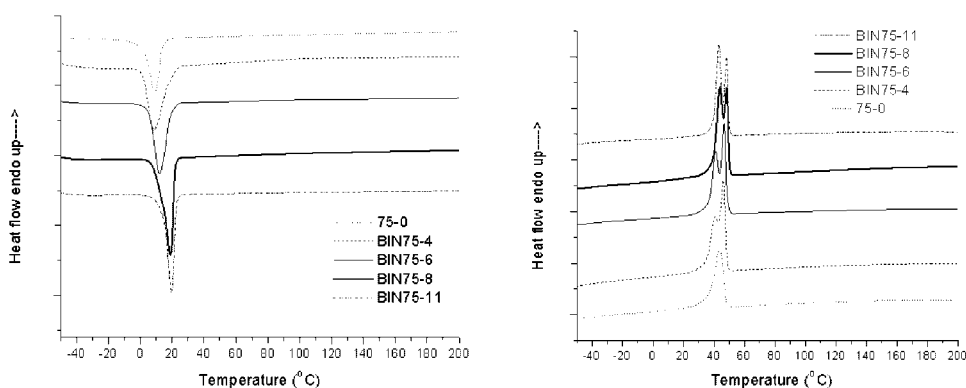

Figure 3 Cooling scan (left) and reheating scan (right) of BIN series SMPU cationomer.

TABLE III
Thermal Properties of SMPU Cationomer

Sample code	First heating at 10°C/min			Second heating at 10°C/min			Cooling at 10°C/min	
	T_{ms} (°C)	ΔH_{ms} (J/g)	Crystallinity (%)*	T_{ms} (°C)	ΔH_{ms} (J/g)	Crystallinity (%)*	T_{cs} (°C)	ΔH_{cs} (J/g)
75-0	49.20	39.37	38.6	43.46	35.62	34.9	9.17	32.33
NMDA75-2	51.82	48.15	47.2	44.66	45.36	44.4	6.75	38.97
NMDA75-4	52.12	49.73	48.7	46.81 (41.97)	46.86	45.9	10.18	42.59
NMDA75-8	50.43	52.72	51.7	47.14 (41.96)	46.59	45.6	12.65	43.61
BIN75-4	50.16	43.80	42.9	45.99 (40.75)	48.93	47.9	8.74	46.56
BIN75-6	46.94	39.81	39.0	46.63 (41.09)	50.60	49.6	12.14	44.87
BIN75-8	50.01	44.94	44.0	48.13 (43.79)	51.37	50.3	18.93	46.24
BIN75-11	47.46	41.75	40.9	48.50 (43.29)	49.45	48.5	19.59	43.97

* Calculated according to the enthalpy of fusion of 100% crystallization PCL: 32.4 cal/g.

deformation fixity and subsequently improve the fixity ratio. Besides, it is worth noting that there are double-melting features in all the DSC reheating thermograms shown in Figures 2 and 3. Similar signature was also observed on the 30/70 DGEBA/PCL blend,[19] binary blends of solution-chlorinated polyethylenes (CPE) with polycaprolactone (PCL), and blends of poly(hydroxyl ether of bisphenol A) (Phenoxy) with polycaprolactone (PCL),[20,21] PCL/SAN investigated by Rim and Runt.[22] In the study of Phenoxy/PCL by Defieuw,[21] the isothermal crystallization process was interrupted after different time intervals and the DSC melting trace was immediately recorded. The higher melting endotherm is of a fixed temperature after short isothermal crystallization times (primary crystallization), while the lower melting peak only appears after much longer crystallization times (secondary crystallization). The secondary crystallization is supposed to occur in the amorphous phase segregated during the primary crystallization of PCL, resulting in a slower crystallization process as this happens in the presence of a higher Phenoxy concentration. In our study, a similar routine was used to investigate the double melting behavior of SMPU cationomer. To remove the effect of recrystallization in cooling process, the sample was quenched to T_c

(isothermal crystallization temperature) from 120°C with enough high cooling rate. The isothermal crystallization temperatures are 10 and 20°C for testing BIN75-11 as shown in Figure 4(a,b) respectively. Just like the result in the investigation of Phenoxy/PCL blends studied by Defieuw,[21] from Figure 4(a), it can be observed that the highest melting endotherm resides in the a constant area and position (48.7°C) in the heating scan after isothermal crystallization for various time intervals; instead, the lower melting keeps moving upward from 42.57 to 43.37°C with the increase of isothermal crystallization time from 1 to 60 min. After the isothermal crystallization at $T_c = 20°C$, this evolution becomes more obvious though the highest melting peak is nearly overlapped with the lower melting peak when the isothermal crystallization time is longer than 50 min. Therefore, the lower melting peak of soft segment in SMPU cationomer in this study was tentatively attributed to the secondary crystallization. Namely, the effect of the presence of ionic group within hard segments can be found to induce more secondary crystallization, subsequently increasing the total crystallinity that can be observed from the increase of endothermic enthalpy in reheating scan shown in Figure 3.
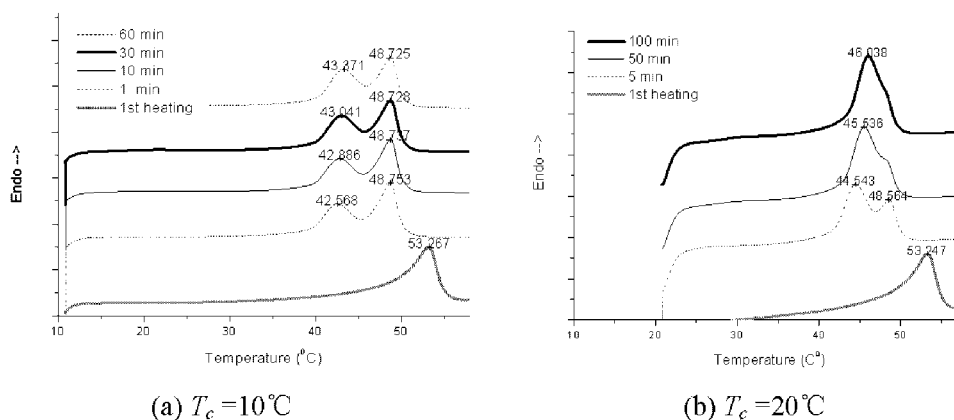

(a) $T_c = 10°C$ (b) $T_c = 20°C$

Figure 4 Double melting behavior of BIN75-11 isothermally crystallized at (a) 10°C and (b) 20°C for various time intervals.
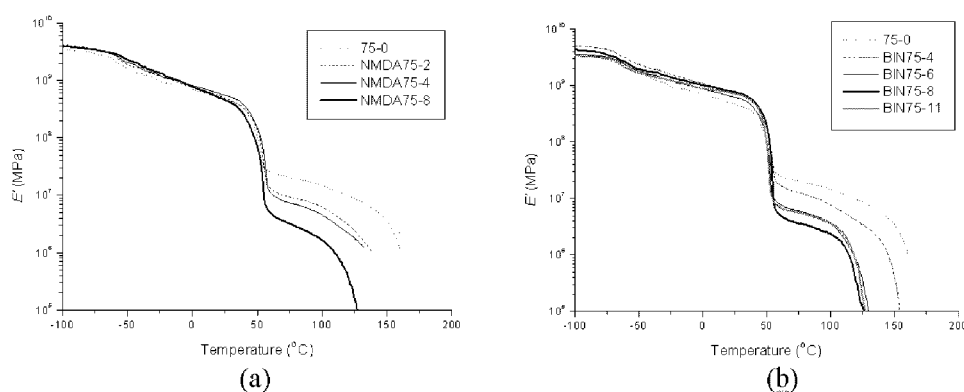
Figure 5 Storage modulus (E') of NMDA and BIN series SMPU cationomer.

Dynamic mechanical analysis

Figure 5 shows the storage modulus (E') from dynamic mechanical analysis of NMDA and BIN series. The result suggests that there is an important difference in the storage modulus in the temperature range from 40 to 50°C within which a sharp transition is rendered to the SMPU cationomers. This transition is attributed to the melting of crystallization of soft segments according to the result of DSC aforementioned. Below the melting point of soft segments (T_{ms}), the crystalline state of soft domain together with the glass state of amorphous hard domain ensures a high modulus of the film.[4] However, when the temperature is above T_{ms}, the entropic elasticity of the molecular chain and physical crosslinking among hard segments jointly contribute the rubbery state modulus.[4,6,23,24]

For hard segment rich phase, although the formation of hard domains cannot be characterized in DSC, the DMA offers indirect evidence with the temperature dependence of dynamic modulus.[23] E' of all SMPU ionomers is nearly 1×10^9 MPa at room temperature range. After the melting of soft segment, the rubbery plateau of E' is located in 1×10^7 MPa around, indicating the existence of physical crosslinks in SMPU ionomer. It is also observed that the rubbery plateau of E' at temperature above T_{ms} tends to be shorter and lower with increasing ionic group content, when asymmetric extender is incorporated into hard segments, showing the decrease of the packing extent of hard domains in NMDA series. Different scenario observed in BIN series is that the E' plateau is shortened and lowered with the increase of BIN content when BIN content is < 8%, but tends to be longer and higher subsequently when the BIN content is above 8 wt %. Such a turning point of the variation of E' with the increase of ionic group content also can be observed in segmented PU anionomer in our previous study.[25] It suggests that the charged ionic groups could enhance the cohesion among hard segments especially in high ionic group content. Figure 6 illustrates the dependence of E' on ionic groups content detected with DMA at 20 and 70°C respectively, in which E' of two series PU ionomer increases slightly with the ionic group content at 20°C, whereas it decreases significantly with the ionic group content at 70°C. Substantially, the turning point at 8 wt % BIN also can be found clearly just like aforementioned. Therefore, it can be concluded that the modulus ratio that was defined as $E'_{at\ 20°C}/E'_{at\ 70°C}$ increased with the increase of ionic group content. The slight increase of elastic modulus at 20°C with ionic group content in constant soft segment content specimen is due to the greater soft segment crystallization induced by ionic groups within hard segments. The immense depression of elastic modulus at 70°C with ionic group content should be attributed to the effect of ionic group on the extent of the order of hard domain.

As shown in Figure 7, in comparison between SMPU cationomers and noncationomers, the SMPU cationomers all have longer and higher rubbery plateau than that of the corresponding noncationomers,
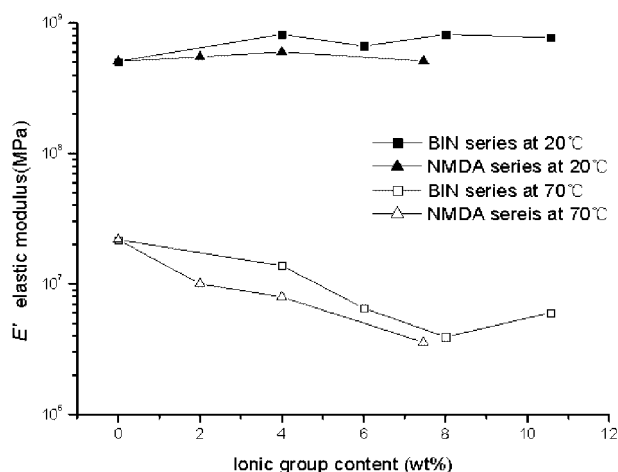

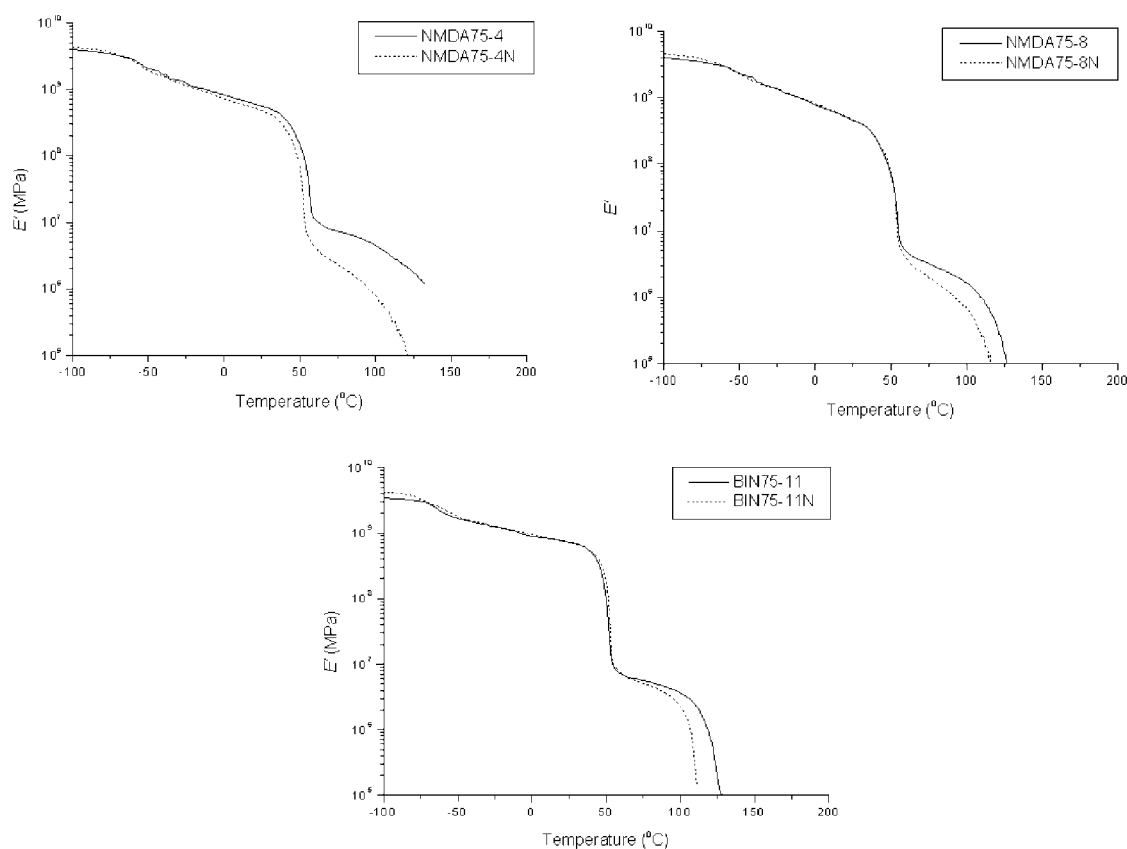**Figure 6** Elastic modulus of NMDA and BIN series SMPU cationomer at 20 and 70°C.

Figure 7 Comparison of E' between SMPU cationomer and the corresponding noncationomer.

illustrating the existence of Coulombic force among cationic groups and the increased cohesion among hard segments after ionization.

Considering the importance of the formation of hard segment domains as a structural characteristic for shape memory function, a deep study about the influence of ionic group within hard segment on hard domain is necessary. The glass transition temperature of hard segment MDI–BDO in polyurethane was ever reported to be located at around 125°C.[26] The melting point of MDI–BDO crystal is in the range of 200–240°C.[27] Although DSC cannot provide the information about the transition of hard segment, we still can detect T_{gh} together with the various transition of soft segment with DMA. Figure 8 shows the dependence of loss tangent (tan δ) on temperature of NMDA and BIN series SMPU ionomer. The peak locating around −60°C belongs to the glass transition temperature of soft segment (T_{gs}); the sharp rise at 50°C is attributed to the melting of soft segment crystallization; the peak appearing at the temperature above 100°C shown in Figure 8(b) is attributed to the glass transition of hard segment rich phase (T_{gh}).[16,28,29] Since tan δ reflects the strain energy of dissipated by viscous friction, a larger tan δ suggests the materials are more viscous and far from elastic.[4] Therefore, when heated above the melting point of

soft segment (T_{ms}), generally the SMPU ionomer with high ionic group content having the higher tan δ is more viscous than the specimen with low ionic group content. For BIN series, as shown in Figure 8(b) and Table IV, the T_{gh} is monotonously depressed from 158.87 to 130.52°C with the increase of ionic group content in hard segment from 4 to 8%, which indicates the insertion of ionic groups increase the disorder of hard domain, disrupt the order of the hard domain and lower the packing extent of hard domains. When the increase of ionic groups content persist to the maximum allowable value, 10.56 wt % from 8 wt %, T_{gh} can be move upward to 132.87°C from 130.52°C. This trend is quite similar with the result of the study on TDI series PU cationomers reported by Chen and Chan.[16] In their research, T_{gh} first decreases and then increases with increasing ionic content. The fall and rise of T_{gh} was explained by an increased extent of disordering due to disruption by ionization and an overcompensation of the increased cohesion due to the increased extent of ionization. Therefore, it is believed that the dependence of T_{gh} on ionic group content is caused by the two opposite effects: disruption of hard domain by insertion of ionic groups and the increased cohesion among hard segments. When BIN content is high enough, as in BIN75-11,
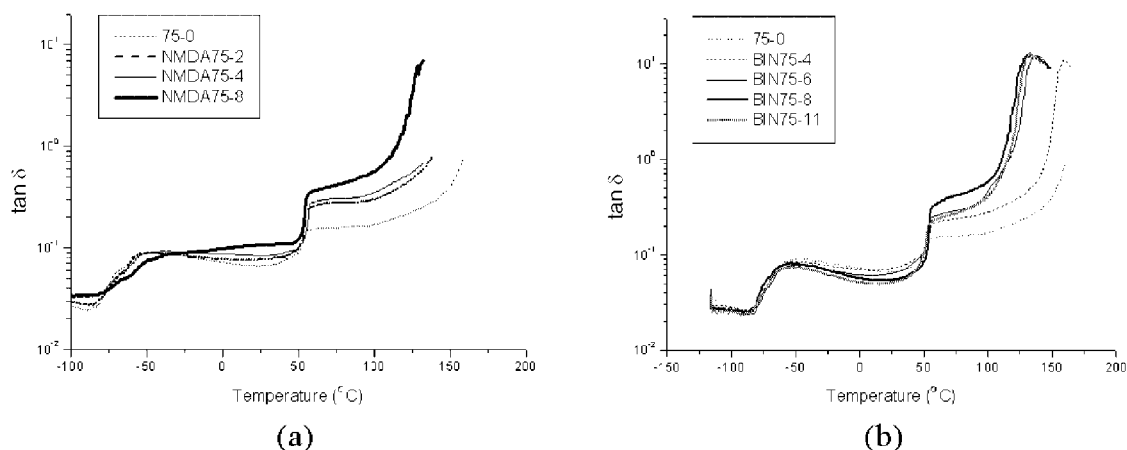
Figure 8 Loss tangent (tan δ) of NMDA (a) and BIN (b) series SMPU cationomer.

the increased cohesion caused by Coulombic force among ionic groups is dominant compared with the sample BIN75-8, which also can be observed from the comparison of tan δ value in rubbery plateau range, in which the BIN-11 is more elastic than BIN75-8, judging from the relative low tan δ value of BIN-11.

Besides, the disruption effect of ionic groups on the order of hard domain could be manifested by the decrease of rubbery region extension with increasing ionic group content as shown in Figure 5. The short rubbery plateau region is due to the insufficient reinforcing effects from the hard segments. In addition, the first decrease and the subsequent increase trends in E' rubbery plateau shown in Figure 5(b) aforementioned in BIN series might be also due to the disruption effect induced by ionization and the compensation of the increased cohesion caused by Coulombic force. In NMDA series, the E' plateau continuously decreases with the increase of ionic group content. Therefore, it illustrates that the disruption of the order of hard domain induced by ionic component insertion within hard segment should be predominant in this case.

Cyclic thermomechanical investigation

Shape memory effect of segmented PU films with ionic groups on hard segments can be studied with cyclic tensile test with emphasis on the cyclic hard-

ening caused by the orientation of PU segments during extension. The stress–strain relationship of the segmented PU film becomes stable after several cycles and with no significant variation in further cycles as reported before.[4,12–14,17] It can be explained with the destruction of weak netpoints in the initial several cycles in deformation process, and the subsequent formation of ideal elastic network.[1]

Chen has reported that the incorporation of ionic extender during synthesis, to some extent, disrupts the order of hard domain,[16] which also can be observed from the resulting data of DMA in this study. Whereas the hard domain is usually considered as having a physical crosslinking structure in the two phase morphology, contributing the overall thermal stimulated deformation recovery process as fixed phase.[4,12,30–32] Therefore, the insertion of ionic groups in hard segment possibly has the huge influence on the shape memory function. Moreover, the Coulombic force among ionic groups might partly compensate the loss of physical crosslinks among hard segments caused by disruptive effect of ionization. Based on the analysis by DMA and DSC for the two series of SMPU cationomers, the effect of ionic group content on the shape memory property in segmented PU cationomer might be illustrated as follows: Figures 9 and 10 demonstrate the cyclic stress–stain behavior of the NMDA and BIN series. The characteristics of shape memory properties on segmented PU ever reported by other researchers,[4,33] such as strain hardening and insensitivity of cyclic property with cycle number can also observed in our investigation. According to the feature of cyclic thermal tensile test on shape memory polymer, the stress–strain relations can be seen in the first several cycles. The quantitative comparison of shape memory effect in this study was made solely by examining the second cycle and the parameters such as

TABLE IV
T_{gh} **of Hard Segment of BIN Series Detected from the Peak of Loss Tangent (tan δ)**

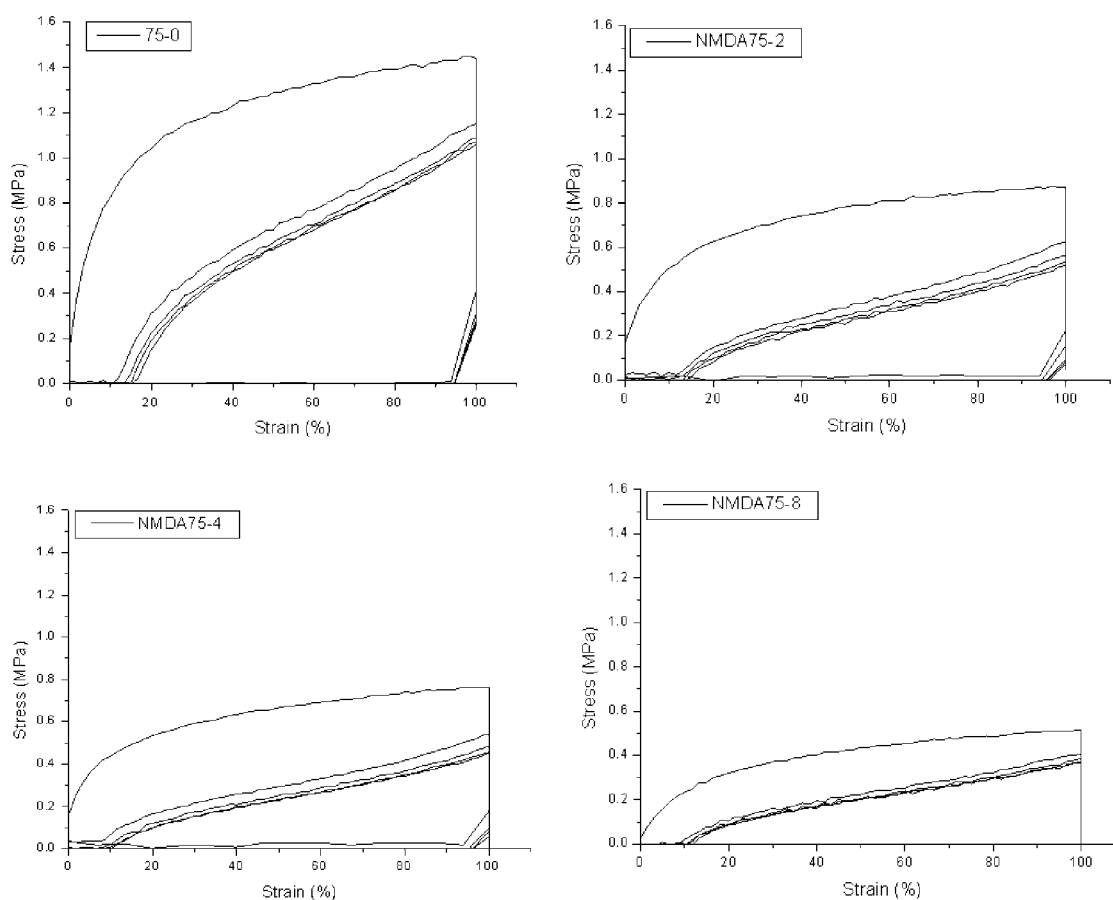| Sample no.	75-0	BIN75-4	BIN75-6	BIN75-8	BIN75-11
T_{gh} (°C)		158.87	136.15	130.52	132.87

Figure 9 Cyclic tensile behavior of NMDA series SMPU cationomer.

stress at 100% elongation, recovery ratio (R_r) and fixity ratio (R_f).

Firstly, we can observe that the ionic group content has large influence on the stress at 100% elongation for the two series. Figure 11 shows the effect of variation of ionic group content on stress at 100% elongation in the second tensile cycle, illustrating that the stress in BIN series was decreased with BIN content initially, and subsequently increased, which is consistent with the variation trends of E' at rubbery plateau in DMA analysis. For NMDA series, the stress values decrease with increasing NMDA content monotonously. In general, the stress in NMDA family is lower than that of BIN family, suggesting the presence of neutralized NMDA into hard segment offers more adverse effect to the order of hard domain in comparison with that from BIN. Therefore, the BIN series SMPU cationomer can withstand higher tensile force in deforming process, whereas in NMDA series, samples are readily deformed at higher temperature.

Figure 12 shows the dependency of fixity ratio and recovery ratio on the NMDA and BIN contents in SMPU cationomer in the second tensile testing cycle. In the NMDA series, the fixity ability of speci-

mens to temporary deformation can be improved effectively with incorporation of ionic groups. Increasing NMDA content from 0% to the maximum allowable value causes the fixity ratio to increase from 93.87 to 100%, meanwhile facilitating the recovery ability. On the other hand, for BIN series, the fixity ratio was not affected significantly by the BIN content, although the presence of neutralized BIN can give rise to a higher crystallinity of soft segment (as shown in Table III). The recovery ratio in BIN family initially increased from 88.43 to 91.76% and subsequently decreased to 88.43%. The variation in the recovery ratio in this series is not significant.

Comparison between the result of cyclic tensile test of the NMDA and BIN families suggests that the categories, together with the content of ionic group have huge influence on the shape memory properties of SMPU cationomer. In the BIN series, the cationic groups are formed from the quaternization of pyridine ring in BIN[34] regardless of the presence of the amine group in the polymer backbone. Instead, in the NMDA series, the cationic groups are located in the backbone.[16] In our specimens studied, the cationic moiety in the backbone (NMDA) seem to decrease the extent of the order of the hard domain
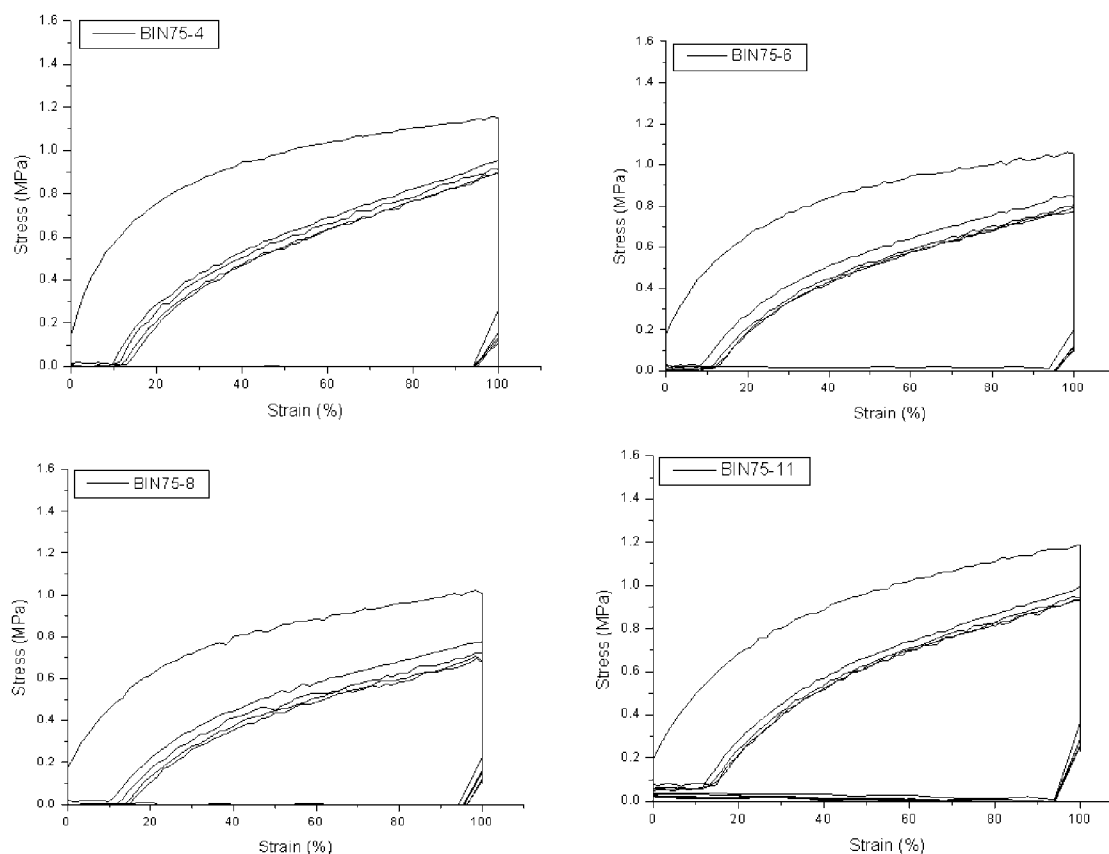
Figure 10   Cyclic tensile behavior of BIN series SMPU cationomer.

and cause more loss of the elastic modulus of the sample at a temperature higher than T_{ms} detected with DMA. Coming back to the BIN series, in addition to the physical crosslinking points, the Coulombic force induced by the cationic pendant groups might be strong enough to compensate the loss of the cohesion owing to the disruptive effect of ioniza-
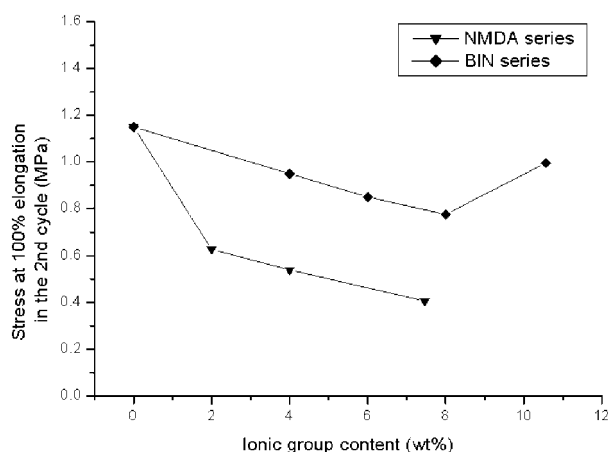

Figure 11   Stress at 100% elongation in the second tensile cycle of NMDA and BIN series.

tion aforementioned, and then withstands the relative high load in the cyclic test. However, it is hard to give an explicit explanation about the variation of fixity ratio in BIN series SMPU ionomer compared with that of NMDA series. Usually the crystallization of soft segment is regarded as being responsible for memorizing the temporary deformation. In NMDA series SMPU ionomer, the fixity ratio substantially increased with NMDA content owning to the higher crystallinity as shown in Table III. Therefore, in BIN series, the higher crystallinity induced by ionic groups was expected to give rise to higher fixity ratio for the temporary deformation. Nevertheless, the fixity ratio is almost unchanged when BIN weight content increased from 0% to the maximum allowable value. Actually, from the reported literature about the molecular mechanism of the shape memory effect of polymer, we can know that, if the thermal transition chosen to fix the deformation is the melting temperature of soft segment, the strain-induced crystallization of soft segment can be initiated by cooling process.[1] After deformation, the crystallite of soft segment prevents the immediate recovery to the coil-like structure or the permanent shape defined by the netpoints of fixed phase. Therefore, the fixity and recovery ability usually called
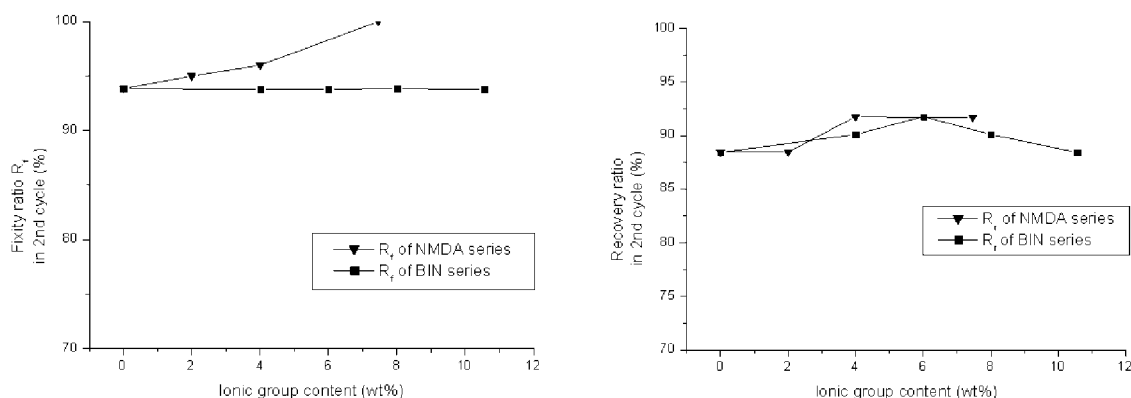
Figure 12 Fixity ratio and recovery ratio in the second tensile cycle of NMDA and BIN series.

'memory effect' is closely related to not only the crystallinity of soft segment, but the trends to the return to the original shape. In our two series SMPU ionomer, though the crystallinity of soft segment is increased significantly with ionic groups, the effect of ionic group within hard segment on the cohesion among hard segments is not neglectable. Because the stronger cohesion among hard segments possibly causes the higher recovery ability, it meanwhile leads to more difficulty in fixing the temporary deformation. Therefore, in the case of BIN, the fixity ratio is not improved significantly even the crystallinity of soft segment is enhanced. So, it is noticeable that the physical crosslinking among hard segments has deep influence on the fixity ability.

CONCLUSIONS

PCL-based segmented PU cationomer series were synthesized to study the effect of cationic groups within hard segments on the shape memory effect, with emphasis being on the shape recovery and fixity ability of the segmented PU cationomer films. DMA and DSC results suggest that the two PU series exhibit improved crystallizability by the presence of cationic groups; on the other hand, the cationic groups on hard segments enhance the cohesion among them through the Coulombic force compared with the corresponding PU noncationomer. The cationic groups on hard segments play a two-fold effect: (i) the disruption of the order of hard domain, and (ii) the enhancement of cohesion among hard segments. The effect of cationic groups on the hard segments is manifested by the reduction of the stress in sample at 100% elongation at high temperature and the depression of the overall rubbery state modulus. Cyclic tensile test result suggests that when the cationic groups in the NMDA series, both the fixity ratio and recovery ratio can be improved simultaneously. However, in the BIN series, cationic pendant groups

have less effect on the fixity ratio and shape recovery ratio. Our studies demonstrate that the content and category of cationic group have deep influence on the shape memory effect in segmented PU cationomer. This article reports a simple methodology for the design of novel shape memory PU cationomers with specific tailored shape memory function.

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