Thermosetting Polyurethanes with Water-Swollen and Shape Memory Properties

WEI CHEN,[1] CHENGYE ZHU,[2] XUERONG GU[2]

[1] Center for Research on Surface and Interface Chemical Engineering and Technology, Nanjing University, Nanjing, 210093, People's Repulic of China

[2] Department of Polymer Science and Engineering, Nanjing University, Nanjing, 210093, People's Republic of China

ABSTRACT: A series of shape memory polyurethanes (SPU) with different component ratio of PEG, MDI, BDO, and crosslinker DEA were synthesized by stepwise polymerization in DMF. WAXD, SAXS, DMTA, and DTA were used to study the microphase structure of SPU. No obvious phase-separation and crystalline evidence of the PEG soft segment and hard segment were obtained in this work. The water-swollen ratio increases with both the increasing molecular weight of PEG soft segment and the decreasing density of the chemical crossbonding. All the samples show good thermally stimulated shape memory properties. When the molar ratio of soft segment to hard segment is close, the shape recovery time reduces along with the increasing density of the chemical crossbonding. When the densities of the chemical crossbonding are similar, the shape recovery time reduces with the increasing molecular weight of the PEG soft segment. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 1504–1512, 2002; DOI 10.1002/app.10357

Key words: polyurethanes; swelling; thermal properties

INTRODUCTION

Shape memory polymers (SMP) are a novel class of functional materials that developed quickly in the last decades. Among them, the thermally stimulated shape memory polymers, whose shape can be easily changed and resumed through the temperature domination, have tremendous potential applications in the fields of medical treatment, health service, packing and architectural industry.[1,2]

Because it is easy to design special polyurethane (PU) to meet the practical needs by altering the type and the ratio of the components, PU becomes naturally an important category of SMP. The relationship between the microstructure of thermoplastic PU and its thermally stimulated shape memory properties has been widely studied recently.[3–6] Moreover, the commercial products of thermoplastic polyurethane with shape memory properties are available.[2] However, there are few reports about the thermosetting shape memory polyurethane (SPU).

The thermosetting SPU not only has the stronger stress of shape recovery than the thermoplastic one, but also can easily form hydrogel by inducing hydrophilic soft segment or ionic groups. The similarity of hydrogel to organic tissues has been well known for a long time, and the research on hydrogel with shape memory properties has received much attention in recent years.[7,8] However, in the case of synthesis, most crosslinked

polymers, for example, polyacryamides, polyacrylates, polyvinylalcohols[9], and their graft copolymers or interpenetrating networks with PU,[10,11] are synthesized through radical polymerization, while other methods of synthesizing PU hydrogel by using hydrophilic soft segments or inducing hydrophilic groups to the backbone of chain, are seldom used.

However, it is expected that PU materials with both the shape memory and the hydrogel properties should have very wide prospects of the application in the area of medical treatments and health services. In this work, we successfully synthesized a series of PU materials with different chemical crosslink densities by using poly(ethylene glycol) as the soft segment. The effects of the microstructure on water absorptivity and thermally stimulated shape memory properties were discussed.

EXPERIMENTAL

Materials

4,4′-Diphenylmethane diisocyanate (MDI) and 1,4-butanediol (BDO) were purified by vacuum distillation. Poly(ethylene glycol) (PEG) and diethanolamine (DEA) were dehydrated by refluxing with toluene (toluene was then removed by vacuum distillation), and dried in a vacuum oven at 20°C for 24 h; molecular weights (M_n) of PEG were determined with VPO. N,N'-Dimethylformamide (DMF) was dried with molecular sieves and purified by vacuum distillation. Stannous octoate catalyst was used as received.

Sample Preparation

A series of SPU were synthesized from PEG, MDI, BDO, and DEA by a three-step method. The prepolymer was prepared by reacting stoichiometric MDI with PEG and 2‰ of catalyst in DMF at 50–60°C for 1–1.5 h with the continuous pass of dry nitrogen gas. The process of reaction was determined by using a standard di-n-butylamine back titration method.[12] After the theoretical NCO value reached, the reaction mixture was heated up to 70°C, and BDO was added dropwise. This chain extension step was also determined by the titration method mentioned above. When the theoretical NCO value reached, the temperature was lowered down to 50°C and the DMF solution of DEA was rapidly added into the system with

vigorous stirring. The resulted viscous liquid was then poured into a preheated Teflon mold with a cover plate. The mold was shifted into a vacuum oven. After continuing reaction in the mould at 80°C for 4 h, the cover plate was taken away and the solvent was removed by slowly decompressing evaporation. All the dried films were immersed in water for 2 days to extract small molecules and dried in vacuum oven at 60°C for 1 week.

The molar-ratio values of raw materials and the content of soft segment and cross linker of samples are shown in Table I. The samples are referenced in this reports by a letter P (polyurethane) with a subscript, which means the soft segments molecular weight in hundreds, and by the molar ratio of MDI, PEG, BD, and DEA. For example, the P_4 3 : 2 : 3/4 : 1/6 represents a PU sample that has PEG400 as the soft segment, and its molar ratio of MDI, PEG, BD, and DEA is 3 : 2 : 3/4 : 1/6.

Characterization

WAXD and SAXS

Wide-angle X-ray diffraction and small-angle X-ray scattering were performed with a Rigaku D/MAX-RA rotating anode X-ray generator with a copper target at 40 kV or 50 kV cathode potential and 50 or180 mA emission current, respectively. The X-rays were collimated into a beam (10 mm × 70 μm) with a Kratky camera, and the scattered X rays were detected with a Sc-30 scintillation counter probe. Cu Kα X-rays were selected by detector pulse-height analysis.

DMTA

Dynamic mechanical investigation was performed using a Rheovibron DDV-II dynamic viscoelastometer (TOYO Baldwin Co.) over a temperature range from −50 to 150°C, with a heating rate of 2°C/min and a working frequency of 110 Hz.

DTA

Differential thermal analysis was carried out over a temperature range from 25 to 200°C, using a CDR-1 differential thermal analyzer at a heating rate of 5°C/min. The standard substance was Al_2O_3.

Measurement of Equilibrium Swelling Ratio

Preweighted dry square films were immersed in DMF or water respectively at 40°C and periodi-

Table I Formulation of Shape Memory Polyurethanes

| | | | | Molar Ratio | | | | Weight Ratio (%) | |
| | | | | | PEG | | | | |
Sample	MDI	BD	DEA	400 (360)	780 (800)	1870 (2000)	Soft segment	Cross linker
P$_4$ 3 : 2 : 1 : 0	3	1	0	2			46.15	0
P$_4$ 3 : 2 : 3/4 : 1/6	3	3/4	1/6	2			46.3	1.1
P$_4$ 3 : 2 : 1/2 : 1/3	3	1/2	1/3	2			46.45	2.2
P$_4$ 3 : 2 : 1/4 : 2/4	3	1/4	2/4	2			46.6	3.4
P$_4$ 2 : 1 : 1/2 : 1/3	2	1/2	1/3	1			38.3	3.7
P$_4$ 4 : 3 : 1/2 : 1/3	4	1/2	1/3	3			50	1.6
P$_4$ 5 : 4 : 1/2 : 1/3	5	1/2	1/3	4			52	1.3
P$_8$ 3 : 2 : 1 : 0	3	1	0		2		65.0	0
P$_8$ 3 : 2 : 3/4 : 1/6	3	3/4	1/6		2		65.1	0.7
P$_8$ 3 : 2 : 1/2 : 1/3	3	1/2	1/3		2		65.3	1.5
P$_8$ 3 : 2 : 1/4 : 2/4	3	1/4	2/4		2		65.4	2.2
P$_8$ 3 : 2 : 0 : 2/3	3	0	2/3		2		65.5	2.9
P$_8$ 2 : 1 : 1/2 : 1/3	2	1/2	1/3		1		57.4	2.6
P$_8$ 4 : 3 : 1/2 : 1/3	4	1/2	1/3		3		68.4	1.0
P$_8$ 5 : 4 : 1/2 : 1/3	5	1/2	1/3		4		70.1	0.8
P$_{20}$ 3 : 2 : 1 : 0	3	1	0			2	81.7	0
P$_{20}$ 3 : 2 : 0 : 2/3	3	0	2/3			2	82.0	1.54
P$_{20}$ 2 : 1 : 1 : 0	2	1	0			1	76.0	0
P$_{20}$ 2 : 1 : 0 : 2/3	2	0	2/3			1	76.6	2.87

The listed figures in the brackets are PEG's molecular weights determined with VPO.

cally (every 4 h or 1 day) removed from the solvent, blotted with laboratory tissue, and weighted until the constant weight was achieved.

The equilibrium swelling ratio in DMF and water were expressed as Q and q, respectively.

$$Q(q) = W_2/W_1 \times 100\%$$

where W_1 is the the weight of dry sample and W_2 is the the weight of achieved equilibrium swelling sample.

Measurement of Shape Memory Property

Fully water-swollen films were carefully cut into narrow strips with the dimension of 3.5 × 0.3 × 0.2 cm. A 2 cm-long region in the middle part of the strip was marked and elongated to 3 cm in a 60°C water bath. Then the strips were fixed by clamps in both ends on glass plates with a scale and putted into a low-temperature bath. After 15 min, the clamp was removed from one end. If the length of the strip was kept constant, which indicated that the temperature of the bath must be below the sample's T_g, the strip was immediately

shifted into a thermostatic bath and the recovery time was recorded.

RESULTS AND DISCUSSION

Morphology

To make clear the relationship between the shape memory function and the morphological structure of our PU samples, the morphology was studied through WAXD, SAXS, DMTA, and DTA.

WAXD

As shown in Figure 1, the testing of all the PU samples resulted in a broad diffraction peak at 2θ from 5° to 30°, which is characteristic of amorphous polyether.[13] Because no sharp diffraction peak that indicates crystal structure is found, we conclude that under the condition of this study, no crystal structure was formed in both the soft and the hard segments of the obtained PU. This is probably because both the hard and the soft segments (except that of the P$_{20}$ series) in the series

samples are relatively short, and the interaction between soft and hard segments—the hydrogen bond is relatively strong, which make the microphase separation of soft and hard segments not well conducted. The hard segments do not aggregate mutually and arrange orderly, and cannot form a crystal structure. The soft segments, unlike pure PEG, cannot crystallize well either, because they are tied up by hard segments, the crosslinker, and the hydrogen bonds, which prevent them from being nicely arranged. The soft segment's length is the shorter, and the content of cross linker is the higher; the bigger is the effect tied up in the soft segments, and the smaller is the probability of the ordered arrangement among the soft segments, i.e., the lower is the degree of short-range order.

SAXS

The results of small-angle X-ray scattering (SAXS) show that the scattering curves of all the samples are similar, with the only exception of the increasing tendency of the descend in the curve tail along with the increasing content of the soft segments and the decreasing content of the crosslinker. As shown in Figure 2, the tail of $P_{20}3$: 2 : 1 : 0 descends slowly, while that of $P_{4}3 : 2 : 0$: 2/3 is almost parallel to the crossaxle. A diffraction peak at $2\theta \approx 0.4-0.7°$ typically should be observed for PU. The more perfect the phase separation, the sharper the peak, which is caused by the diffraction between the hard segments and the soft segments domains of PU.[14] However, this kind of peak doesnot appear in the SAXS curves

Figure 2 SAXS pattern of three PU samples with different components.

of all our samples, which indicates there is no obvious microphase separation in these PU samples. The reason is probably that the same is as described above in WAXD. All the samples in this study have relatively short hard segments, and because proportion of the oxygen atom in soft segments is high, the formation probability of hydrogen bond with the hard segments is great. These reasons make the hard segments disperse in soft segments instead of aggregating and forming a domain. But the probability of the close arrangements of two or three hard segments cannot be eliminated. The reason for the small changes in the curve's tail along with the altered composition is still unclear.

DMTA

DMTA results are expressed as the loss tangent (tan δ) vs. temperature. Over the temperature range from −50 to 160°C, each sample has an α peak at low temperature. It has been widely accepted that the peak should be attributed to the glass transition of PU's soft segments,[3,10] and the corresponding temperature is the soft segment's glass transition temperature. The glass transition temperatures of several sample groups are listed in Table II. From these data it is clear that glass transition temperature decreases with the increase of soft segment PEG's molecular weight when the composition ratio is the same. As shown in Figure 3, the glass transition temperature of $P_{20}3 : 2 : 0 : 2/3$ is 34°C lower than that of $P_{8}3 : 2$: 0 : 2/3, and 84°C lower than that of $P_{4}3 : 2 : 0$: 2/3. The glass transition temperature also decreases along with the increase of soft segment's
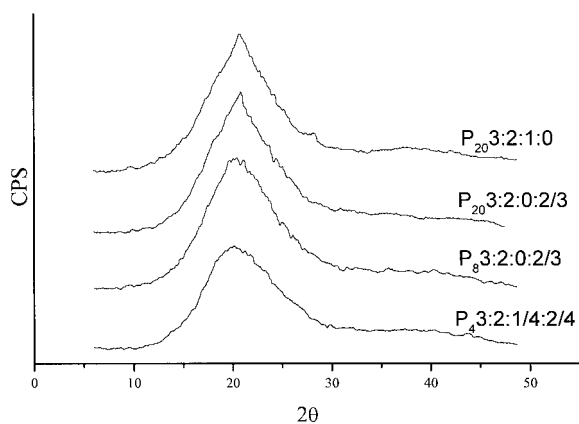

Figure 1 WAXD pattern of three thermosetting PUs with different molecular weights of PEG and a thermoplastic PU. Note that each curve has been successively shifted by 500 CPS for clarity.
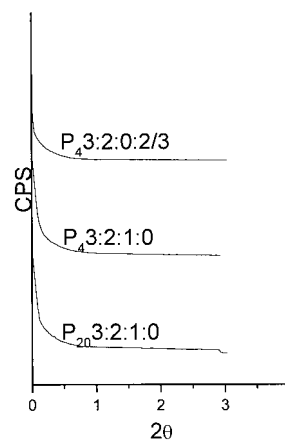
Table II The Temperature of α Peaks (T_g) from DMTA

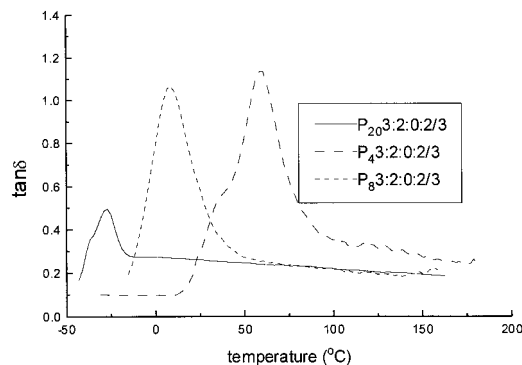| Sample	P_4 3:2:1:0	P_4 3:2:1/2:1/3	P_4 3:2:0:2/3	P_4 4:3:1/2:1/3	P_8 2:1:1:0	P_8 3:2:1:0	P_8 3:2:0:2/3	P_{20} 2:1:1:0	P_{20} 2:1:0:2/3	P_{20} 3:2:0:2/3
T_g (°C)	36	45	56	43	2	−19	7	−25	−12	−27

Figure 3 DMTA spectra of three samples with the same molar ratio of components and differnt molecular weights of PEG: tan δ–T curves.

content. For example, $P_8$2 : 1 : 1 : 0 with 57% of the soft segment has a T_g of 2°C, while $P_8$3 : 2 : 1 : 0 with 65% of the soft segment has a T_g as low as −19°C. When the ratios of soft segment to hard segment are similar, T_g raises as the crosslinker's content increases. As shown in Figure 4, the T_gs of crosslinked $P_4$3 : 2 : 0 : 2/3 and $P_8$3 : 2 : 0 : 2/3 are higher than those of the corresponding linear ones—$P_4$3 : 2 : 1 : 0 and $P_8$3 : 2 : 1 : 0 by 20 and 26°C, respectively.

All the results indicate that the movement of soft segment is tied up by the hard segment. When the soft segment is shorter or the content of the hard segment is higher, the force is stronger and the necessary energy to overcome the resistance is higher, or the soft segment–hard segment phase separation is less distinct.[5,6] As a result, T_g moves toward a higher temperature. At room temperature, the series samples of P_4 exist in their plastic form because of the low molecular weight of their soft segments. The resistant effect
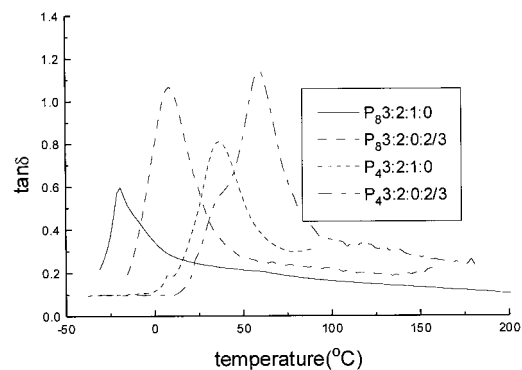

Figure 4 DMTA spectra of the thermoplastic PU and thermosetting PU: tan δ–T curves.

from the crosslinker is bigger than that from the hard segment's content and the length of the soft segment, because crossbonding limits the space situation of the chain segments.

DTA

Each sample shows an endothermic peak (which is assumed as a β peak) in the DTA spectrum over a range from room temperature to 160°C. The corresponding temperature of the β peak is listed in Table III.

From the data in this table, it is clear that the molecular weight and content of the soft segment have little effect on the position of the β peak. Along with the increase of the soft segment PEG's molecular weight, the β peak moves a little toward low temperature. The effect from the crosslinker's content are almost not noticed. These results are in accordance with the DSC result from Takahashi[3] in which the series SPU are synthesized from MDI, BDO, and low molecular weighted PEA. They are also in accordance with Foks's DSC results of the PU films cast at different temperatures.[15] However, the attributions of this β peak are not agreed upon among scientists. Cooper thought it should be attributed to the dissolving of short-range order in the hard segments domain of PU,[16] T. Takahashi assigned them to the glass transition of hard segments,[3] while Foks thought they should be attribute to the melting of the crystal in the soft segments.[15] The peak is also attributed to the endotherm of dehydration in the polymer.[17]

To check the attribution of this peak, we immersed the samples in 60°C water for 24 h, then used DTA to analyze them with corresponding dry ones under the same condition, and found the situation and the shape of the β peak in the wet samples were not changed while a big endotherm peak (γ peak) appeared at approximately 95°C (Fig. 5). We also treated samples by annealing them at 135 or 150°C for 2 h, and performed the DTA tests under the same condition as the corresponding untreated ones. The result showed both the annealed and the untreated samples had almost the same DTA curves, and the position of the β peak was not altered. The phenomenon of this peak's movement to higher temperature after annealing, which was described in Cooper's article, did not emerge in our experiments. So this β peak cannot be attributed to water. It cannot be attributed to the short-range disorder of hard segments in the hard segment domain either, i.e.,

Table III The Temperature of β Peaks from DTA

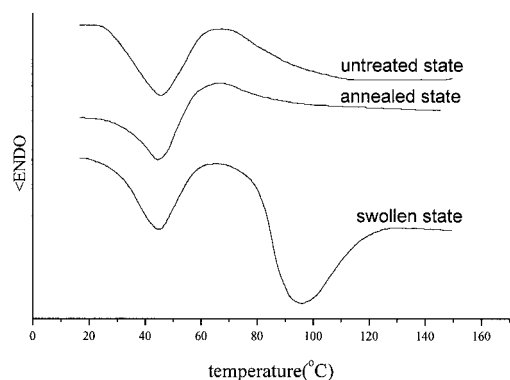| Sample	P_4 3:2:1:0	P_4 3:2:1/4:2/4	P_4 3:2:0:2/3	P_4 2:1:1/2:1/3	P_8 3:2:1:0	P_8 3:2:1/4:2/4	P_8 3:2:0:2/3	P_{20} 3:2:1:0	P_{20} 3:2:0:2/3
T (°C)	49	50	50	49	48	49	49	44	45

Figure 5 DTA curves for dry and wet samples of $P_{20}3$: 2 : 0 : 2/3.

there is no hard segment domain in our samples, which is consistent with the result of SAXS. Because the result of WAXD discussed above indicates that both the hard and the soft segments are not crystallized, this β peak cannot be attributed to the melting of the soft segment's crystal. We attribute this peak to the dissociation of the interaction among two or three hard segments. This interaction also can be called the glass transition of the hard segments.

As shown in Figure 6, the movement of chain segments along with the change of temperature is inferred as follows. When the temperature is raised up to a certain degree, the soft segments begin to move, while the relative positions of hard segments are unaltered, i.e., the hard segments are not moved at that temperature. When the temperature is raised to a higher degree, the hard segments (two or three of them are aggregated together) overcome the interaction among themselves and begin to move with the soft segments.

Degree of Swelling in DMF (Q) and Water (q)

DMF is a good solvent for PU. The result of swelling experiment shows all the samples achieve their swelling balance in 12 h at room temperature. The degrees of swelling (Q) of all the samples are listed in Table IV.

The result shows that the samples without the crosslinker dissolved completely, while the ones with a crosslinker were swollen. The degree of swelling (Q) decreases along with the increase of the crosslinker's content in the series of polymers with the same PEG molecular weight. For samples with the same component of molecular ratio, Q increases with the raising of the PEG molecular weight. The later two situations are actually the

same in the relationship between Q and crosslinker's density, i.e., Q increases when the relative content of the crosslinker decreases, which induces the increase of average molecular weight between two crosslinked points (Mc).[18] From these results, it seems that the polymerization is progressed according to the feeding ratio and the sequence. The products' components are well distributed.

All the samples are also immersed in water. Their time to achieve swelling balance and the balanced water swelling ratio (q) are listed in Table IV. Figure 7 shows the q curves of samples with different Mc vs. time. The first pair of samples are P_43 : 2 : 1/4 : 2/4 and P_83 : 2 : 0 : 2/3, the second pair are P_43 : 2 : 3/4 : 1/6 and P_84 : 3 : 1/2 : 1/3, and the third pair are P_83 : 2 : 1/2 : 1/3 and $P_{20}3$: 2:0 : 2/3. The samples in each pair have similar Mc.

From Table IV and Figure 7, we concluded that: (1) in the samples with similar Mc, equilibrium swelling ratio of water (q) increases and the time to achieve balance reduces along with the increase molecular weight of the soft segment PEG. The samples with PEG molecular weight less than 2000 have a equilibrium q less than 130%, while the samples of PEG 2000 have a balanced q greater than 150%. (2) When the contents of soft segment are close, water swelling ability increases with the increase of Mc. For example, the soft segment contents of P_83 : 2 : 3/4 : 1/6 and P_83 : 2 : 0 : 2/3 are close (65.1 and 65.5%, respectively), but because their Mc are different (the former is 9510 while the later is 2310), their q values are 122 vs. 114%, respectively.

From the structure analysis above, we can draw the conclusion that there is no crystal in
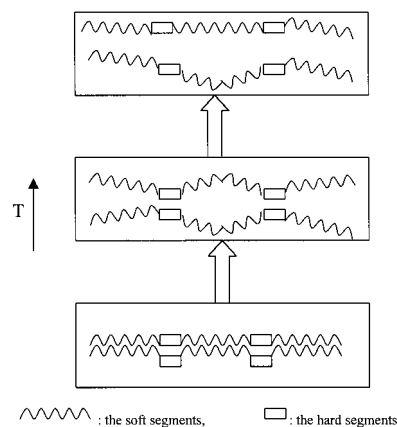

$\diagup\!\diagdown\!\diagup\!\diagdown$: the soft segments, $\square$: the hard segments

Figure 6 Scheme of chain segment movement.

Table IV The Equilibrium about Swelling Ratio in DMF and with Respectively, the Time of Equilibrium about Water Absorption and the Time of Shape Memory for the Various Samples
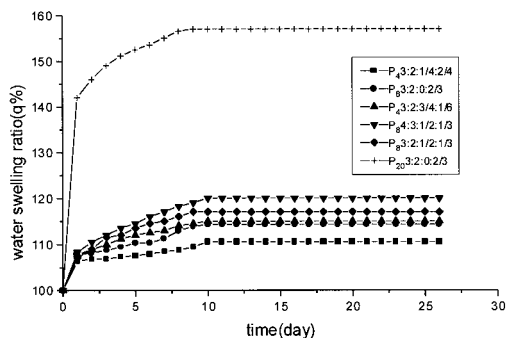
Sample	Q (%) (in DMF)	q (%) (in Water)	t^a (Days)	Times of Shape Recovery (sec.)		Mc
				70°C	t_2^b	
P_4 3 : 2 : 1 : 0	dissolved	122	10	36.8	19.9	—
P_4 3 : 2 : 3/4 : 1/6	900	115	10	30.9	18.0	6150
P_4 3 : 2 : 1/2 : 1/3	610	113	11	15.7	9.9	3030
P_4 3 : 2 : 1/4 : 2/4	440	111	13	13.2	6.1	2250
P_4 2 : 1 : 1/2 : 1/3	231	108	12	12.0	9.4	1810
P_4 4 : 3 : 1/2 : 1/3	710	116	11	18.7	16.3	4250
P_4 5 : 4 : 1/2 : 1/3	1140	123	10	23.1	17.9	5470
P_8 3 : 2 : 1 : 0	dissolved	119	10	20.3	28.4	—
P_8 3 : 2 : 3/4 : 1/6	1140	122	10	15.6	19.3	9510
P_8 3 : 2 : 1/2 : 1/3	680	117	9	7.9	13.5	4710
P_8 3 : 2 : 1/4 : 2/4	612	116	9	7.8	10.5	4010
P_8 3 : 2 : 0 : 2/3	480	114	12	5.8	7.4	2310
P_8 2 : 1 : 1/2 : 1/3	421	108	13	4.1	10.6	2650
P_8 4 : 3 : 1/2 : 1/3	1000	120	10	12.1	16.8	6770
P_8 5 : 4 : 1/2 : 1/3	1220	127	8	15.0	21.5	8830
P_{20} 2 : 1 : 1 : 0	dissolved	148	6	13.5	23.6	—
P_{20} 3 : 2 : 0 : 2/3	1500	158	7	3.7	6.7	4750

[a] The time to get water-absorb equilibrium.
[b] It was 80°C for the P_4 series, 50°C for the P_8 and P_{20} series.

both the soft and the hard segment. The polymers are amorphous. Because the soft segments consisting of PEG are hydrophilic while the hard segments consisting of MDI and BDO are hydrophobic, the absorptivity of water depends on the association through hydrogen bonds between the oxygen atom of PEG chain and the hydrogen atom of water. As previously confirmed, because the soft segments do not crystallize under the experiment condition in this work, the quantity of the absorbed water increases with the increase of soft segment content. The greater the PEG's molecu-

lar weight, the smaller effect affected by hard segments' hydrophobic ability and the greater is the water absorptivity. On the other hand, when crosslink's density is higher, the limitation of the soft segments' movement is bigger, which makes it difficult to provide enough free volume for association with water. So the absorptivity of water decreases. All the results also indicate bigger balanced water absorptivity is obtained with minor extent of phase separation.[5] Because the lower the soft segment content, the smaller the PEG molecular weight and the higher the cross linker's density, the minor is the soft segment-hard segment phase separation.

The Function of Shape Memory

All of our samples have shape memory function.

The samples with fixed deformation through low temperature are put into a thermostatic bath with a temperature of 70°C or T_2. The recovery time is listed in Table IV. (T_2 is 80°C for the P_4 series and 50°C for the P_8 and P_{20} series.)

It can be easily stated that the recovery time is in inverse ratio with the recovery temperature. The reason lies in that the higher temperature can provide more energy, which accelerates the

Figure 7 Time-dependent water swelling ratio of three groups of samples.

relax rate of the chain segment. As to the series samples with the same PEG molecular weight, the recovery time decreases along with the increase of crosslinker's content in the molecule (or the decrease of Mc). But when Mc are similar, the recovery time at 70°C decreases with the increase of the soft segment's length (e.g., the molecular weight of PEG). For example, the Mc of $P_4 4 : 3 : 1/2 : 1/3$, $P_8 3 : 2 : 1/2 : 1/3$, and $P_{20} 3 : 2 : 0 : 2/3$ are similar (about 4500), while the shape recovery time is 18.7, 7.9, and 3.7 s, respectively. That is to say, the moving rate of the chain segment with high molecular weight PEG is faster than the one with low molecular weight PEG.

Because the substance of the shape memory process is an entropically elastic rejuvenation of rubber, the recovery rate is determined by the intensity of the recovery stress. The samples with higher content of crosslinker have shorter recovery time because the elastic recovery stress of the chemical crosslinking bond is stronger than that of the physical bond. As to the segments with similar Mc, the higher the contained PEG's molecular weight, the lower the necessary energy for the segments' movement (this has been confirmed by the results of DMTA) and the shorter the recovery time at the same temperature. The reason is the same with what has been used above to explain why the higher the recovery temperature, the shorter the recovery time.

CONCLUSION

1. The designed PU materials with PEG soft segments were synthesized in the presence of diethanolamine as a crosslinker by the stepwise polymerization in DMF. Because of the short hard segments and the strong interaction between the soft and hard segments, the microphase separation in all samples is not observed, and there is no crystal structure of soft or hard segments.
2. All the PU samples have water absorptivity that increases with the increase of soft segment's content and the decrease of crosslink density.
3. All the PU samples have thermally stimulated shape memory property. The recovery time reduces with the increase of chemical crosslink's density when the ratios of the soft segment to the hard segment are similar. It also reduces with the increase of PEG molecular weight when the chemical crosslink densities are similar.

REFERENCES

1. Hayashi, S.; Kondo, S. Plastics Eng 1996, 2,29.
2. Lee, C.; Hwang, J.; Chae, B. U.S. Pat. 5,442,037 (1994).
3. Takahaxhi, T.; Harashi, N. J Appl Polym Sci 1996, 60,1061.
4. Li, F.; Zhang, X.; Hou, J.; Zhu, W.; Mao, X.; Luo, X.; Mao, D. Acta Polym Sinica 1996, 8, 45.
5. Jeong, H. M., et al. J Polym Sci Polym Phys 2000, 38, 3009.
6. Kim, B. K., et al. J Polym Sci Polym Phys 2000, 38, 2652.
7. Osada, Y.; Matsuda, A. Nature 1995, 376, 219.
8. Matsuda, A.; Sato, J.; Yasunage, H.; Osada, Y. Maracomolecules 1995, 27, 7695.
9. Toshihiro, H. Kobunshi 1991, 40, 524.
10. Ying, Y.; Gu, X. R.; Yang, C. Z. J Appl Polym Sci 1999, 70, 1047.
11. Kim, B. K.; Park, S. H. J Polym Sci Polym Chem 1999, 37, 2703.
12. David, D. J. Analytical Chemistry of Polyurethane; Wiley-Interscience: New York, 1969.
13. He, X.; Jia, X.; Yu, X. J Appl Polym Sci 1994, 54, 207.
14. Yang, C. Z.; Grasel, T. G.; Bell, J. L.; Reghter, R. A.; Cooper, S. L. J Polym Sci Polym Phys 1991, 29, 581.
15. Foks, J.; Jonik, H.; Russo, R. Eur Polym J 1990, 26, 309.
16. Soymour, R. W.; Cooper, S. L. Maracomolecules 1973, 6, 48.
17. Brozoski, B. A. Maracomolecules 1984, 17, 230.
18. Flory, P. J. Principles of Polymer Chemistry; Cornell Univ. Press: New York, 1953.