Study on the Liquefied-MDI-Based Shape Memory Polyurethanes

Qi Cao,[1] Shaojun Chen,[1,2] Jinlian Hu,[2] Pengsheng Liu[1]

[1]Institute of Polymer Science and Engineering, College of Chemistry, Xiangtan University, Xiangtan, Hunan 411105, People's Republic of China
[2]Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hung Hum, Kowloon, Hong Kong, People's Republic of China

ABSTRACT: A series of liquefied-MDI-based polyurethanes having shape memory behavior, with various soft segments, chain extenders, and micro-phase separation promoters were synthesized. Their morphology and properties were investigated in terms of thermal properties, dynamic mechanical properties, and shape recovery behavior. The results indicate that the soft segment formed with longer chain segment incline to crystallize during the cooling scans and the resulting SMPU have the higher crystallinity. Meanwhile, the chain extenders, which can enhance the polarity of hard segment, incline to have excellent shape memory properties with bigger storage modulus in rubbery state too. It was also found that the micro-phase separation promoters have great influence on the shape memory behavior due to the enhancement of micro-phase separation of SMPU. Furthermore, it was proved again that SMPU with longer soft segment and lower hard segment contents usually showed good shape memory behavior. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 993–1000, 2007

Key words: polyurethane; shape memory; molecular design; micro-phase separation; liquefied-MDI

INTRODUCTION

Material scientists predict a prominent role of intelligent materials in the future. In the last few years, this concept has been found growing interest as a result of the rise of a new class of materials. One of them is so-called shape memory materials. Shape memory materials are smart materials having stimulus-responsive ability, e.g., temperature, force, electro-magnetism or solvent etc. via adjusting their shapes, positions or strains.[1–3] They mainly include shape memory ceramics, shape memory metal alloys, and shape memory polymers (SMPs).[3] Of particular interest in this article is SMPs having some novel properties, e.g., deformation capacity, adjustable shape recovery temperature, electric/heat insulation, to mention a few.

Shape memory polyurethanes (SMPUs) are the typical thermosensitive SMPs, which were extensively studied in the past decades.[1–14] Generally, the segmented polyurethanes (PU) have a good micro-phase separation structures consisting of hard domains and soft domains due to the thermodynamic immiscibility of soft segment and hard segment.[2] The hard segments acting as frozen phase can bind themselves via hydrogen bonding or crystallization, making the SMPUs very solid below T_m. The reversible phase transformation of soft segments acting as reversible phase is reported to be responsible for shape memory effect.[2] In this way, the shape memory effect can be controlled via molecular weight of soft segment, mole ratio between hard segment and soft segment, and polymerization process.

In an early report of our work,[15] it is found that micro-phase separation can be enhanced significantly by the micro-phase separation promoters, such as 1-octadecanol (ODO), liquid paraffin (LP). Because ODO molecules are capped at the end of PU chains, and the alkyl chains ($-C_{18}H_{37}$) of ODO are dispersed at the interface of the two phases in PU system due to immiscibility, this facilitates the micro-phase separation of hard segments from soft segmental phase; moreover, it lubricates PU chains in further solidification process. In comparison, LP is macro-phase separated from PU system, acting as an outer lubricant; thus it also promotes micro-phase separation of PU. However, the micro-phase separation promoters are not the sole factor to determine the shape memory behaviors of SMPs.

Understanding the relationship between the morphology and shape memory behavior of SMPs are crucial for the worldwide development of smart materials.[10–12] In previous literatures, 1,4-phenylene

TABLE I
Synthesis Parameters for SMPU with Different Compositions

No.	Soft segment (M_n, g mol^{-1})	Chain extender	[NCO]/[OH][a]	HS content[b] (wt %)	ODO% (wt %)	LP% (wt %)
P1	PEAG (3200)	BDO	1.0	25	0	0
P2	PBAG (3700)	BDO	1.0	25	0	0
P3	PCL (3100)	BDO	1.0	25	0	0
P4	PHAG (3500)	BDO	1.0	25	0	0
P5	PHAG (3500)	BDO	1.0	20	0	0
P6	PHAG (3500)	BPA	1.0	20	0	0
P7	PHAG (3500)	BPA	1.02	20	0.9	0
P8	PHAG (3500)	BPA	1.02	20	0.9	3.0
P9	PHAG (3500)	BPA	1.02	30	0.9	3.0
P10	PHAG (3500)	BPA	1.02	35	0.9	3.0
P11	PHAG (2000)	BPA	1.02	20	0.9	3.0
P12	PHAG (2000)	BPA	1.02	25	0.9	3.0
P13	PHAG (2000)	BPA	1.02	35	0.9	3.0
P14	PHAG (2000)	BPA	1.02	40	0.9	3.0

HS, hard segments; ODO, 1-octadecanol; LP, liquid paraffin; BDO, 1, 4-butanediol; BPA, bisphenol A.
[a] Feed molar ratio of isocyanate groups to hydroxyl groups.
[b] Calculated according the feed weight ratio: HS content $= [(W_{L-MDI} + W_{BDO})/(W_{L-MDI} + W_{BDO} + W_{polyester})] * 100\%$

diisocyanate (PDI),[9] 2,4-toluene diisocyanate(TDI),[10] 4, 4-methylene bis(phenylisocyanate) (MDI),[2,11–13] and hexamethylene diisocyanate(HDI)[7,14] were all used to synthesize SMPUs, but less report of liquefied-MDI(L-MDI), which is a liquid modified product of MDI at room temperature, is available.[16] Besides, there are so much soft segment polyglycols, such as Polycaprolactone (PCL),[5] polytetramethylene oxide(PTMO),[2,4] poly (ethylene adipate) glycol (PEAG),[10] poly (butylenes adipate) glycol (PBAG), and[12] poly (hexaylene adipate) glycol (PHAG),[13] and so much little molecular glycols are used as chain extenders in the synthesis of SMPUs. But there are still no clear comparison studies of their shape memory behaviors in all kinds of SMPUs.

In the present work, we focus on the investigation of liquefied-MDI-based SMPUs, since the L-MDI have superior fluidity and good storage stability at room temperature, and it is a promise materials for the application of RIM (reaction injection molding) technology in the preparation of SMPUs in industry.[16] Besides, several kinds of soft segments, chain extenders and micro-phase separation promoters are used to synthesize SMPUs for comparing investigations.

EXPERIMENTAL SECTION

Materials

PEAG(M_n = 3200 from Shanfen PU factory, China), PBAG (M_n = 3700 from Shanfen PU factory, China), PHAG(M_n = 3500, from Shanfeng PU factory, China), PCL(M_n = 3100, from Shanfeng PU factory, China), ODO(from Shanghai Medicine Reagent, China) and Bisphenol A (BPA, from Shanghai Leshong trade, China) were dried under vacuum at 80°C for 24 h; 1,4-butanediol (BDO, from Shanghai

Medical Chemical Reagent, China), N, N-dimethyl-formamide (DMF, from Shantou Guanghua Chemical Reagent, China), liquid paraffin (LP) were dehydrated at ambient temperature using a 0.4 nm molecular sieve for 2 days. The L-MDI with 23 wt % isocyanates was obtained by the liquefactions of MDI in the presence of little molecular glycol-dominant reaction reagents in our laboratory.[16]

Synthesis of SMPU

The general procedure is as follows:[15] dehydrated polyglycol (PEAG or PBAG, PHAG, PCL) and one molar excess of L-MDI in 20 wt % DMF were charged in a four-necked round-bottom flask equipped with mechanical stirrer, nitrogen inlet, thermometer, and condenser with drying tube. The reaction mixture was stirred at 80°C in dried nitrogen atmosphere for 2 h, followed by the addition of chain extender (BDO or BPA) and stirred at 80°C for 2 h. ODO (or LP) was added into the reaction mixture and stirred at 80°C for 2 h. Feed molar ratio of NCO/OH was controlled to 1.02 to ensure that ODO was capped at the end of polyurethane. No characteristic absorption peak of isocyanates at 2273 cm^{-1} was detected from FTIR spectra confirms this attachment. The resulting solution was cast on a glass plate, further evaporated DMF solvent in a dried vacuum oven at 80°C for 2 days to give PU films with 0.5 mm thickness. According to their soft segment types, such as PCL, PEA, PBA, PHA, the resulting SMPU samples here are named PCL-based SMPU (CLPU), PEA-based SMPU (EAPU), PBA-based SMPU (BAPU), and PHA-based SMPU (HAPU), respectively. The feed ratios for the resulting SMPU samples are summarized in Table I.

X-ray diffraction

The X-ray test was carried out using a Rigaku D/ MAX-3B with an X-ray wavelength of 0.154 nm at a scanning rate of $3°$ min^{-1}. Specimens with 0.5 mm thickness were prepared for these measurements.

Differential scanning calorimetry

The differential scanning calorimetry (DSC) test was performed on a PE Q10 DSC instrument at a heating or cooling rate of $20°C$ min^{-1}. Prior to the DSC measurements, after slowly cooling down from $120°C$, the samples were kept in a dried vacuum oven at $35°C$ for two weeks to eliminate the thermal history[16]. Second heating/cooling scanning curves from -70 to $150°C$ was recorded.

Dynamic mechanical analysis

The dynamic mechanical analysis (DMA) test was carried out using a PE DMTA-V dynamic mechanical thermal analyzer in the tensile mode at a fixed frequency of 1.0 Hz. Specimens were heated from 0 to $80°C$ at a heating rate of $3.0°C$ min^{-1}.

Shape memory behavior test

Rectangular specimens with 20 mm length, 5 mm width, and 0.5 mm thickness were prepared for these measurements. Stretching the film to the elongation of 600% at $80°C$ (T > Tm of the soft-segment domains), quickly cooled down to $0°C$ under stretching conditions. The specimens were then placed on the desk at ambient temperature for 5 min. The strain recovery was measured in an oil bath with a hot stage at a heating rate of $2.5°C$ min^{-1}. The length at different temperatures was recorded directly from the ruler in oil, and then the shape recovery (R_T), maximum shape recovery (R_{max}), shape fixity (F), shape stability (S) is defined as follows:

$$R_T = (L_S - L_T)/(L_S - L_0) \times 100\% \tag{1}$$

$$R_{max} = (L_S - L_R)/(L_S - L_0) \times 100\% \tag{2}$$

$$F = (L_F - L_0)/(L_{max} - L_0) \times 100\% \tag{3}$$

$$S = (L_S - L_0)/(L_{max} - L_0) \times 100\% \tag{4}$$

where, L_0 is the original length, L_{max} is the maximum stretched length, L_F is the fixed length at $0°C$, L_S is the stable length at ambient temperature, L_T is the length at a certain temperature (T) during the heating process, L_R is the recovery length.[13,15]
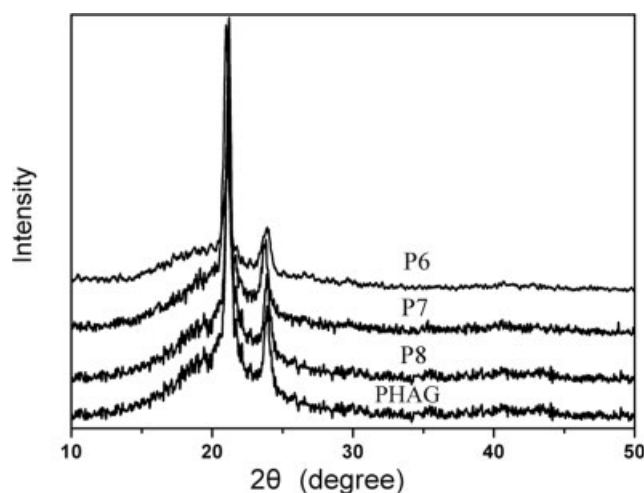

Figure 1 X-ray diffraction profiles of PHA based SMPU with or without addition of ODO or LP.

RESULTS AND DISCUSSION

X-ray diffraction studies

Figure 1 present the X-ray diffraction profiles of HAPU comparing with pure soft segment PHAG. The diffused diffraction peaks are observed to appear at $\sim 2\theta = 21.07°$ and $23.86°$ in the pure PHAG while appear at ~ 21.02 and $23.86°$ with a decreased intensity of crystal peaks in the pure HAPU sample (See Fig. 1, PHAG and P6). It means that the crystallization of SMPU mainly ascribes to their soft segment; the crystal of soft segments in the HAPU is disturbed significantly because of the hindrance of hard segments.[17,18] In contrast, the microseparation promoters can efficiently improve the phase-separation of polyurethane as reported in literature.[15] Thus, it is observed that the addition of small amount (0.9 wt %) of ODO or LP can significantly improve the crystallization of these soft segments, giving rise to a strikingly sharp X-ray diffraction peak at $21.07°$ as well as at $23.86°$ in Figure 1.

DSC studies

Li et al.[5] had pointed out that the high crystallinity of the soft segment regions at room temperature and the formation of stable hard-segment domains acting as physical crosslinker in the temperature range above the melting temperature (T_m) of the soft segment crystal were the two necessary conditions. Hereby, from the molecular structure, it can be expected that polyurethane formed with good crystallizability soft segment will show excellent shape memory effects. The thermal properties of SMPU with various soft segment types are shown in Figure 2(a). It can be observed that HAPU sample (See P4) presents a prominent T_m at $51.44°C$ with
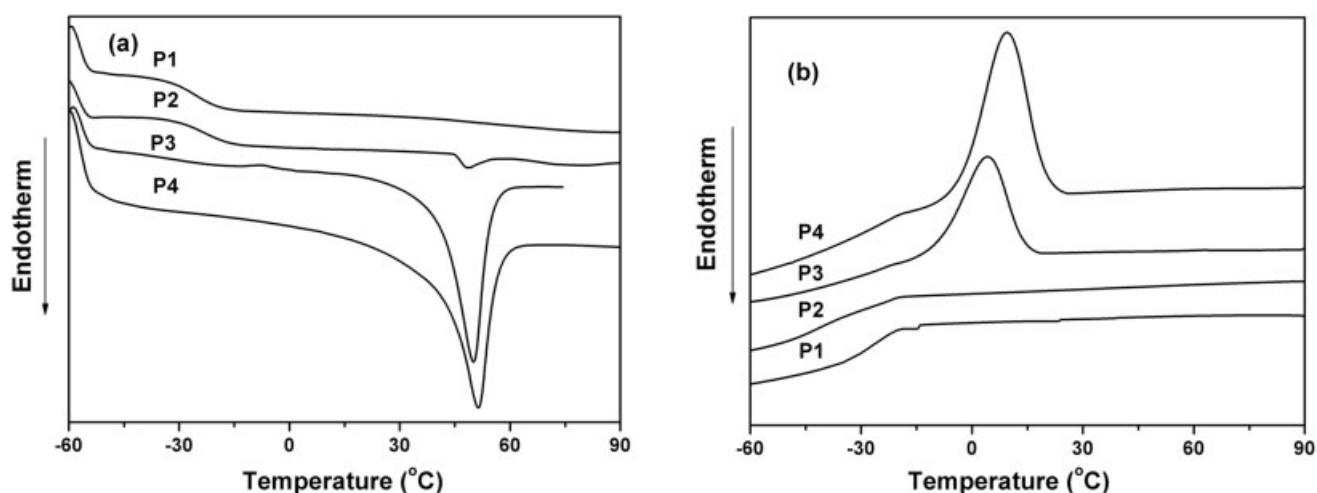
Figure 2 DSC heating curves of PU with different soft segment: (a) Heating curves; (b) cooling curves.

higher enthalpy like that of CLPU (see P3), while EAPU (see P1) and BAPU (see P2) exhibit no melting peak or little enthalpy at the heating scans. Besides, at their cooling scans [shown in Fig. 2(b)], the re-crystallizing peak appears at 12.88°C in HAPU sample, while there is still no peak in EAPU and BAPU; even in CLPU sample, the re-crystallizing peak appears at a lower temperature with less enthalpy, which explains that the PHA-based SMPU have better crystallizability comparing to PCL-based SMPU, PEA-based SMPU and PBA-based SMPU.

To investigate the micro-phase separation structure of L-MDI based SMPU, different chain extenders and micro-phase separation promoters with various hard segment content (HSC) and soft segment length (SSL) are used here on the base of selecting the PHA soft segment. The thermal properties of L-MDI based SMPU are shown in Figure 3. In Figure 3(a), it could be observed that PHAG precursor shows a melting

peak at ca.63°C with melting enthalpy (ΔH_m) of 106.5 J/g. In contrast, the T_m of soft segment of HAPU samples (see P5-P12) moves to a lower temperature, and the associated ΔH_m gets smaller, which implies that the crystallinity of SMPU decreases due to the hindrance of hard segment as proved by x-ray. Similar results were also observed in CLPU,[13,14] which was also ascribed to micro-phase mixing of hard segments and soft segments. Especially, when BPA containing rigid structure is used as chain extender, this influence is more prominent [shown in Fig. 3(a)], presumably attributed to the less mobility of hard segments formed with BPA.

Meanwhile, it can be found that T_m and T_c of HAPU both decrease with the HSC in Figure 4; and HAPU formed with shorter SSL usually shows a lower T_m at heating scans and no T_c at cooling scans (see Fig. 3 for P12), which is consisted with the results of literature.[2,7,19] In addition, a clear exothermic peak
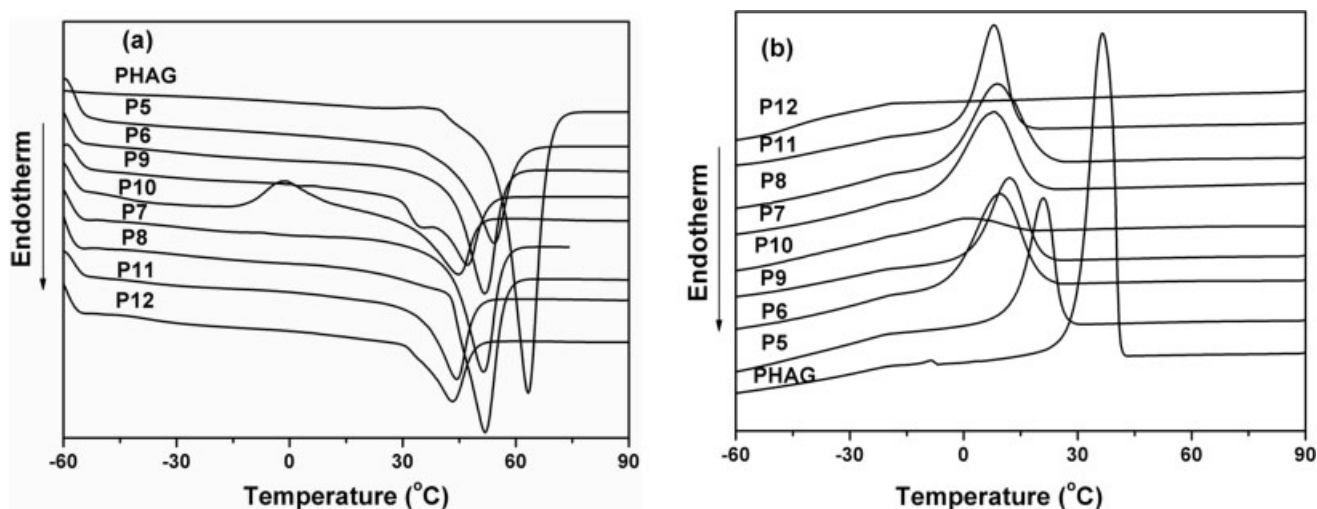

Figure 3 DSC scanning curves of PU and their soft segment precursor: (a) Heating curves; (b) cooling curves.
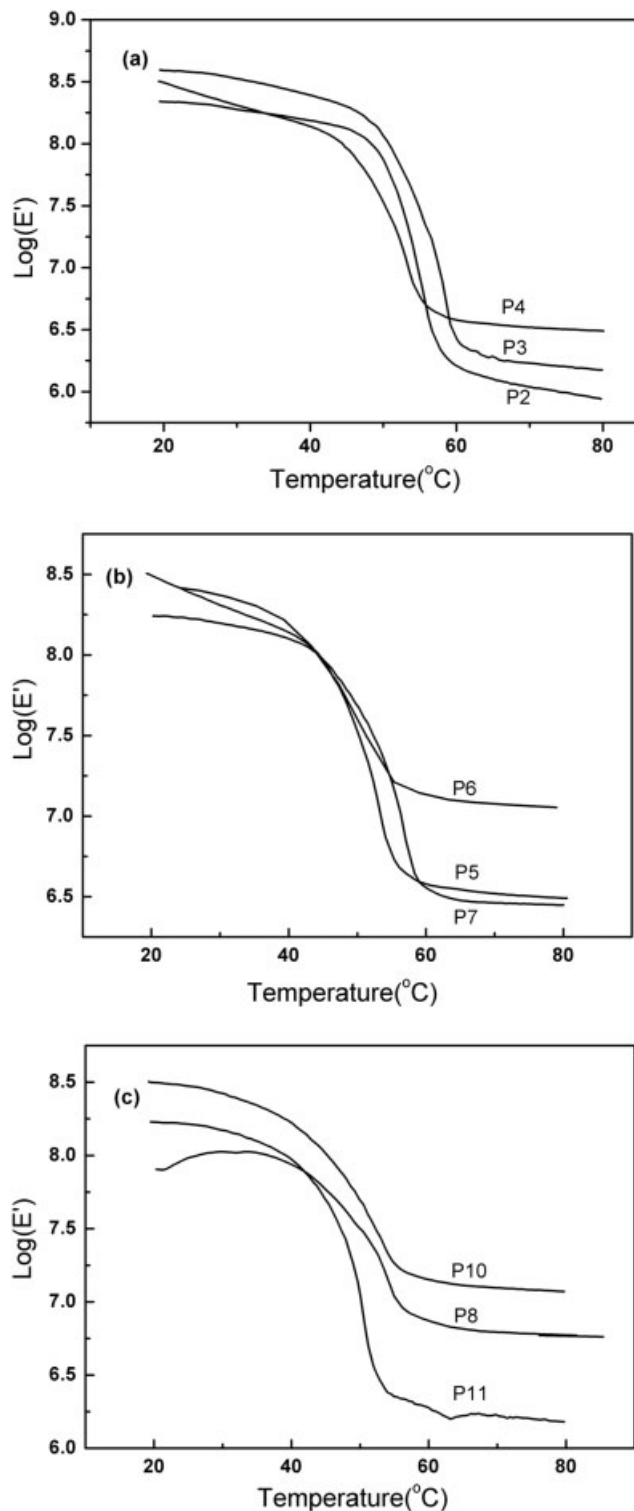
Figure 4 Storage modulus (E') of SMPU samples as function of temperature.

appears at the cooling scans in the HAPU samples with addition of small amount of ODO or ODO/LP. And it shifts to relatively higher temperature as the micro-phase separation promoter content increases. In a molecular level, the reason is because these

micro-phase separation promoters contain long alkane chains ($-CH_2-$) and can disperse in the interface between soft segment domains and hard segment domains because of the thermodynamic immiscibility with PU chain. It also can lubricate PU chain during the extension solidification process because of its flexibility; In contrast, ODO is a reactable lubricant that can be grafted to molecular chain as inner lubricant, while LP only can be dispersed among the chains acting as an outer lubricant.[15] Therefore, it can be expected that T_c, T_m of SMPU, added these two micro-phase separation promoters together, will shift to a further higher temperature [see sample P8 in Fig. 3(a)]. This confirms the crystallization promotion effect of ODO or ODO/LP on PHA soft segments as discussed in X-ray diffraction studies.

DMA studies

The dynamic mechanical properties of L-MDI based SMPU are shown in Figures 4 and 5. Generally, the storage modulus at crystalline state (named E'_m here) or at glass state (named E'_g here) mainly result from both the crystal structure or amorphous structure of soft segment and amorphous structure of hard segment, while the storage modulus at rubber state (named E'_r here) only depends on the amorphous structure of the hard segment. Thereby, a dramatic decrease of their storage modulus at T_m of soft segment here is detected in Figure 4. This transition is desirable for the thermosensitive shape memory behavior. Since these most likely lead to the deformed material recovery to its original shape in a relatively narrow temperature range on heating close to T_m, some difference is found among different samples discussed as follows.

Figure 4(a–c) present the influence of soft segment types, chain extender types, and HSC, SSL on the storage modulus of L-MDI based SMPU. It can be observed that the E_m' of HAPU is equivalent to that of BAPU, slightly lower than CLPU. It suggests that CLPU materials are most rigid among these three materials at crystalline state. While the E'_r value of HAPU is higher than BAPU and CLPU, that is, the HAPU materials have better mechanical properties at higher temperature comparing to BAPU and CLPU. Similarly, it can also be observed that E'_r of BPA extended SMPU is much higher than that of BDO extended SMPU in Figure 4(b) because of its hard segment consisting of more rigid structures. Thus, HAPU extended by BPA have more wide applications at a higher temperature. Besides, in Figure 4(b), it can be observed that the addition of small amount of ODO in HAPU dramatically decreases their E'_r, while their E'_m is still close to that of the pure HAPU [see Fig. 4(b): P6, P7]. It means that the modulus ratio (E'_m/E'_r) of ODO/LP-modified SMPU
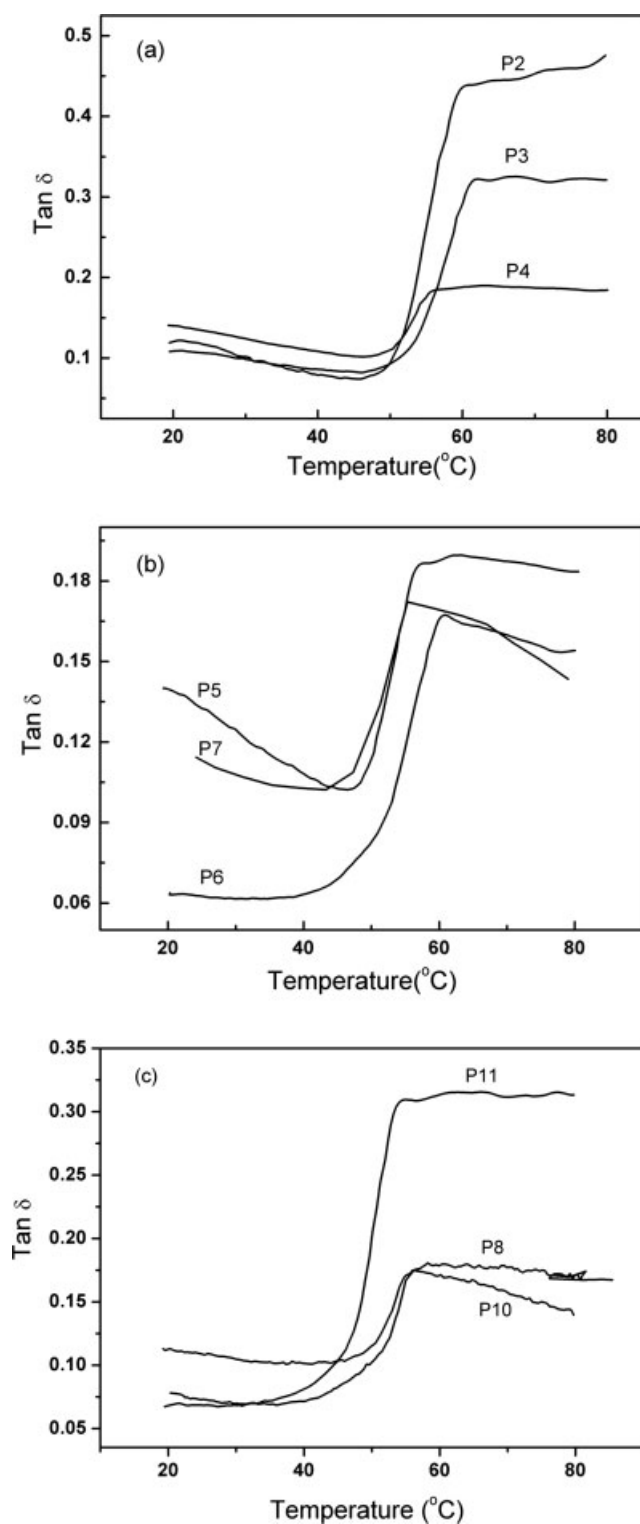
Figure 5 Tanδ of SMPU samples as function of temperature.

remarkably increases. Thus higher shape fixity is expected in the following shape memory behavior test. Meanwhile, in Figure 4(c), because the crystallinity of long SSL formed SMPU is higher than that of short SSL formed SMPU as proved in DSC test,

the E' of L-MDI based SMPU with longer SSL is higher than that of shorter SSL samples both at glass state and at rubber state. The crystal is the reinforced filler to materials just like that the hard segment domains are the reinforced filler to soft segment domains. Therefore, the E' also increases with HSC like the common segmental polyurethanes; and L-MDI based SMPU becomes more rigid either as the HSC increases or as the SSL increases both at glass state and at rubber state.

Generally, the tanδ reflects the movement of molecular chain. Molecular chain segments of polyurethane almost are frozen at glass state. Thereby, the tanδ at glass state is lower and change slightly, while the tanδ at rubber state improves greatly because of the increase of micro-brown movement soft segment above T_m.[2] In Figure 5(a), it is observed that the tanδ of HAPU at rubber state is little, below 0.2, while tanδ of CLPU approaches to 0.5. Meanwhile, the tanδ of BPA extended SMPU is much bigger than that of BDO-extended SMPU at glass state as well as at rubber state [shown in Fig. 5(b)], ascribing to the rigid hard segment restricts the movement of molecular chain. In addition, the soft segmental mobility is observed at ~ 50°C, and the tanδ at crystalline state is observed to increase significantly with addition of ODO. Similar effect is also observed in the LP-modified HAPU samples in Figure 5(b). This is another proof that the micro-phase separation promoter lubricates and improves the movement of molecular chain. In Figure 5(c), higher tanδ value is observed in the HAPU with shorter SSL at rubber state; while little difference at glass state. As the HSC increases, the tanδ at glass state increases, and no significant difference can be found at rubber state. These results indicate that the tanδ at rubber state mainly results from the movement of soft segment.

Shape memory behavior

Figure 6 shows the thermal recovery curves of L-MDI based SMPU. As mentioned above, long SSL and suitable HSC are necessary for SMPU having excellent shape memory behavior.[7] The shape recovery temperature (T_r)[7] is also related to the reversible phase transition temperature ascribed to the crystal melting of soft segment. Therefore, it is observed in Figure 6(a) that the T_r of HAPU is ~ 50°C, corresponding to its T_m tested by DSC above. It means that the shape recovery process really results from the phase transition of soft segment in the L-MDI based SMPU.

It is worth noting here that only slight shape memory effect is observed in the samples containing 20 wt % HSC samples because of its less perfect micro-phase separation. However, the addition of small amount of ODO can significantly modify its micro-phase separation without changing the

composition of samples.[15] Therefore, in Figure 6(b), it is observed that the T_r of HAPU sample increases with the addition of ODO and LP due to the enhancement of micro-phase separation, resulting
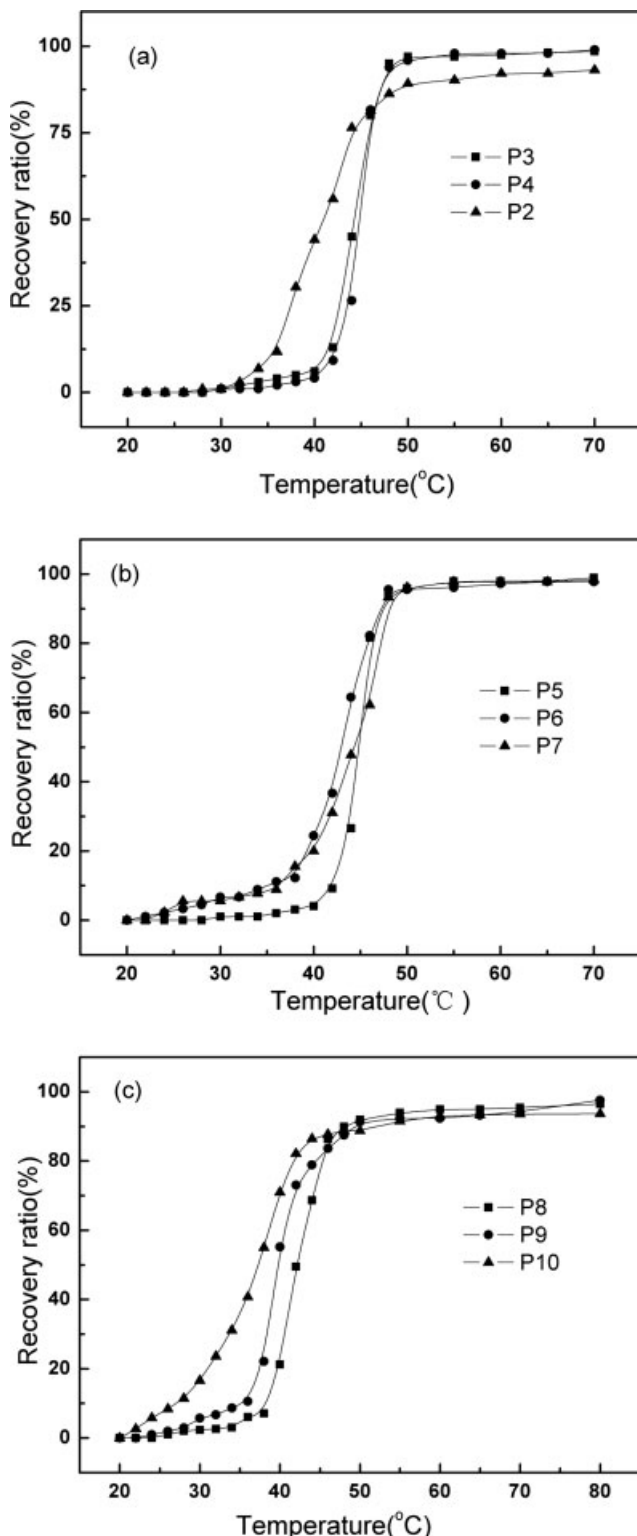

Figure 6 Strain recovery curves of SMPU (a, with different soft segment; b, with or without addition of 1-octadecanol; c, with different hard segment contents).

TABLE II
The Shape Fixity of Liquefied-MDI Based SMPU Samples

Samples	P6	P7	P8	P9	P10	P11	P12	P13	P14
Shape fixity (%)		96.0	97.2	100.0	97.5	96.9	99.5	95.0	91.5	86.3

from the inter lubricant and outer lubricant. Besides, it can be found that the BPA-extended SMPU [seen P6, P7 in Fig. 6(b)] recovery slowly with lower T_r comparing with BDO-extended SMPU [seen P5 in Fig. 6(b)]. It implies that PBA-extended SMPU reinforces the hard segment domains accompany by the interruption of soft segment crystallizability, which are also proved in DSC discussion above. Similar to other SMPU, the Figure 6(c) presents that the T_r of L-MDI based SMPU decreases with the HSC but increases with SSL. In fact, it is also ascribes to the enhancement of micro-phase separation either the HSC decease or the SSL increase.

In this experiment, because HAPU and CLPU both have good micro-phase separation structure as proved in DMA test, no significant difference of final recovery ratio can be found in the HAPU samples except that BAPU show a lower shape recovery ratio comparing with CLPU and HAPU. However, great differences are found in their shape fixity properties due to their different crystallizability with various HSC, SSL, and ODO or LP. The shape fixity of HAPU is given in Table II. It can be observed that the pure HAPU shows 96% shape fixity, whereas, addition of small amount of ODO/LP significantly improves its fixity to 100%, because the micro-phase separation promoters improve crystallizability of the soft segment. Moreover, just as shown in Figure 5, there is a large elasticity release at T_m, which is contributed to the shape fixity of SMPU.[2] Therefore, with the addition of micro-phase separation promoters, the shape fixity increases to 100%. Meanwhile, it is found that the shape fixity of HAPU decreases as the HSC increases or SSL decreases (shown in Table II).

CONCLUSIONS

A series of SMPU based on L-MDI are synthesized with four types of soft segments (PCL, PHA, PEA, PBA), two types of chain extenders (BPA and BDO), and two micro-phase separation promoters (ODO and LP). The morphology and properties of liquefied-MDI based SMPU were investigated in details. The following conclusions can be summarized:

1. SMPU having good crystallizability soft segments, especially, the soft segment formed with long chain segment, and SMPU extended by rigid chain

extenders more incline to crystallize. Then these SMPU show higher T_r and better shape fixity.

2. The L-MDI based SMPU extended by rigid chain extenders like BPA inclines to show higher storage modulus both at glass state and at rubber state. But the T_r of rigid chain extended SMPU is lower.

3. The degree of micro-phase separation structure influences the shape memory properties greatly. Generally, the T_r increases with addition of micro-phase separation promoters as well as increase with SSL instead of decrease with HSC. Besides, higher shape fixity is observed in the samples with higher SSL, lower HSC samples, and addition of ODO or LP.

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