Effect of Microphase-Separation Promoters on the Shape-Memory Behavior of Polyurethane

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ABSTRACT: A series of segmented polyurethanes (PUs) with novel thermosensitive shape-memory behavior were synthesized via the *in situ* addition of a small amount of 1-octadecanol (ODO) to a PU system. For comparison, liquid paraffin (LP) modified PUs were also synthesized. The effects of a small amount of ODO or LP on the PU suprastructure and the thermosensitive shape-memory properties were studied with X-ray diffraction, differential scanning calorimetry, dynamic mechanical analysis, and shape-memory studies. The results indicated that the *in situ* addition of a small amount of ODO (e.g., 0.3 wt %) remarkably promoted microphase separation, facilitating the ordered packing of soft segments and the formation of perfect hard-segment domains and thus significantly improving the shape-memory properties. In contrast, LP had less significant influence on the shape-memory behavior because of the macrophase separation of these nonpolar alkyl chains from the PU system. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 5224–5231, 2006

Key words: crystallization; interfaces; modification; polyurethanes; stimuli-sensitive polymers

INTRODUCTION

Shape-memory materials are smart materials that can respond to environmental variations, such as the temperature, force, electromagnetism, and solvent, through the adjustment of their shape, position, or strain. These functional materials have been extensively applied in the fields of intelligence and alertness.[1–3] Shape-memory materials mainly include shape-memory ceramics, shape-memory metal alloys, and shape-memory polymers (SMPs).[3] SMPs have attracted extensive attention because of their novel properties, such as their deformation capacity, adjustable shape-recovery temperature, and electric/heat insulation. Of particular interest in this article is the so-called shape-memory polyurethane (SMPU).

SMPU shows a typical microphase-separated suprastructure because of its thermodynamic immiscibility: Hard segments aggregate via strong hydrogen bonding to form stable, dispersed domains, acting as physical crosslinkers. Soft segments are generally responsible for their shape-memory behavior. The shape-memory behavior can be controlled through the adjustment of the type or content of the soft segment and the optimization of the polymerization proce-

dure.[2] Kim's group[4,5] reported that the strain recovery of SMPUs was attributable to their microphase-separated structure and the formation of stable hard-segment domains. They synthesized a series of SMPUs with excellent thermosensitive shape-memory behavior by enforcing microphase separation via the incorporation of ionized hard segments.[6–8]

Of particular relevance to this work is the effect of low-molecular-weight lubricants, such as 1-octadecanol (ODO) and liquid paraffin (LP), on the microphase separation and antiplasticization of polyurethane (PU) elastomers.[9,10] ODO molecules are capped at the end of PU chains via a urethane reaction between isocyanate-capped PU prepolymers and hydroxyl groups of ODO; the alkyl chains ($—C_{18}H_{37}$) of ODO are dispersed at the interface of the two phases in a PU system because of immiscibility. This facilitates the microphase separation of hard segments from the soft-segment phase; Moreover, it lubricates PU chains in a further solidification process.[9,10] In comparison, LP is macrophase-separated from a PU system, acting as an outer lubricant, and thus also promotes the microphase separation of PU.

In previous communications, we briefly presented the synthesis of novel SMPUs with shape-memory behavior via the *in situ* addition of low-molecular-weight lubricants to conventional PU.[11] This article focuses on the effect of a small amount of ODO or LP on the microphase-separated structure and accordingly the thermosensitive shape-memory properties of PU.

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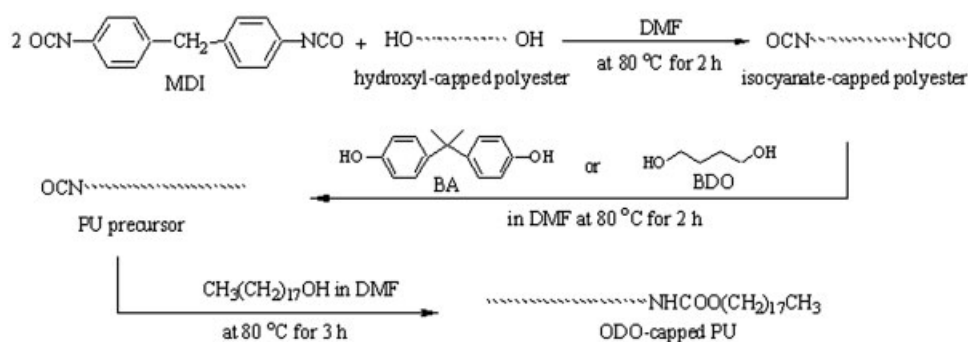
Scheme 1 Synthetic scheme of ODO-capped PU.

EXPERIMENTAL

Materials

Poly(1,4-butylene adipate) glycol [PBAG; number-average molecular weight (M_n) = 2800 g/mol] and poly (hexamethylene adipate) glycol (PHAG; M_n = 2000 or 3500 g/mol; Yanhu City, China) were purchased from Shanfeng PU Factory and used without further purification; 1,4-butanediol (BDO; 99%) and bisphenol A (BA; 99%) were purchased from Shanghai Reagent Co. (Shanghai, China) and dehydrated *in vacuo* at 80°C for 24 h before use. ODO (99%) and LP (99%) were purchased from Shanghai Reagent (Shanghai, China) and used without further purification; *N,N*-dimethylformamide (DMF; 99%) was purchased from Shanghai Reagent, dehydrated at the ambient temperature with a dried 4-Å molecular sieve for 2 days, and distilled under reduced pressure before use. Liquefied 4,4-methylene bis(phenylisocyanate) (L-MDI) with 23.0 wt % isocyanate was synthesized in our laboratory.[12]

Synthesis of SMPUs

The synthesis route for ODO-capped SMPUs is shown in Scheme 1. The SMPU feed molar ratios are summarized in Table I. The general procedure was as follows. Dehydrated PBAG or PHAG and 1 molar excess of L-MDI were dissolved in dried DMF (20 wt %) in a four-necked, round-bottom flask equipped with a mechanical stirrer, nitrogen inlet, thermometer, and condenser with a drying tube. The reaction mixture was stirred at 80°C in dried nitrogen atmosphere for 2 h. BDO or BA was charged into the flask, and the reaction solution was stirred at 80°C for 2 h. ODO or LP was charged into the flask, and the reaction was stirred at 80°C for 2 h. The feed molar ratio of the isocyanate groups to the hydroxyl groups ([NCO]/[OH]) was controlled at 1.02 to ensure that ODO was capped at the end of PU. The resulting solution was cast onto a glass plate. DMF was evaporated in a dried vacuum oven at 80°C for 2 days to give PU films with a 0.5-mm thickness.

TABLE I
Synthetic Parameters for SMPUs with Various Compositions

No.	Soft segment [M_n (g/mol)]	Chain extender	[NCO]/[OH]	HSC (wt %)[a]	ODO (wt %)	LP (wt %)
S1	PBAG (2800)	BDO	1.00	25	0	0
S2	PBAG (2800)	BDO	1.02	25	0.3	0
S3	PBAG (2800)	BDO	1.02	25	0.6	0
S4	PBAG (2800)	BDO	1.02	25	0.9	0
S5	PBAG (2800)	BDO	1.02	25	0	1.0
S6	PBAG (2800)	BDO	1.02	25	0	5.0
S7	PHAG (3500)	BDO	1.00	20	0	0
S8	PHAG (3500)	BDO	1.02	20	0.3	0
S9	PHAG (3500)	BDO	1.02	20	0.6	0
S10	PHAG (3500)	BDO	1.02	20	0.9	0
S11	PHAG (3500)	BA	1.00	20	0	0
S12	PHAG (3500)	BA	1.02	20	0.9	0
S13	PHAG (3500)	BA	1.02	20	0.9	3.0
S14	PHAG (3500)	BA	1.02	28	0.9	3.0
S15	PHAG (3500)	BA	1.02	33	0.9	3.0
S16	PHAG (2000)	BA	1.02	20	0.9	3.0

[a] Hard-segment content calculated according to the feed weight ratio: HSC = [($W_{\text{L-MDI}}$ + W_{BDO})/($W_{\text{L-MDI}}$ + W_{BDO} + $W_{\text{polyester}}$)] × 100%.
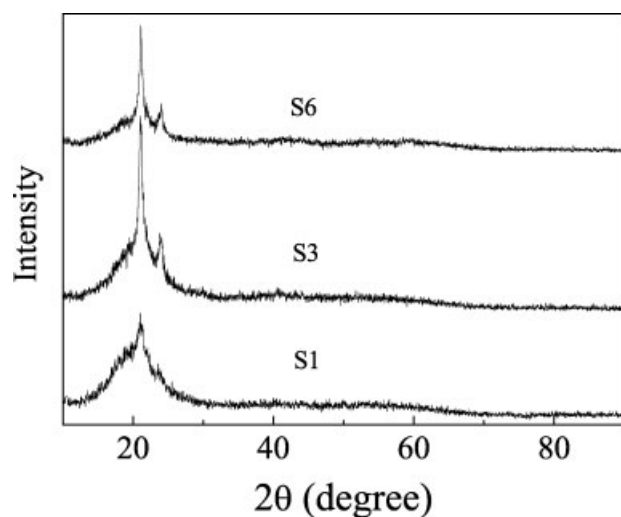
Figure 1 X-ray diffraction profiles of PBAG-based SMPUs with or without the addition of ODO or LP.

Differential scanning calorimetry (DSC)

DSC was performed on a PE Q10 DSC instrument at a heating or cooling rate of 20°C/min. The samples were heated to 120°C and then placed in a dried vacuum oven at 35°C for 2 weeks to eliminate the thermal history before DSC measurements.[13] Second-heating/cooling scanning from −70 to 150°C was recorded.

Dynamic mechanical analysis (DMA)

DMA was performed on 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.
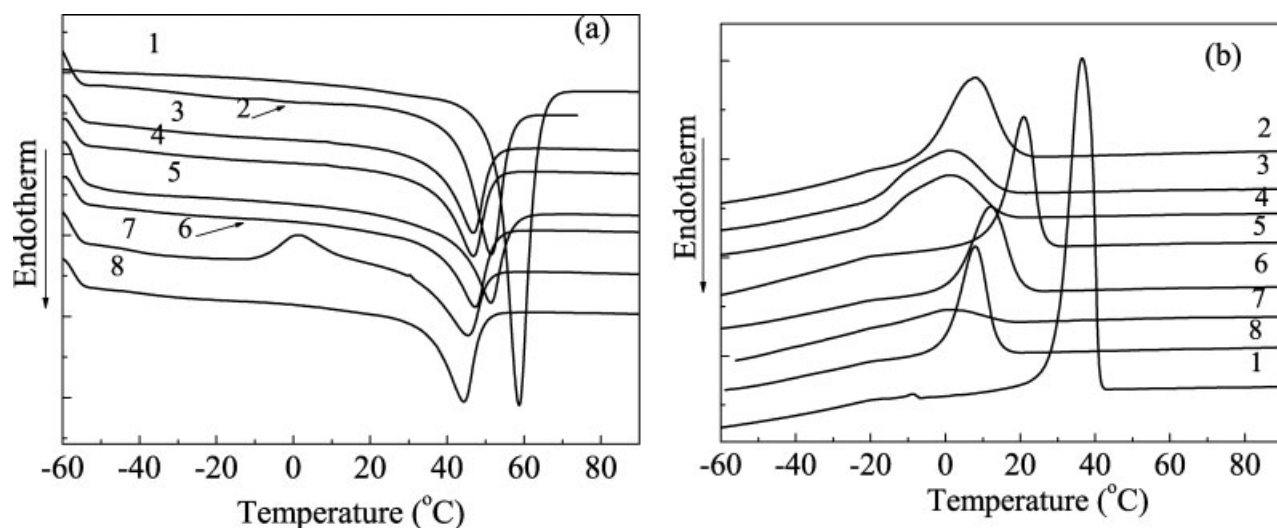
X-ray diffraction

X-ray diffraction measurements were performed on a Rigaku D/MAX-3B with an X-ray wavelength of 0.154 nm at a scanning rate of 3°/min. Specimens 0.5 mm thick were prepared for these measurements.

Shape-memory-behavior studies

Rectangular SMPU films (20 × 5 × 0.5 mm) were employed for these measurements. The films were stretched to 600% elongation at 80°C and then were quickly cooled to 0°C and kept at 0°C for 5 min; these films flowed by their placement on a desk at 25°C for 5 min. The strain recovery of these films was recorded by the placement of these films in an oil bath with a hot stage at a heating rate of 2.5°C/min. The shape fixity (F), shape stability (S), and shape recovery (R) are defined as follows:[2,4,5]

$$F = \varepsilon_f/\varepsilon_m \times 100\% \tag{1}$$

$$S = \varepsilon_s/\varepsilon_m \times 100\% \tag{2}$$

$$R = (\varepsilon_m - \varepsilon_p)/\varepsilon_m \times 100\% \tag{3}$$

where ε_f is the fixed strain at 0°C, ε_s is the stable strain at 25°C, ε_m is the maximum strain, and ε_p is the residual strain after recovery at 80°C.

RESULTS AND DISCUSSION

X-ray diffraction studies

PBAG is a crystalline polymer with X-ray diffraction at 2θ values of 21.5, 22, and 24°.[14] However, the aggregation of hard segments in the PBAG-based PU

Figure 2 DSC (a) heating and (b) cooling scanning curves for PU and soft-segment precursors: (1) pure PHAG (3500), (2) S7, (3) S11, (4) S12, (5) S13, (6) S14, (7) S15, and (8) S16.
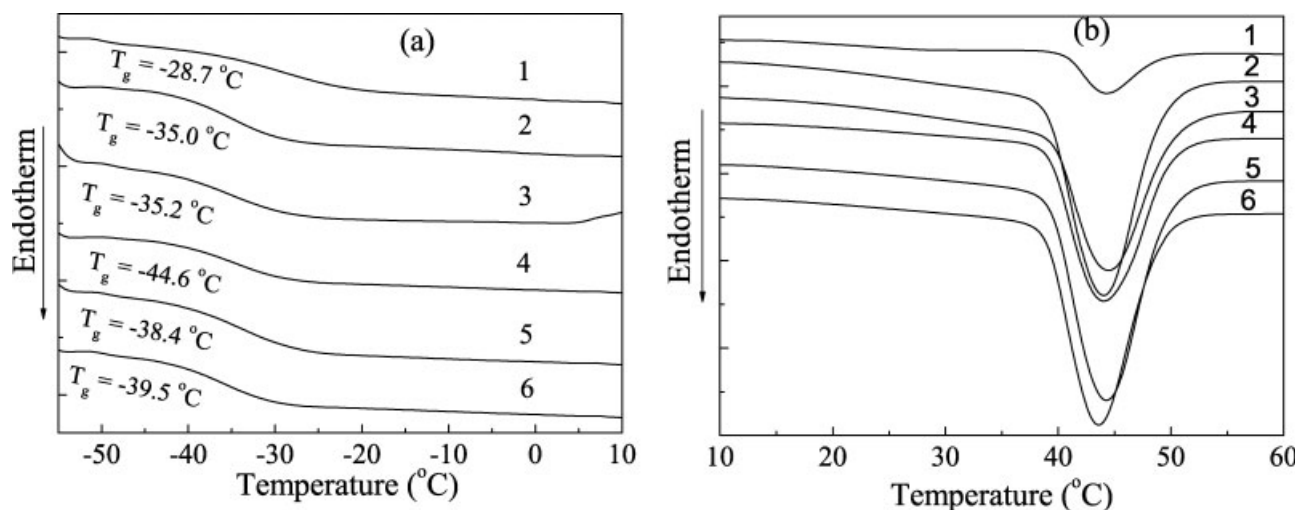
Figure 3 DSC scanning curves for PBAG-based PUs: (1) S1, (2) S2, (3) S3, (4) S4, (5) S5, and (6) S6.

system significantly disturbs the ordered packing of PBAG segments,[15] leading to imperfect crystallization of the segments. Only a weak diffraction overlapping the diffusion peak at about $2\theta = 21.0°$ was detected from its X-ray diffraction profile (Fig. 1 for S1). However, the addition of a small amount of ODO (e.g., 0.6 wt %) significantly improves the ordered packing of PBAG segments, giving rise to a strikingly sharp X-ray diffraction peak at 21.1° and diffraction peaks at 22.0 and 24.1°(Fig. 1 for S3).

In comparison, the nonpolar alkyl chains (LP) also improve the crystallization of PBAG segments in the PU system, but much less significantly than ODO: 5.0 wt % LP is needed to achieve an effect similar to that of 0.6 wt % ODO (Fig. 1 for S6). This indicates that the enforced dispersion of alkyl chains by attachment to the end of PU chains can significantly improve this lubricant effect, thus promoting the microphase separation of PU.

DSC studies

As shown in Figure 2(a), the PHAG precursor shows a melting peak at 59°C [melting enthalpy (ΔH_m) = 106.5 J/g]. In contrast, the PHAG-based PU shows a lower melting temperature (T_m; ≤ 52°C) and lower ΔH_m value (≤ 41.59 J/g), indicating the imperfect crystallization of PHAG segments in the PU system. Similar results were also observed for poly(ε-caprolactone)-based PU.[16] This influence is more pronounced when BA is incorporated into PU [Fig. 2(a) for S11–S16], presumably because of the lower mobility of the hard segments with the rigid moiety of BA, leading to the microphase-separation retardation of hard segments from the soft-segment phase.

Only weak crystallization was detected for PU with 33% hard segments in the cooling process [Fig. 2(b)

for S15], and a recrystallization process was observed at about 1°C in the heating process [Fig. 2(a) for S15]. This suggests that excess hard segments do not always provide a well-ordered structure.[2] Also, PU with low-molecular-weight soft segments (e.g., M_n = 2000 g/mol) showed a low T_m value (<44°C), as expected.[2,7]

The addition of ODO or LP can significantly improve T_m and the crystallization temperature (T_c), which can be close to that of the pure soft-segment precursor. For instance, T_m and T_c of S11 are 46.7 and 1.2°C, respectively. Upon the addition of 0.9 wt % ODO and 3% LP, they increase to 51.7 and 21.0°C, respectively, which are quite close to T_m (58.7°C) and T_c (35.9°C) of pure PHAG (3500 g/mol). This indicates that, upon the addition of ODO or LP, the ordered packing of soft segments is remarkably enhanced.
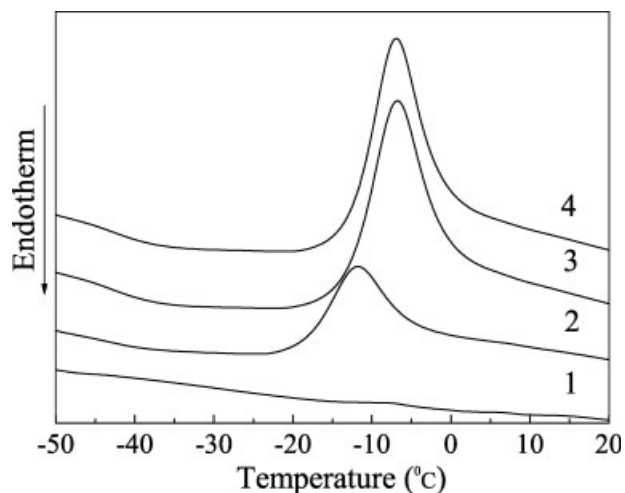

Figure 4 DSC scanning curves for PHAG-based PUs: (1) S7, (2) S10, (3) S9, and (4) S8.
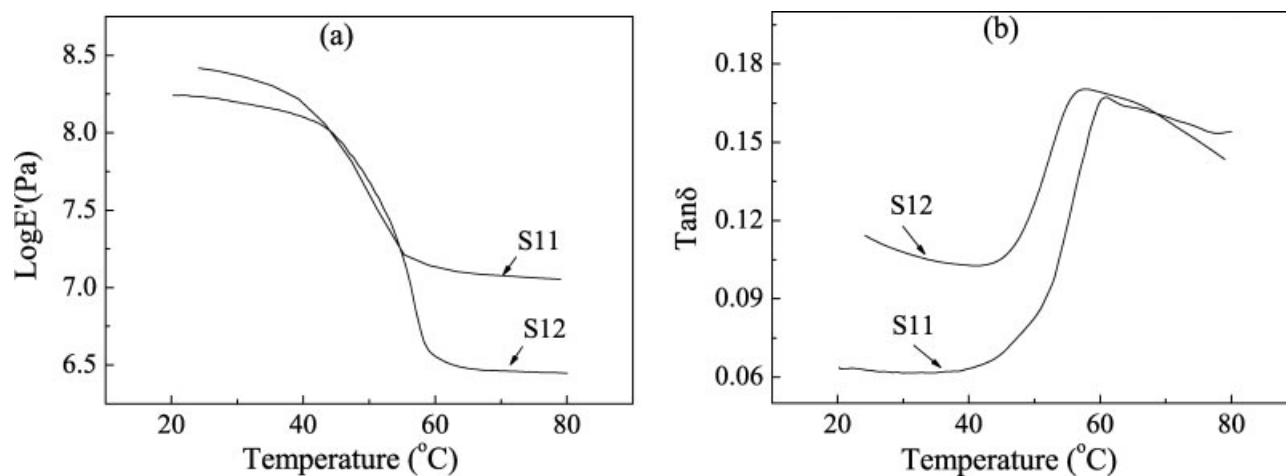
Figure 5 (a) E' and (b) tan δ of PHAG-based SMPUs (S11 and S12) as a function of temperature.

Similarly to what is described in the literature,[17] no obvious glass transition was detected in PHAG-based PUs from DSC curves, presumably because of the perfectly ordered packing of the segments [Fig. 2(a)]. However, for the PBAG-based PU with less perfectly ordered packing of PBAG segments, the glass transition is quite clear. As shown in Figure 3(a), the glass-transition temperature (T_g) of PBAG-based PU decreases upon the addition of ODO or LP. Their ΔH_m values (> 39.7 J/g) are significantly larger than that of pure PU [$\Delta H_m = 3.09$ J/g; Fig. 3(b)]. This indicates that the addition of ODO or LP improves the crystallization of PBAG segments.

As shown in Figure 4, only a slightly exothermic peak was detected from the DSC curve of pure PHAG-based PU. However, an exothermic peak at −6.8°C appears upon the addition of 0.3 wt % ODO. The addition of 0.6 wt % ODO leads to an exothermic

peak at −6.8°C. However, the addition of 0.9 wt % ODO to PU reduces this T_c to −11.7°C. This difference is presumably attributable to a different mechanism: for PU with ODO in the range of 0.3–0.6 wt %, the alkyl chains act as crystal nuclei, which induce the heterogeneous crystallization of PHAG segments in the PU system. As the ODO concentration increases to 0.9 wt %, the lubricating effect of ODO in the PU system should be significant, and this facilitates the microphase separation of the segments in the PU system. Further studies are needed to clarify this variation.

DMA

As shown in Figure 5(a), a dramatic decrease in the storage modulus (E') of PHAG-based PU at about 50°C (T_m of the PHAG segment domains) was
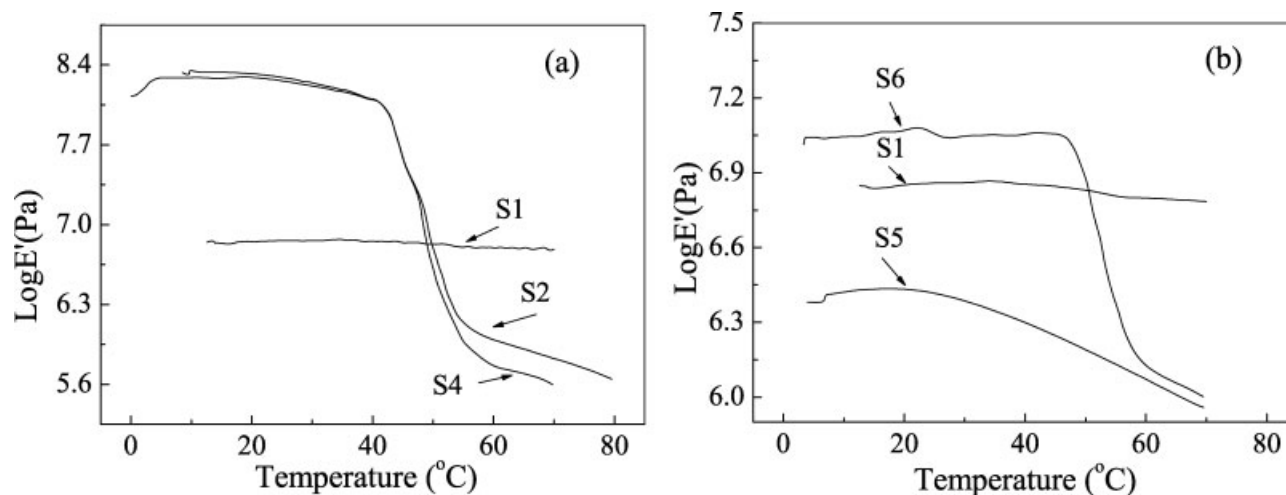

Figure 6 E' of PBAG-based SMPUs as a function of temperature: (a) PU with or without the addition of ODO and (b) PU with or without the addition of LP.
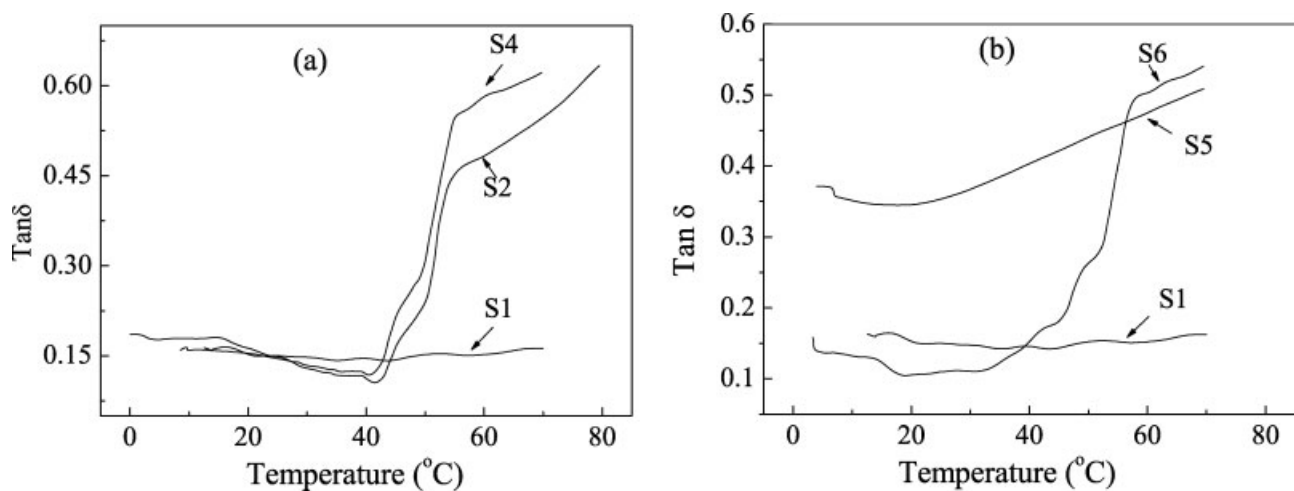
Figure 7 Tan δ of PBAG-based SMPUs as a function of temperature: (a) PU with or without the addition of ODO and (b) PU with or without the addition of LP.

detected. This transition is desirable for thermosensitive shape-memory behavior because it most likely leads to the deformed material recovering its original shape in a relatively narrow temperature scale (ca. T_m). Moreover, the addition of a small amount of ODO to the PU system dramatically decreases the rubbery-state modulus (E'_r), whereas the crystalline-state modulus (E'_m) is still close to that of pure PU [Fig. 5(a)]. Thus, the modulus ratio (E'_m/E'_r) of PU remarkably increases upon the addition of ODO. In addition, the mobility of soft segments (α transition) can be observed at about 50°C [Fig. 5(b)], and tan δ in the crystalline state significantly increases with the addition of ODO because of the enhancement of the soft-segment mobility. A similar effect was also observed in DMA curves of LP-modified PU. For example, upon the addition of 4.0 wt % LP, E'_m/E'_r of PU

increases from 85 to 250, tan δ in the crystalline state increases from 0.13 to 0.18, and tan δ in the rubbery state increases from 0.18 to 0.4 [Fig. 5(b)].

For the pure PBAG-based PU, the critical molecular weight of the PBAG precursor for showing a shape-memory effect is about 2800 g/mol.[16,18,19] No crystallization was detected for PU samples without an annealing process.[20,21] No significant E' variation of the pure PBAG-based PU was detected in the range of 20–80°C (Fig. 6), and this suggests that the soft-segment phase of this pure PU is predominantly amorphous. The strain-recovery process is just a thermosensitive shrinkage process. However, a sharp transition was observed at about 50°C for PU with the addition of 0.3 wt % ODO (Fig. 7). The modulus ratio between 30 and 70°C is 429, significantly larger than that reported in the literature.[4,6,14] This leads
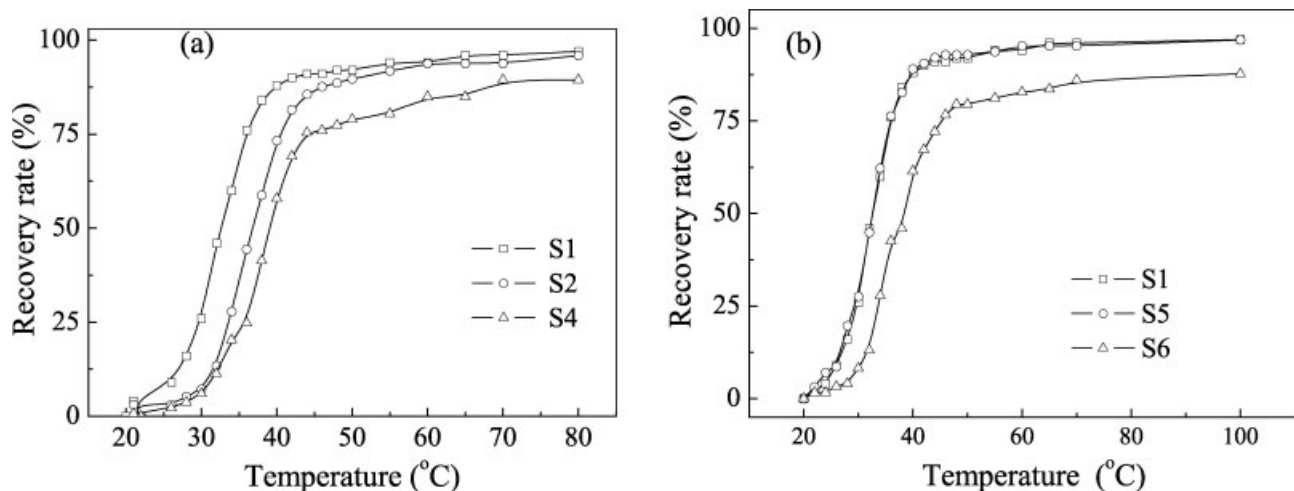

Figure 8 Strain-recovery curves of PBAG-based PUs with various contents of microphase-separation promoters: (a) with or without the addition of ODO and (b) with or without the addition of LP.
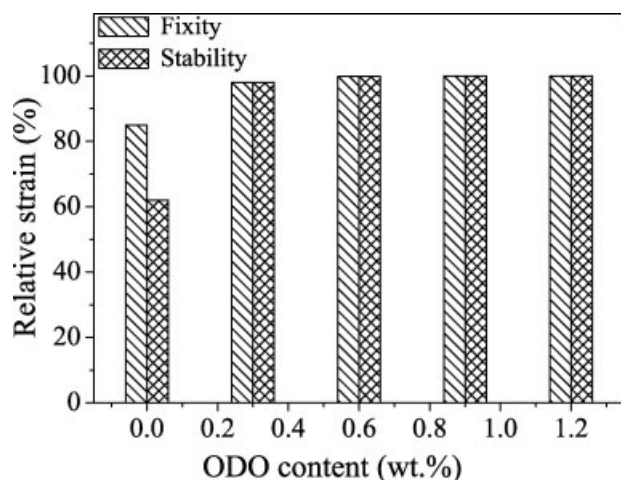
Figure 9 Shape fixity and stability versus the weight percentage of ODO in PBAG-based PUs.

to the improvement of their fixity, as discussed later. On the basis of our experimental results, the effect of LP on the dynamic mechanical properties is less significant than that of ODO.

Shape-memory-behavior studies

Generally, relatively long soft segments and suitable hard-segment contents are necessary for PU with excellent shape-memory behavior or final recovery memory.[4–7,16] The recovery temperature (T_r) is related to the reversible phase-transition temperature, the melting process of the soft-segment phase. Previous studies have revealed that an improvement in microphase separation leads to an increase of T_r.[4–7,16]

For a pure PBAG-based PU with 25 wt % hard segments and short PBAG soft segments (M_n = 2800 g/mol), only a slight shape-memory behavior was observed because of its imperfect microphase-separation structure. However, without any change in the composition or type of the two segments, the addition of a small amount of ODO significantly influences the shape-memory properties; for example, T_r increases upon the addition of ODO or LP (Fig. 8). ODO shows more significant influence than LP, such as $\Delta T_r > 6°C$ upon the addition of 0.6 wt % ODO [Fig. 8(a)], whereas no ΔT_r can be detected upon the addition of 1.0 wt % LP [Fig. 8(b)]: 5.0 wt % LP is needed to increase ΔT_r to about 4.5°C [Fig. 8(b)].

Most strikingly, under the same conditions, the maximum elongation of the pure PBAG-based PU is less than 400% at 80°C, and its fixity at the ambient temperature is less than 60%, whereas the maximum elongation of ODO-modified PU at 80°C is larger than 600%, and its fixity at the ambient temperature is almost 100%. A similar effect was also observed for the PHAG-based PU. The strain of pure PU was recovered immediately with heating to 50°C. How-

ever, for ODO- or LP-modified PU, especially for LP-modified PU, there was still a little strain without recovery because of the deterioration of physical cross-linkers in the PU system under a large draw ratio (>600%).[4,16,22] Under large elongation, the lubricating effect of ODO or LP also induces partially plastic deformation, thus undermining the shape-recovery ability.

Two parameters, the shape fixity and shape stability, are employed for the characterization of shape retention. The shape fixity and shape stability of PBAG-based PUs with the variation of the ODO content are summarized in Figure 9. The pure PU, synthesized via the reaction of PBAG (M_n = 2800 g/mol) with MDI–BDO (hard-segment concentration = 25%), has shape fixity (ca. 85%) and shape stability (ca. 61%). Upon the addition of 0.3 wt % ODO, both the shape fixity and stability increase to 100%.

In summary, the shape retention of PU is significantly reinforced by the *in situ* addition of a small amount of ODO, without any change in the type or composition of the two segments of PU. This implies that the segmented polymers are able to be modified to show shape-memory behavior via the addition of small amounts of microphase promoters to enhance their multiple-phase suprastructures.

CONCLUSIONS

The incorporation of a small amount of ODO into conventional PU can significantly improve the microphase-separation structure, thus enforcing the shape-memory behavior (e.g., the increase in T_r, the shape fixity, and the shape stability). LP can also reinforce the shape-memory behavior but less pronouncedly than ODO because of its physical blending or macrophase separation with the PU system. This novel strategy provides a facile route to the synthesis and further upscaling of this type of smart polymer. It is envisaged that this strategy is also suitable for modifying microphase-separated segmented polymers toward shape-memory behavior.

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