

## Thermal and shape memory properties of cyanate/polybutadiene epoxy/polysebacic polyanhydride copolymer

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**ABSTRACT:** A novel thermal-induced shape memory polymer was synthesized by copolymerization of a new kind of epoxy resin-polybutadiene epoxy (PBEP), bisphenol A-type cyanate ester (BACE), and polysebacic polyanhydride (PSPA) with different mass ratios. Fourier transform infrared spectroscopy (FTIR), bending test, dynamic mechanical analysis (DMA), and shape memory property were investigated systematically. It was found that the PSPA significantly enhanced the bending strength and flexural modulus. The DMA results showed that the glass transition temperature reduced with increasing content of PSPA. Furthermore, the shape memory tests proved that the copolymer possessed excellent shape memory properties. The shape recovery time decreased with increasing content of PSPA and temperature. The shape memory rate increased as the PSPA content increased. The shape recovery ratio decreased with increasing cycle times. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42045.

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### INTRODUCTION

The shape memory polymer (SMP) is a new type of intelligent polymer. It can rapidly recover from a temporary shape with an appropriate stimulus such as temperature, X-ray, specific ions, electron, pH, magnetic field, or enzyme.<sup>1–8</sup> Compared with shape memory alloy and shape memory ceramic, SMP possesses the merits of light weight, low cost, good processing, high deformation speed, and tailored transition temperature.<sup>9–14</sup> Since the 1990s, SMPs have been rapidly developed and widely applied in smart textiles and apparels,<sup>15,16</sup> intelligent medical treatments,<sup>17</sup> and self-deployable structures in spacecrafts.<sup>18</sup> It is known that the shape memory theory of SMP relies on the cooperation of the reversible and irreversible phases of the copolymer.<sup>19</sup> Phase separation is necessary in this principle. Irreversible phase should be the cross-links and reversible phase should be flexible and act as the transition.<sup>20</sup>

Liu Yuyan *et al.*<sup>21</sup> prepared shape memory epoxy composites by blending with activity polyurethane. They found that modified blends have lower cross-linking density and lower glass transition temperature for shape memory property. R. Biju *et al.*<sup>22</sup> reported shape memory cyanate ester/epoxy/poly(tetramethylenoxide) copolymer. The obtained glass transition temperature was about 100°C. There are numerous reports on shape memory epoxy throughout the world.<sup>23–26</sup> However, there are a few

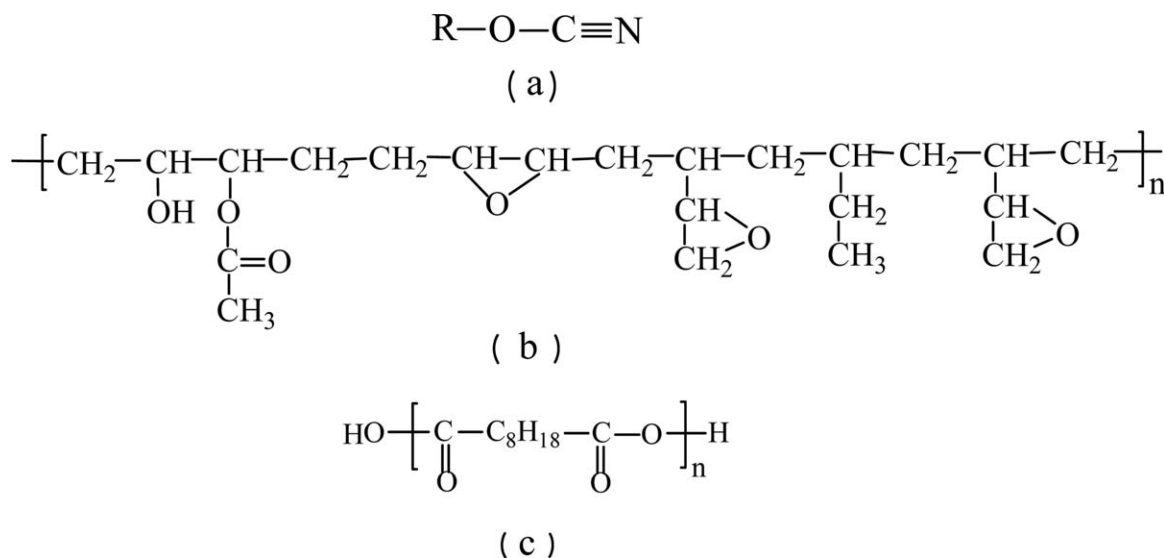
reports on cyanate ester higher transformation temperature for shape memory function.

This study aims to prepare shape memory cyanate with higher transformation temperature. We favor bisphenol A-type cyanate ester (BACE) which form highly cross-linked triazine ring structure resulting in high glass transition temperature. And the triazine ring structure can act as irreversible phase. Moreover, we introduce a newly manufactured epoxy-polybutadiene epoxy (PBEP) and polysebacic polyanhydride (PSPA) that can act as reversible phase. PBEP and PSPA possess flexible aliphatic chains to control the ratio of reversible and irreversible phase in preparing SMP. And the mechanical and thermal properties of BACE can be improved by interacting with PBEP and PSPA.

### EXPERIMENTAL

#### Materials

Bisphenol A-type cyanate ester (BACE), white crystal with purity of more than 99.5% and molecular weight of  $278 \times \text{g mol}^{-1}$  was obtained from Zhejiang Victory Biological Chemical Co., Ltd. Polybutadiene epoxy (PBEP), amber sticky liquid with a molecular weight of  $2000 \times \text{g mol}^{-1}$ , with hydroxyl weight fraction of 2% to 3%, was obtained from WuHan Shi-Zishan Paint Manufactory Co., Ltd. Polysebacic polyanhydride



**Scheme 1.** The chemical structures of BACE, PBEP, and PSPA (a) BACE, (b) PBEP, (c) PSPA.

(PSPA), brown wax and molecular weight of  $5000 \times \text{gmol}^{-1}$ , was obtained from WenZhou Clear and Bright Chemical Co., Ltd. PTFE film, stuck to the glass mold for stripping, was obtained from ShenZhen FenLiDa Plastic Products Co., LTD. The chemical structure of BACE, PBEP and PSPA is shown in S1 Scheme 1.

#### Preparation of SMP Casting

BACE, PBEP, and PSPA were mixed according to the different formulations in Table I. As shown in Table I, the material A3 is defined as the molar ratio of BACE, PBEP, and PSPA is 0.1 : 0.015 : 0.00072. The mixture was stirred thoroughly at  $90^\circ\text{C}$  and poured into a preheated glass mold. Then, the glass mold was put in the vacuum drying oven with constant temperature at  $80^\circ\text{C}$  for 40 min to remove the air bubbles. The curing process was  $100^\circ\text{C}/3\text{h} + 120^\circ\text{C}/2\text{h} + 160^\circ\text{C}/1\text{h}$ . After serial curing, the resulting cast was naturally cooled down inside the furnace.

#### Characterization

**Fourier Transform Infrared Spectroscopy.** Uncured copolymer was dissolved in acetone to prepare the samples for FTIR analysis by casting thin films on KBr discs. A small amount of powder was obtained from the surface of the cured copolymer using a file and mixed with KBr powder. Then, the mixture was grinded in a grinding dish and tableted through a rotary tablet press. FTIR was carried out on a Perkin-Elmer spectrum GXA model between  $500 \text{ cm}^{-1}$  and  $4000 \text{ cm}^{-1}$  under a resolution ratio of  $4 \text{ cm}^{-1}$ .

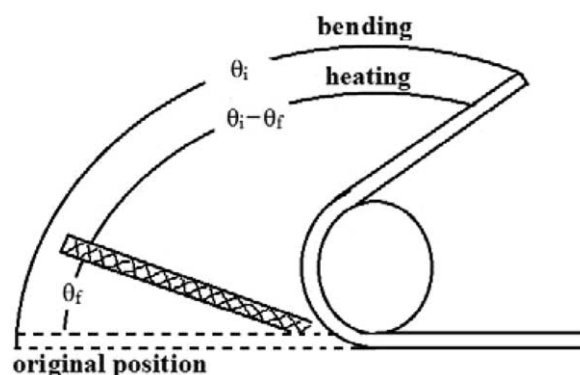
**Gelation Time.** A specimen of the uncured resin system was placed on a steel surface at constant temperature ( $100^\circ\text{C}$ ,

$120^\circ\text{C}$ ,  $140^\circ\text{C}$ ,  $160^\circ\text{C}$ , and  $180^\circ\text{C}$ ), and a knife was used to test gelation. Gel time is defined as the time interval from the resin is initially set until when its gel wire drawing ability is lost.

**Bending Tests.** Bending tests were performed at room temperature using the bending test equipment (SANS Power Test, Shenzhen SANS Material Test Instrument Co., Ltd., China) with a test rate of  $10 \text{ mm min}^{-1}$ . Five specimens for each formulation were measured to achieve the average value. Flexural modulus and bending strength results were recorded during the experiment.

**Dynamic Mechanical Analysis.** DMA samples were cut to dimensions of  $3 \times 12 \times 35 \text{ mm}^3$ . The glass transition temperature ( $T_g$ ) and storage modulus ( $E'$ ) were determined using an instrument TA Q800 in single cantilever clamping fixture. The temperature was ranged from  $25^\circ\text{C}$  to  $260^\circ\text{C}$  at a frequency of 1 Hz and a heating rate  $3^\circ\text{Cmin}^{-1}$ .

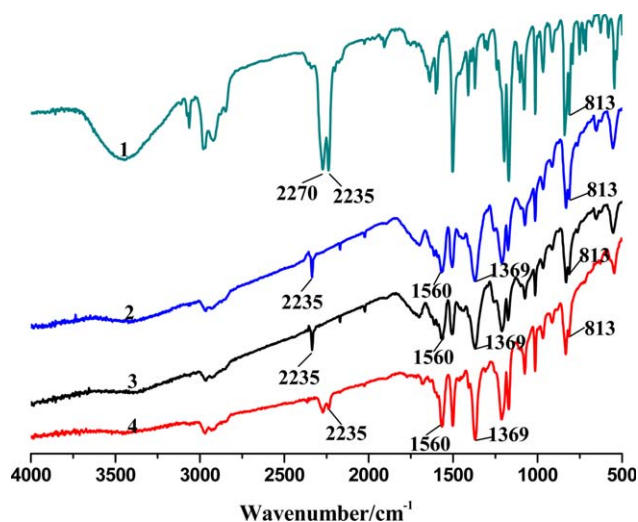
**Shape Memory Properties.** Rectangular specimens ( $35 \text{ mm} \times 15 \text{ mm} \times 3 \text{ mm}$ ) were used to evaluate the shape memory property of BACE/PBEP/PSPA copolymer. Shape memory tests were conducted under the following procedures. (1) The samples were heated up to the transformation temperature



**Figure 1.** Deformation model of shape memory effect.

**Table I.** The Different Formulations of Copolymerization System

Samples	A1	A2	A3	A4	A5
BACE (mole)	0.1	0.1	0.1	0.1	0.1
PBEP (mole)	0.015	0.015	0.015	0.015	0.015
PSPA (mole)	0.00024	0.00048	0.00072	0.00096	0.0012



**Figure 2.** FTIR of A3 before and after curing (1) before curing, (2) after curing (100/3 h), (3) after curing (100°C/3h + 120°C/2h), and (4) after curing (100°C/3h + 120°C/2h + 160°C/1h). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

( $T_{\text{trans}}$ ,  $T_{\text{trans}} = T_g$ ,  $T_g + 10^\circ\text{C}$ ,  $T_g + 20^\circ\text{C}$ ) above the  $T_g$  in an oven for 10 min for full heating. (2) As it is shown in Figure 1, the samples were deformed to an angle  $\theta_i$  ( $\theta_i = 180^\circ$ ) and was rapidly quenched in cold water. Consequently, the deformation was restored. (3) The sample was heat up to  $T_{\text{trans}}$  again, and the shape recovery process was observed. When the angle does not change the shape, recovery time was recorded. The shape recovery rate at corresponding temperature is defined as  $\theta_i/t$ , and the shape recovery ratio is defined as  $(\theta_i - \theta_f)/\theta_i \times 100\%$ .

## RESULTS AND DISCUSSION

### Cure Characteristic of BACE/PBEP/PSPA

In this study, FTIR was conducted to clearly know the reaction between the groups of the copolymerization system. Figure 2 illustrated us FTIR curves of the uncured and cured of A3. It can be seen from Figure 2 that the absorption peaks of functional groups were significantly different before and after the copolymerization reaction.

Without the promoter, a small amount of curing agent, such as acid anhydride, reacts with the hydroxyl group in the epoxy resin to produce the monoester containing a carboxyl group, which in tune triggered the reaction of PBEP.<sup>27</sup> And the reaction rate between acid anhydride and hydroxyl group has relationship with the concentration of the hydroxyl group in the epoxy resin. In this experiment, the weight fraction of hydroxyl group in the epoxy resin is 2% to 3%. Therefore, the reaction between acid anhydride and hydroxyl group in the epoxy resin is slow. It was confirmed from the disappearance of the hydroxyl group ( $3460\text{ cm}^{-1}$ ) and the appearance of the monoester group ( $1735\text{ cm}^{-1}$ – $1806\text{ cm}^{-1}$ ).

In addition, the curing of the epoxy groups ( $811\text{ cm}^{-1}$ ) and CE groups ( $2270\text{ cm}^{-1}$  to  $2235\text{ cm}^{-1}$ ) in the system was verified from the disappearance of peak. It was confirmed again from the formation of triazine groups at  $1560$  and  $1369\text{ cm}^{-1}$  and oxazoline ketone group at  $1680\text{ cm}^{-1}$ . Ketone group

(interaction between epoxy and CE) was arising continually as the reaction proceeded. Triazine ring ( $1369\text{ cm}^{-1}$ ) showed the similar trend.

Therefore, FTIR clearly showed the changes of the functional groups before and after curing. Taking benzene ring group ( $830\text{ cm}^{-1}$ ) as internal standard, the apparent conversion ratio<sup>27</sup> is defined:

$$X = 1 - \frac{H(t)_R \times H(t_0)_{830}}{H(t_0)_R \times H(t)_{830}}$$

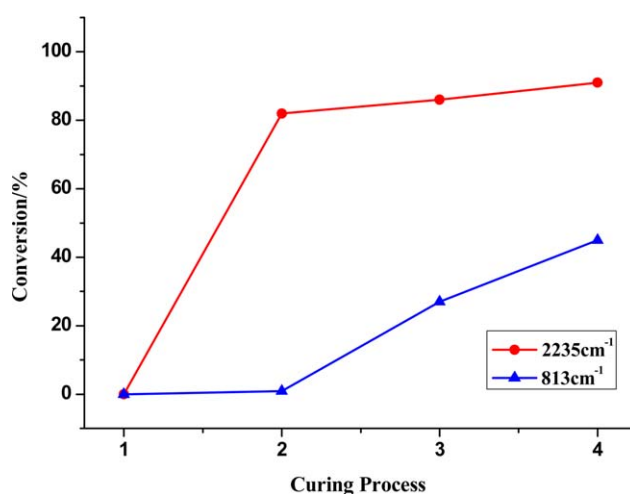
Where  $H(t_0)_R$ ,  $H(t)_R$ ,  $H(t_0)_{830}$ , and  $H(t)_{830}$  are the peak height of R and benzene ring before and after curing, respectively.

Figure 3 showed the conversion of epoxy group and cyanate group before and after a series of curing process. It can be seen from the Figure 3 that at the previous stage of curing process, the reaction rate of cyanate is significantly faster than the epoxy. And the conversion of epoxy group is less than the conversion of cyanate group. The main reaction equations are shown in S2 S3 Schemes 2 and 3.

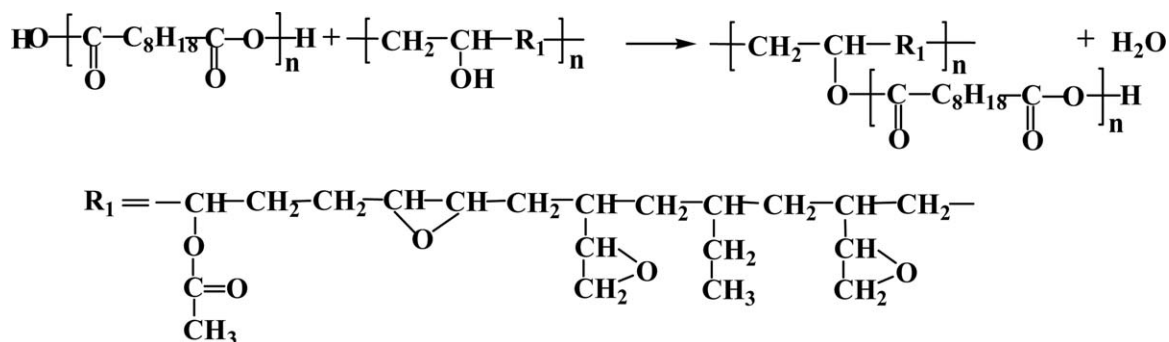
Moreover, Scheme 4 illustrated the microstructure of BACE/PBEP/PSPA copolymer. The cross-linking points can be seen as a triazine ring structure, and the soft segments can be regarded as the flexible aliphatic chains of PBEP and PSPA. When the copolymer is heated above the glass transition temperature, the orientation and deformation of the soft segments will occur under an external force; when the external force is removed, the soft segments will return to the initial state.

### Chemical Reactivity of The Copolymerization System

It is known that the gel time probably illustrates the curing time at corresponding temperature. Figure 4 showed the gel time of the copolymerization system at different temperature. The graph shows that the gel time of copolymerization system with different molar ratio of PSPA decreased as the temperature increased. As shown in Figure 4, the formulation of PSPA-



**Figure 3.** The conversion of epoxy group and cyanate group versus curing process. before curing, (2) after curing (100/3h), (3) after curing (100°C/3h + 120°C/2h), and (4) after curing (100°C/3h + 120°C/2h + 160°C/1h). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



Scheme 2. Graft copolymerization of PBEP and PSPA.

0.00024 will gel in 720 s at 100°C but will gel in only 82 s at 180°C.

In addition, at the same temperature, the gel time of all copolymerization systems decreased as PSPA increased. The PSPA-0, which is the copolymer system without PSPA, will gel in 73 min at 100°C, but PSPA-0.00048, will gel in only 10 min at 100°C. This result indicates that the temperature and the amount of PSPA could promote the chemical reactivity of the copolymerization system.

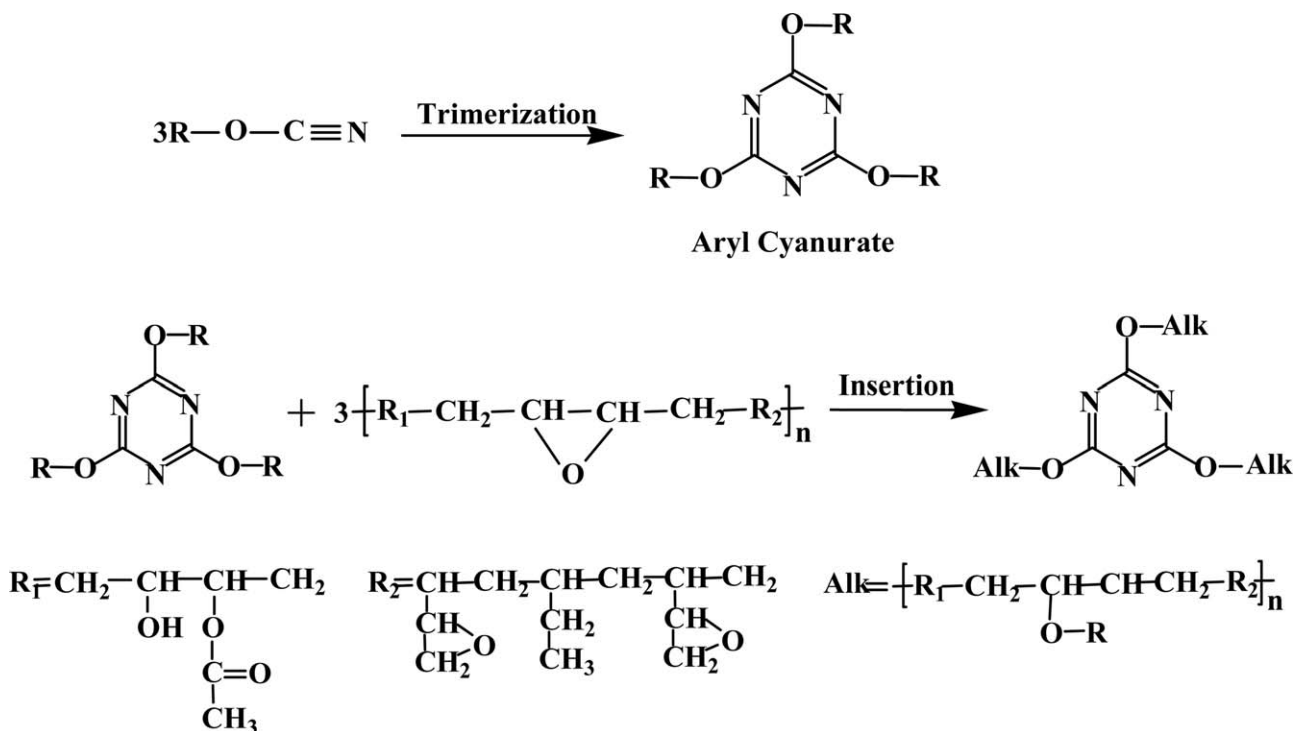
#### Mechanical Analysis

Mechanical property is one of the most important determinants of shape memory BACE/PBEP/PSPA copolymer as smart structural materials.<sup>28</sup> Figure 5 showed the bending strength and flexural modulus of BACE/PBEP/PSPA copolymer at room temperature. It was indicated that the content of PSPA had a significant influence on the mechanical performance of copolymer:

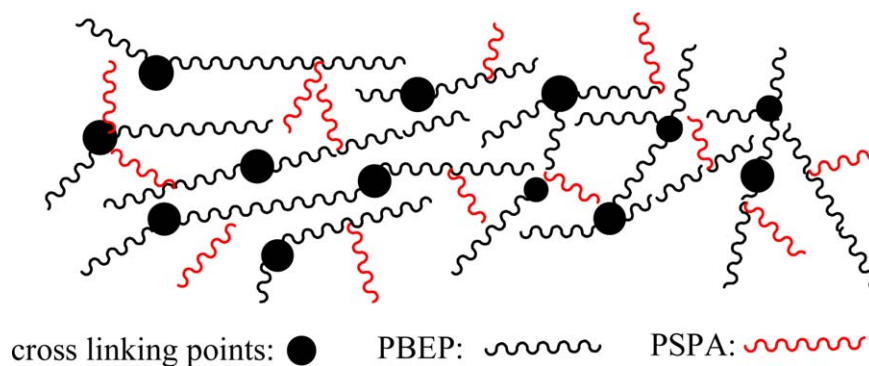
higher bending strength and flexural modulus was observed at higher weight fraction of PSPA. Theoretically, when CE is completely solidified, neat structure containing triazine and oxazoline ketone rings can be obtained to result in higher crystallinity and greater cross-linking density. Moreover, FTIR and gel time illustrated that the curing process of PBEP can be promoted, and curing reaction was more complete in the presence of PSPA. Therefore, both rigidity and bending strength increased. Therefore, the introduction of PSPA could improve the mechanical performance to satisfy the demand of various applications.

#### DMA

In order to determine the transformation temperature for shape memory test,  $T_g$  of different samples was investigated by DMA, and DMA curves of BACE/PBEP/PSPA copolymer are shown in Figures 6 and 7. The  $T_g$  of A1, A3, and A5 are 119°C, 113°C, and 101°C, respectively. Theoretically, the



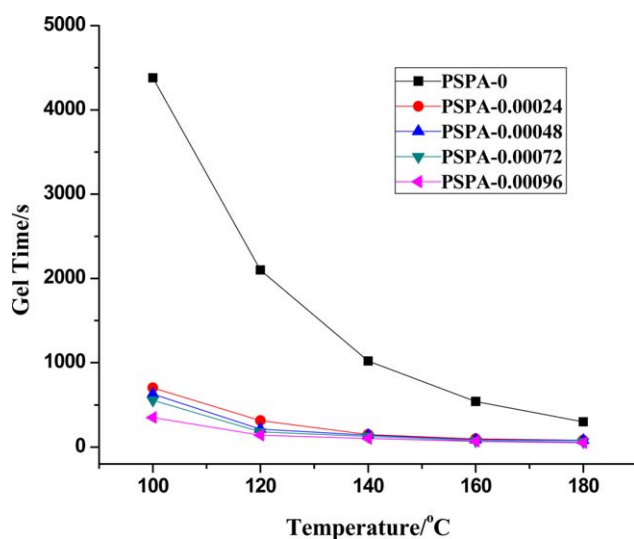
Scheme 3. Synthesis of shape memory BACE/PBEP/PSPA copolymer.



**Scheme 4.** Schematic illustration of microstructure of BACE/PBEP/PSPA copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

flexibility, one of the most important factors influencing  $T_g$ , decreased due to the introduction of PSPA. PSPA includes flexible aliphatic chains and  $-\text{COOH}$  groups. On the one hand, the  $-\text{COOH}$  which is polar group increases  $T_g$ . On the other hand, the flexible aliphatic chains can greatly reduce the  $T_g$ . However, for PSPA with molecular weight of  $5000 \times \text{g mol}^{-1}$ , the effect of the latter is far more than the former. Therefore, the  $T_g$  of BACE/PBEP/PSPA copolymer decreased as the content of PSPA increased. And the anelasticity of molecular chains showed the same trend. Subsequently, the peak of  $\tan \delta$  shifted toward lower temperature.

Moreover, it was generally recognized that the prominent shape memory materials must have a stable high-elastic state, and the mechanical modulus usually changed about two orders of magnitude when the ambient temperature varied.<sup>21</sup> Figure 7 illustrates that the storage modulus of BACE/PBEP/PSPA copolymer below  $T_g$  are about two orders of magnitude larger than that above  $T_g$ . For instance, the A3 sample exhibits a storage modulus of 2275.2 MPa at  $20^\circ\text{C}$ , while it is just 7.5 MPa at  $180^\circ\text{C}$ . It was indicated that the incorporation of PSPA was beneficial for shape memory property.

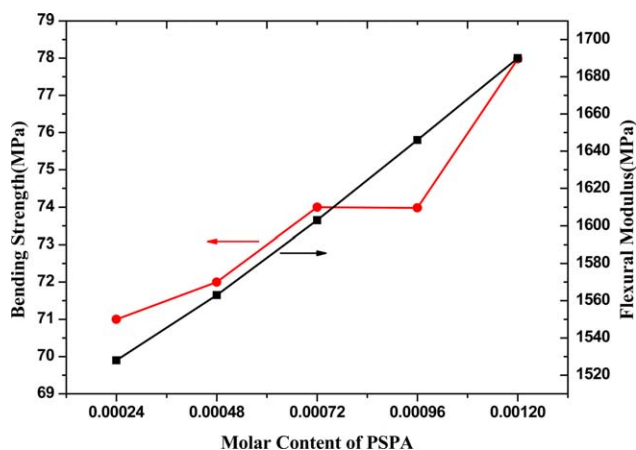


**Figure 4.** Gel time of the different copolymerization systems. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

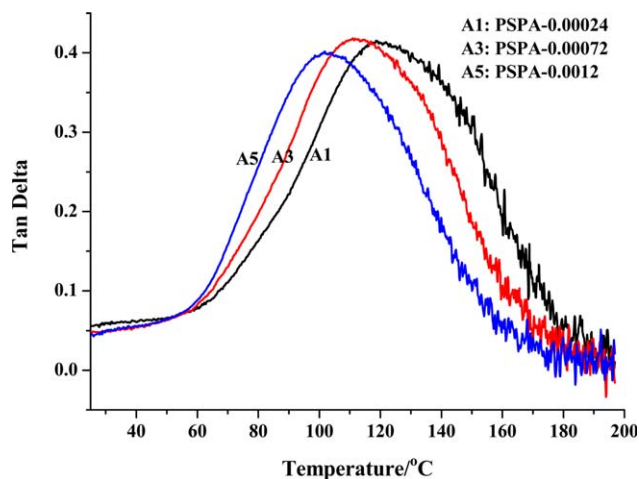
### Shape Memory Properties

The detailed shape memory performances including shape recovery time, shape recovery rate, shape recovery ratio, and the cycle times were revealed in Figures 8–10 and Table II. Figure 8 showed us a whole and clear shape recovery procedure at  $T_g$  for A4. The sample was heated to its  $T_g$  temperature, deformed to the temporary shape, and cooled down to the room temperature to fix the deformation. When the sample was heated to the  $T_g$  temperature again, it automatically recovered to the initial shape and the angle changed from  $180^\circ$  to  $0^\circ$  within 115 s. This simple shape deformation and fast recovery process demonstrate its excellent shape memory effect, and it can be used in thermo-sensitive actuators.

Figure 9 illustrated the relationship between the molar content of PSPA and shape recovery time at  $T_g$ ,  $T_g + 10^\circ\text{C}$  and  $T_g + 20^\circ\text{C}$ . It can be seen from the figure, shape recovery time decreased with increasing content of PSPA. For instance, at  $T_g$ , the A1 recovered to the initial shape within 154 s, while the A5 just took up 109 s. In addition, for the same sample, shape recovery time will be less as the temperature increased. The shape recovery time of A2 was 143 s, 132 s, and 129 s at  $T_g$ ,  $T_g + 10^\circ\text{C}$  and  $T_g + 20^\circ\text{C}$ , respectively. The cycling times were



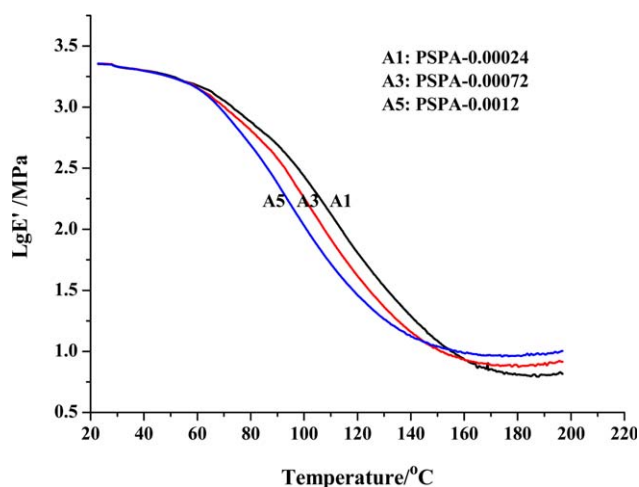
**Figure 5.** Bending strength and flexural modulus at room temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6.**  $\tan\delta$  versus temperature of BACE/PBEP/PSPA copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

an important index of shape memory polymer, characterizing recyclability of shape recovery. Figure 10 showed the relationship between cycling times and shape recovery time. The curves showed that the shape recovery time decreased with increasing number of cycling times. However, five heating/cooling cycles were conducted for all samples without losing shape memory effect. As shown in Table II, the deformation recovery rate was the highest at A5 and slightly decreased with decreasing content of PSPA. Moreover, the shape recovery ratio was almost 100%.

Apparently, shape memory effect improved with flexible linking, and the value of shape recovery speed was in direct proportion with PSPA content. The shape recovery was ascribed to the release of inner stress (the flexible aliphatic chains of PBEP and PSPA), which is applied and memorized during the deformation and the shape-fixing stages, respectively. The recovery behavior of SMP shows strong dependency on PSPA content. Besides the above mechanical and thermal test results, shape memory test



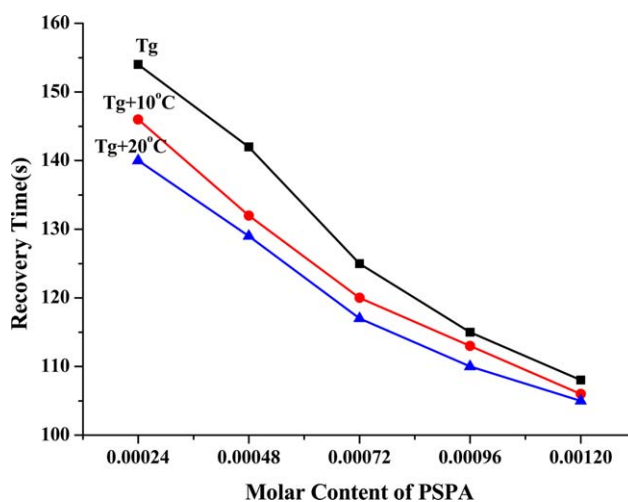
**Figure 7.** Storage modulus versus temperature of BACE/PBEP/PSPA copolymer. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 8.** Visual demonstration of shape memory effect for A4. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

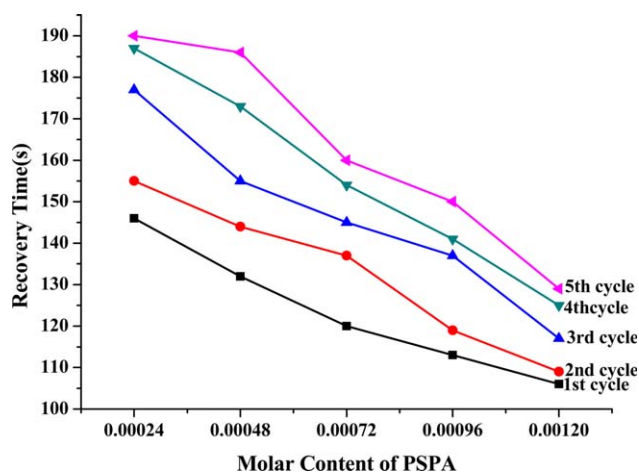
**Table II.** Shape Recovery Rate and Ratio of BACE/PBEP/PSPA Copolymer at  $T_g$

Samples	A1	A2	A3	A4	A5
Shape recovery rate/ $s^{-1}$	0.0204	0.0220	0.0248	0.0273	0.0288
Shape recovery ratio/%	100	98	100	100	100



**Figure 9.** Shape recovery time versus the molar content of PSPA at  $T_g$ ,  $T_g + 10^\circ\text{C}$  and  $T_g + 20^\circ\text{C}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

confirmed that flexible linking of PSPA was helpful in improving its shape memory recovery. Better shape memory recovery was obtained with more flexible linking in the copolymer system. Therefore, the incorporation of PSPA in flexible linking was beneficial for shape recovery properties.



**Figure 10.** Shape recovery time versus the cycling times at  $T_g$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSION

In this study, a novel type of thermal-induced shape memory polymer with good thermal and mechanical performances was copolymerized of BACE, PBEP, and PSPA with different mass ratios. Shape memory properties could be improved by adjusting the matrix ratio. PSPA content had a great beneficial impact on shape recovery behavior. The shape recovery time increased with the growing content of PSPA. The maximum and the minimum shape recovery rate were  $0.0288 \text{ s}^{-1}$  and  $0.0204 \text{ s}^{-1}$ , respectively. Further, the shape recovery ratio was almost 100%. The polymer synthesized in this study is suitable for processing good shape memory composites and is potentially applied in manufacturing intelligent materials and sensors.

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