

CONVENIENT CONTROL OVER HIGH TEMPERATURE SHAPE MEMORY POLYMERS

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ABSTRACT

Glass transition temperature (T_g) is crucial in determining application areas of high temperature shape memory polymers (SMPs), but some T_g s are difficult or uneconomic to be obtained. Here we introduce a facile way to prepare high temperature SMPs with controllable T_g s from 456 to 503 K by copolymerization of polyimides, and relationships between T_g s and diamine components of the shape memory copolyimides agree with Fox Equation. These copolyimides can fix temporary shape and return to original shape nicely, and the possible mechanisms of their high shape fixity and shape recovery are analyzed on the basis of thermomechanical properties and molecular structures. The copolymerization of shape memory polyimides has offered an effective way to obtain high temperature SMPs with desired properties.

1 INTRODUCTION

Stimuli-responsive polymers are playing an important role in various applications as they are smart materials that can respond to external stimuli.^[1-4] Among them, shape memory polymers (SMPs) have attracted more and more attentions as they can recover to initial shape from contemporary shape under external stimuli such as heat, electric, magnetic and light.^[5-9] Heat is the major stimulus for SMPs, and shape transition temperature (T_{trans}) is critical to their applications.^[10-15] High temperature SMPs have potentials in many fields such as deployable space structures and high temperature actuators, and glass transition temperature (T_g) is the basic reference for their T_{trans} .^[16, 17] T_g should be higher than operating temperature to avoid premature shape recovery, but if T_g is too high the shape transition process will cause some damages to the environments.^[18, 19] Therefore, control of T_g is of great importance for high temperature SMPs.

There have been several reports about high temperature SMPs, such as shape memory cyanate, polyimides, and sulfonated poly(ether ether ketone) ionomers.^[20-22] It is observed that some factors such as molecular structure, molecular weight and crosslinking density can affect T_g s of high temperature SMPs.^[23-25] For example, shape memory polyimides of different molecular structures bear certain T_g s.^[23] However, it is not very easy and sometimes impractical to obtain SMP with expected particular T_g s by changing molecular structures due to the lack of suitable reactants. Molecular weight (M_n) can also exert influence on T_g s but the temperature range is usually about 10 K, as samples with M_n lower than the critical molecular weight can't produce shape memory effects.^[24] Higher crosslinking density lead to higher T_g of SMPs, but their shape memory performance will deteriorate obviously when crosslinking density exceeds certain values.^[25] Until now, the control over T_g s of high temperature SMPs within wide temperature range is still lacking.

Here we introduce a facile way to prepare high temperature SMPs with controllable T_g s located from 456 to 503 K by copolymerization of shape memory polyimides. T_g s of the shape memory copolyimides can be tailored by adjusting the diamines components, and the relationships between T_g s and components fit to Fox Equation. The copolyimides can fix the contemporary shape and return to original shape very well, and the possible mechanisms of their shape memory performance are discussed.

2 EXPERIMENTAL SECTION

Materials. 4,4'-(4,4'-Isopropylidenediphenoxy)bis(phthalic anhydride) (BPADA, 98 %) and 4,4'-Bis(4-aminophenoxy)biphenyl (BAPB, 99 %) were purchased from TCI chemicals, 1,3-Bis(3-aminophenoxy)benzene (BAB, 99 %) was purchased from Sigma-Aldrich, and the reactants were used without further purification. Dimethylformamide (DMF) was bought from Sinopharm Group Co. Ltd.

Synthesis of shape memory copolyimides. The mixture of 5 m mol BAB and BAPB were added into 40 ml DMF and stirred under dry nitrogen until completely dissolved to form a homogeneous solution at room temperature. Then a stoichiometric amount of BPADA was added into the solution and stirred 24 h to form poly(amic acid)s (PAAs) at room temperature. The PAA was poured onto the glass plate and evaporated at 50 °C for 5 h, and then underwent step-wise curing at 70, 100, 150, 180, 220 and 260 °C for 2 h, respectively. The samples were detached away from glass in deionized water, and then heated at 100 °C for 5 h.

Structure characterization. Structure of the shape memory copolyimides was characterized with Fourier transform infrared (IR), and the IR spectra were obtained on Thermo Nicolet Nexus 870. Molecular weight was characterized with size exclusion chromatography (SEC) on Waters 2414 equipped with a refractive index detector.

Thermomechanical and thermal characterization. Thermomechanical properties of the shape memory copolyimides were characterized with TA instrument DMA Q800 in tensile mode at the frequency of 1 Hz, and the heating rate was 3 °C/min. Thermal stability was characterized with TA instrument Q500 TGA under nitrogen with heating rate of 10 °C/min.

Shape memory characterization. Shape memory properties of the copolyimides were characterized as follows: (1) The flat polyimide film was twisted around a glass rod at T_g+30 K, (2) the spiral-shaped temporary shape was fixed at room temperature, (3) the spiral was reheated at T_g+30 K and recover to flat film.

3 RESULTS AND DISCUSSION.

Structure of the shape memory copolyimides. The shape memory copolyimides of BPADA/BAB-BAPB were synthesized with two-step polycondensation process by employing BPADA as dianhydride and the combination of BAB and BAPB as diamines, and the sythesis process is shown in Figure 1.

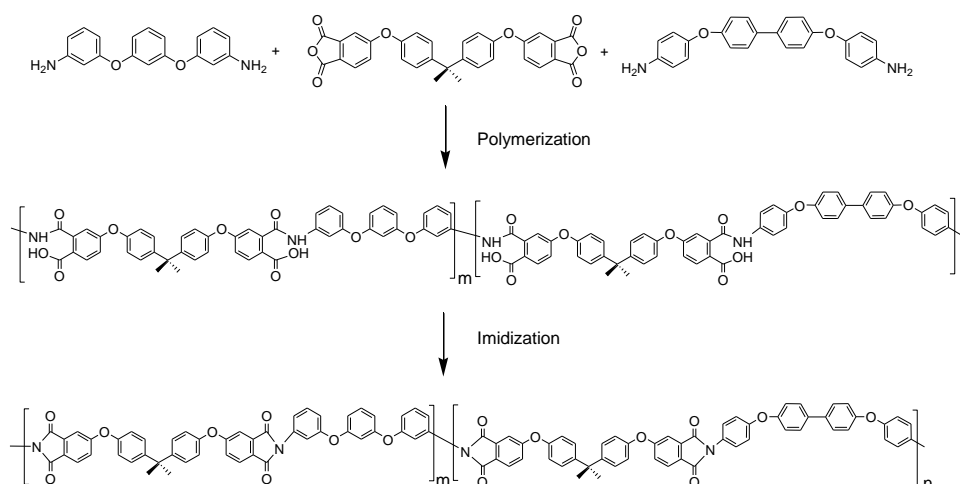


Figure 1. Synthesis process of shape memory copolyimides of BPADA/BAB-BAPB.

Structures of these shape memory copolyimides were characterized with IR, as shown in Figure 2. The asymmetric stretching, symmetric stretching and bending of C=O vibrations, together with C-N-C stretching vibrations of imide ring are located around 1775, 1717, 738 and 1375 cm^{-1} , respectively. These IR peaks confirmed the successful and complete imidization of the shape memory copolyimides.^[26]

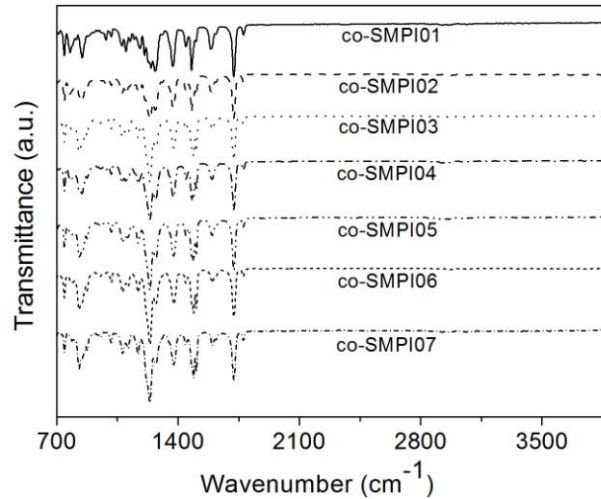


Figure 2. IR spectra of shape memory copolyimides of BPADA/BAB-BAPB.

T_g of the shape memory copolyimides T_g is crucial to high temperature SMPs, and here T_g of the shape memory copolyimides was controlled by adjusting diamine components. The peak of loss factor ($\tan \delta$) obtained with DMA is regarded as their T_g s, as shown in Figure 3a.

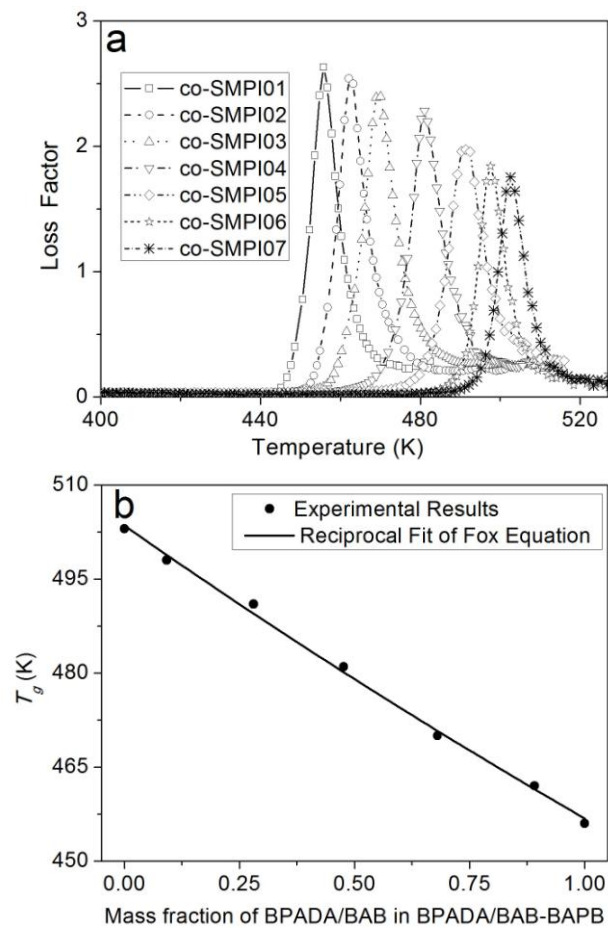


Figure 3. T_g of the shape memory copolyimides. (a) Loss factor versus temperature, (b) T_g as a function of diamine components in BPADA/BAB-BAPB.

All the shape memory copolyimides are random copolyimides, as judged from the single T_g .^[26] It is observed that there is a increase of T_g with the decrease of BAB content, and co-SMPI01, co-SMPI02,

co-SMPI03, co-SMPI04, co-SMPI05, co-SMPI06 and co-SMPI07 exhibit T_g s of 456, 462, 470, 481, 491, 498 and 503 K, respectively. The reduced value of $\tan \delta$ in samples with higher T_g indicates the enhanced elastic feature of the copolyimide the increase of BAPB.

Due to the importance of T_g to polymers, many attempts have been executed to create $T_g(x)$ equations of copolymers and polymer blends, such as Fox Equation, Gordon-Taylor Equation and Kwei Equation.^[27, 28] Among them, Fox Equation is a very important basic equation that can adopt to many systems. For binary systems, Fox Equation can be expressed as Equation 1:

$$\frac{1}{T_g} = \frac{x_1}{T_{g,1}} + \frac{x_2}{T_{g,2}} \quad (1)$$

Here $T_{g,i}$ and T_g are pertinent to the pure component i and copolymer, respectively. The x_i is the mass (weight) fraction of component i , and $x_2=1-x_1$.^[28] Relationship between T_g and content of diamines of the shape memory copolyimide is correlated with Equation. 1, as manifested in Figure 3b. It is observed that T_g s of the copolyimide vary within the temperature range of 47 K, and they adhere to the reciprocal fit of Equation 1 very well. It has been proved that the fitting of T_g s to Fox Equation is mainly caused by the similarity in molecular structures of polymer components of the copolymers.^[27, 28] As manifested in Figure 1, both BAB and BAPB molecules contain two ether linkages connecting benzene rings, and thus there is similarity in the molecular structures of BPADA/BAB and BPADA/BAPB. Accordingly, the copolyimide of BPADA/BAB-BAPB possesses rather uniform structure in its molecular chains. As a result, the similarity in molecular structures of BPADA/BAB, BPADA/BAPB, and BPADA/BAB-BAPB lead to the nice fitting of their T_g s to Fox equation. Therefore, the copolymerization of shape memory polyimides has offered a convenient way to obtain SMPs with controllable high T_g s.

Thermal stability of the shape memory copolyimides.

Thermal stability of the shape memory copolyimides were characterized with TGA, as shown in the supporting information (Figure S1). The temperature at which 5 % weight loss occurs is regarded as decomposition temperature (T_d) of the shape memory copolyimides, and the samples are suitable for high temperature applications with their T_d s higher than 500 °C. Besides, the char yields at 800 °C are all higher than 50 %. These results have manifested that the shape memory copolyimides are highly thermally stable.

Shape memory properties of the copolyimides.

Shape memory properties of the copolyimides were characterized and they showed nice shape memory performances by fixing temporary shape and recovering to original very well. The shape recovery process of co-SMPI04 from temporary spiral shape to original flat shape on hot-stage set at 240 °C are illustrated in Figure 4.

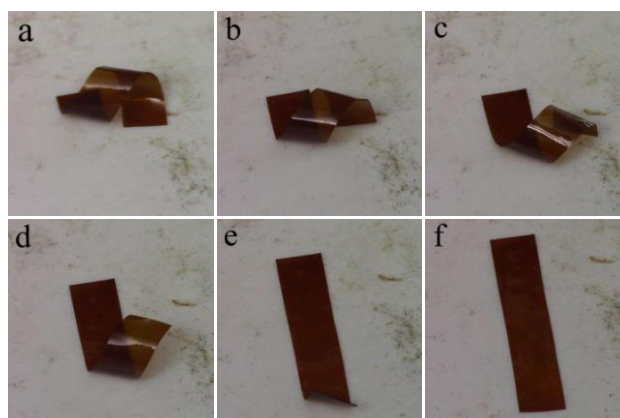


Figure 4. Shape recovery process of shape memory copolyimide. (a) Temporary shape of co-SMPI04, (b) its recovery shape on hot-stage set at 240 °C for 7s, (c) 10s, (d) 15s, (e) 18s, and (f) 26s, respectively.

The shape memory copolyimides can fix the temporary shape very well, i.e., they exhibit high shape fixity. The shape fixity of SMP is concerned with its thermomechanical properties,^[10, 11] and the storage modulus (E') of the shape memory copolyimides are manifested in Figure 5. It is clearly demonstrated that the E' is high and decreases slowly with the increase of temperature at glassy state. For example, the E' of co-SMPI04 is 2.29 GPa and 1.68 GPa at 333 K and 461 K (T_g-20 K), respectively. Then it undergoes a huge drop during glass transition process and is rather low at rubbery state, and the E' of co-SMPI04 is 6.28 MPa at 501 K (T_g+20 K). The low E' favors the deformation of initial shape, while the high value is conducive to fixing of temporary shape.^[10, 11] Therefore, the large difference in E' at rubbery and glassy states of co-SMPI04 account for its nice fixity of temporary shape.

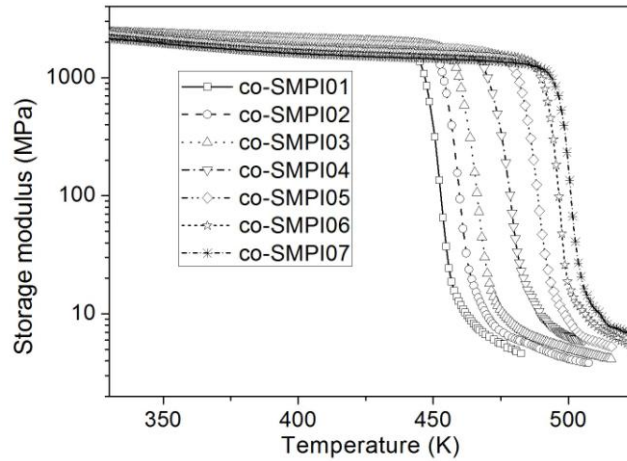


Figure 5. Storage modulus of the shape memory copolyimides.

It is observed from Figure 5 that all the other shape memory copolyimides also exhibit huge gap in E' at rubbery and glassy states. The typical values of E' are summarized in the supporting information as Table S1, and the value at glassy state (T_g-20 K) is more than two hundred times higher than that at rubbery states (T_g+20 K). Therefore, all the shape memory copolyimides manifested high shape fixity rates.

The shape memory copolyimides can return to the original shape completely, indicating that they possess high shape recovery. For SMPs, the shape recovery is mainly determined by the permanent phase composed of chemical or physical crosslinkers.^[10, 11] It has been observed that for thermoplastic shape memory polyimide, both $\pi-\pi$ interactions and chain entanglements can act as permanent phase.^[21, 23, 24] For shape memory copolyimide, the high shape recovery is closely related with permanent phase caused by its molecular structures, as manifested in Figure 6.

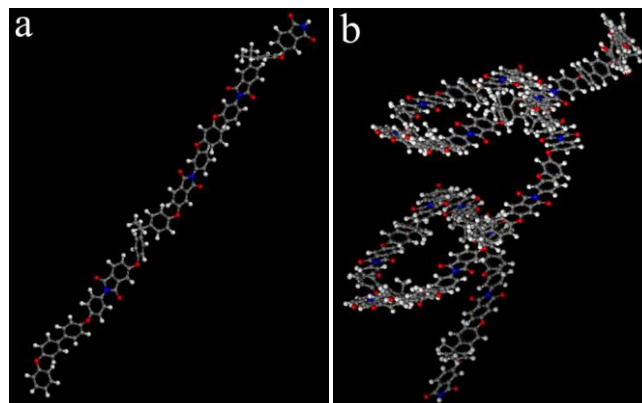


Figure 6. 3D illustration of molecular structures of shape memory copolyimides. (a) Repeating unit and (b) the highly twisted chain of co-SMPI04.

The shape memory copolyimides can produce strong π - π interactions since they bear high degree of aromatic rings, as manifested by three-dimensional (3D) illustration of the repeating unit structure of co-SMPI04 in Figure 6a. The number average molecular weight of co-SMPI04 is measured to be 18.8 kg/mol and the corresponding chain comprises 11 repeating units, and 3D illustration of the chain structure is illustrated in Figure 6b. It is observed that the chain is high twisted, and the aggregation of such chains are apt to form a great deal of chain entanglements. As a result, the shape memory copolyimides exhibit high shape recovery rates with their strong π - π interactions and substantial chain entanglements acting as the permanent phase.

4 CONCLUSIONS

In summary, high temperature shape memory polymers possessing controllable T_g s are obtained by copolymerization of BPADA with diamine combinations of BAB and BAPB. T_g of the shape memory copolyimides can vary from 456 K to 503 K, and the relationship between T_g s and their components fit to Fox Equation very well. The thermally stable copolyimides possess nice shape memory performances and the large difference in storage modulus at glassy and rubbery states mainly accounts for the high shape fixity, while the strong π - π interactions and substantial chain entanglements determine the high shape recovery. The facile copolymerization of shape memory polyimides has been proved to be a useful way to obtain high temperature shape memory polymers with desired properties.

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