Preparation and Properties of Multi-Shape Memory Polyimides with High Strain

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ABSTRACT: A series of polyimides with low crosslink density were obtained by crosslinking with non-coplanar crosllinkers. Polyimides showed the best shape memory effects when the content of crosslinker is 0.5%, and the strain as high as 460%. In addition, based on the study of multi-stage recovery test, we found that the polyimides may have the ability to tune the programming temperature to achieve multiple-shape memory behavior. Moreover, we also investigated this series of low crosslinking density polyimides for the shape memory cycle stability, stress relaxation, thermal properties, mechanical properties, dielectric properties and water absorption.

Keywords: Polyimides; high strain, multiple shape memory effect

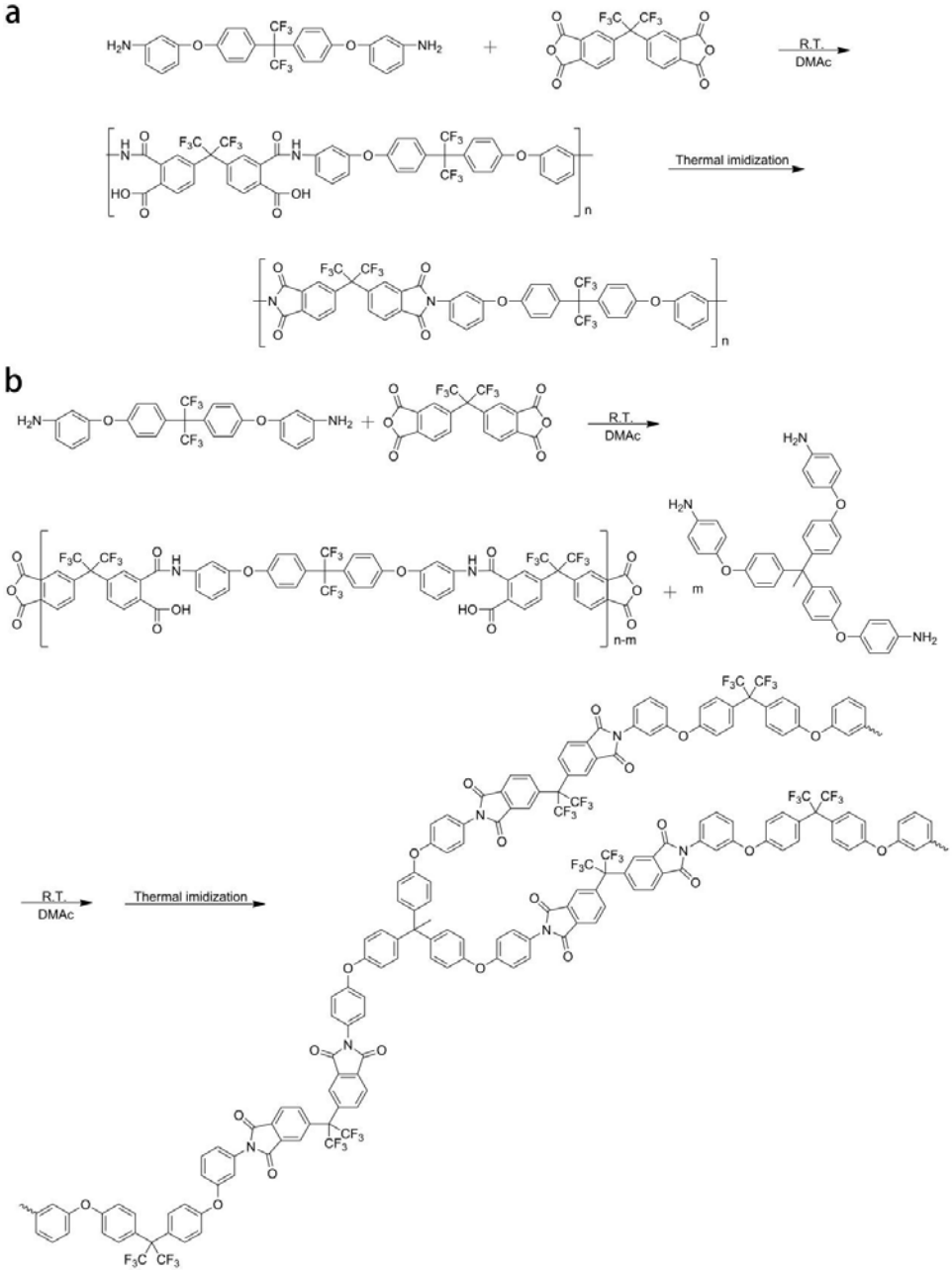
1. INTRODUCTION

Polyimides as a class of thermally responsive SMPs have been widely studied due to the excellent thermal properties and mechanical properties. Neat thermoplastic polyimides possess strong π-π interactions leads to excellent dual-shape memory effect (SME).17 Polyimides with large content of aromatic groups, strong intermolecular interactions, showed high cycle life for bending deformation.18 Leng et al. explored the shape memory polymers with adjustable high glass transition temperature (300 ℃) and make a comparison with the thermoplastic and thermoset polyimides. Besides, PI nanocomposites were also been investigated.19-23 Graphene polyimide nanocomposites exhibited high-temperature shape memory effects.21 Low cross-linked polyimide nanocomposites reinforced by single wall carbon nanotubes showed good shape memory performance with a glass transition temperature of 220 ℃.23 As to multi-shape memory polyimides, one can obtain the target properties using the copolymers which have two glass transition temperatures.24 All of these polyimides showed excellent shape memory properties, however, its strain was no more than 200% up to now.

In this work, we selected kinked diamines containing trifluoromethyl and dianhydrides containing trifluoromethhyl to execute polymerization reactions. A series of polyimides with low crosslink density were obtained by crosslinking with non-coplanar crosllinkers. Swelling property of crosslinked polyimides was investigated, and the crosslinking densities of the materials were calculated by the linear fitting of the stress-strain relationship according to the phenomenon theory. Analyzing the influence on shape memory by crosslink densities, the results showed that polyimides showed the best shape memory effects when the content of crosslinker is 0.5%, and the strain as high as 460%.

2. EXPERIMENTAL

The synthesis of PI-0.5 (m-6FBAPP/6FDA/0.5%mol TAPE) is used as an example to illustrate the general synthetic route as shown in Scheme 1. 1.7770 g 6FDA was added to a solution of 2.0427 g m-6FBAPP in 10 g DMAc with stirred under nitrogen. The reaction mixturtirred at room temperature for 24h to afford a viscous poly(amic acid) (PAA) solution. 0.0232 g TAPE as triamine crosslinker (equimolar with functional groups) and additional 5.4 g DMAc was added to the mixture with stirring for another 12h. The solid concentration of the reaction system was controlled at 20%wt. PI films were prepared by pouring the PAA onto the glass plastes and then heated in air oven with a temperature procedure (50 ℃/24h, 80 ℃/24h) to remove the solvent. In addition, the materials were fully imidized at 100 ℃/2h, 150 ℃/2h, 200 ℃/1h, 250 ℃/1h, and 300 ℃/1h under vacuum. The films were stripped from the plate by soaking into the distilled water they were cooled to room temperature, and the thickness is about 150 μm.



Scheme 1. a) Synthesis route of PI-0. b) Synthesis route of crosslinked PI.

3. RESULTS AND DISCUSSION

In this work, we attempt to design and synthesis a series of high strain multi-shape memory polyimides by

traditional polycondensation as shown in Scheme 1. The degree of crosslinking was controlled by the ratio of monomer and crosslinker. Neat polyimides and four different degrees of crosslinking polyimides were investigated and the detailed recipe is given in Table 1. For the fact that fully aromatic polyimides have rigid chains and strong interchain interactions, the polymers have limited strain when deformation. These strong interactions originate from intra- and interchain charge transfer complex (CTC) formation and electronic polarization. In our strategy, the introduction of $-CF_3$ into polymer chains' alignment and disrupt the formation of efficient CTC, which endow materials with a high strain when deformation. We selected 2,2'-bis[4-(3-aminophenoxy)phenyl]hexafluoropropane (m-6FBAPP) and 4,4'-(hexafluoroisopropylidene) (6FDA) to have polymerization reactions. The formation of the long repeating units and highly kink structures can increase the flexibility of the macromolecular chain and lead to massive chain entanglement, which can provide enough physical crosslink network that an excellent SMP requires. As shown in Figure 1, the red and blue balls represent two different crosslinks of the macromolecular chain. In addition, 1,1,1-tris[4-(aminophenoxy)phenyl]ethane (TAPE) as non-coplanar crosslinker provides lightly chemical crosslinks of the polyimides. The synergistic of physical crosslinks and chemical crosslinks makes the polymer have a good shape memory effect.

Table 1. Physical and thermal properties of the polyimides.

	Cross-linker (mol%)	Gel Content (wt%)	Crosslink density (%)	T_g (°C)	$T_{5\%}$ (°C)[a]
PI-0	0	0	-	226	529
PI-0.5	0.5	93.4	0.24	227	528
PI-1	1.0	93.9	0.25	225	526
PI-2	2.0	94.2	0.27	226	528
PI-5	5.0	98.5	0.29	225	524

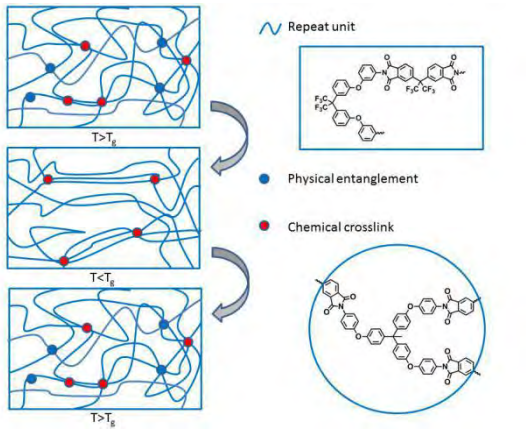


Figure 1. Schematic representation of the molecular mechanism of the thermally induced shape-memory effect for cross-linked polyimides with T_g. Blue dot: physical entanglement. Red dot: chemical crosslink.

Figure 2a describes the dynamic mechanical curves of PI-0.5. At the glass transition, there is a sharp decrease from 1.2×10^9 Pa to 6.0×10^6 Pa, about three orders of magnitude. Above 260 ℃, the curve of storage modulus are increased slowly which should attribute to the incomplete cross-linking of polyimides when thermal imidized. Complete tan δ curves are shown in Figure 2b. There is a trend that with the increasing of crosslink density, the height of tan δ peak was decreased, which is consistent with results from the previously reported thermoset polyimides. Neat polyimides exhibit a glass transition of 217 ℃. Due to the low crosslink density of polyimides, there is little difference of the glass transition temperature (T_g). Figure 2a also provides the information of shape

memory effects. Though the transition is not very broad like other thermoplastic with physical crosslinking, but it also provides a range of 30 ℃ temperature interval. In this temperature region, the crosslinking polyimides can exhibit good multi-shape memory effect.

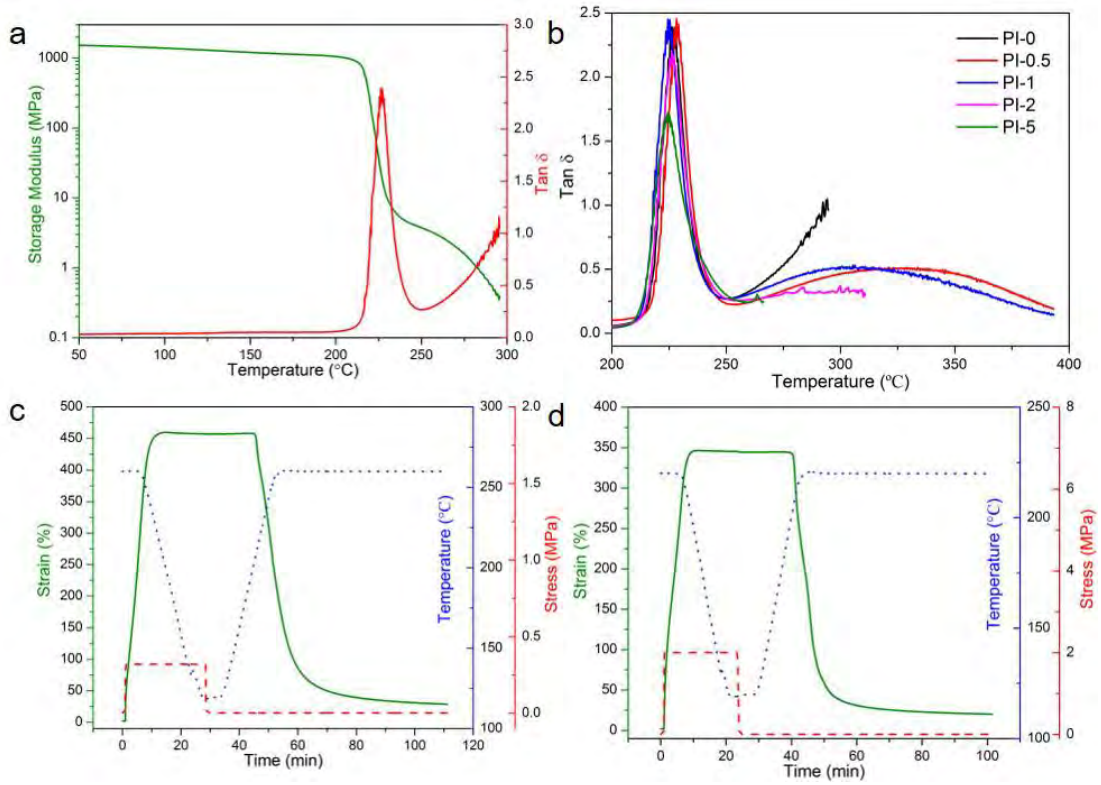


Figure 2. a) Dynamic mechanical analysis curve of PI-0.5. b) Tan δ curves of polyimides. c) Dual shape memory cycle at T_d=T_r=260 ℃. R_f=99.4%, R_r=93.5%. d) Dual shape memory cycle at T_d=T_r=220 ℃. R_f=99.4%, R_r=94.7%. Solid line: strain; dotted line: temperature; dashed line: stress.

Firstly, we evaluated that the dual-SMP of lightly crosslinked polyimides PI-0.5. As shown in Figure 2c, PI-0.5 exhibited a high strain up to 460% with the deformation and recovery temperature (T_d and T_r) at 260 ℃ and the fixing temperature (T_f) at 120 ℃. In this case, PI-0.5 still displays quite high R_f >99% and R_r >93%. Moreover, the dual-SME of PI-0.5 was also investigated at the T_g. PI-0.5 exhibited R_f of 99.4% and R_r of 94.7% with the strain under load of 344% at 220 ℃ as shown in Figure 2d. Dual shape memory effects of different crosslinker content of polyimides were also studied as shown in Figure3a-c.

A multi-stage recovery test was performed to verify the multiple shape memory effect as illustrated in Figure 3d. We found that PI-0.5 could recover to the original shape at different temperature (220, 230, 240, 250, 260 ℃). Therefore, these low density crosslinking polyimides have the ability to tune the programming temperature to achieve multiple-shape memory behavior.

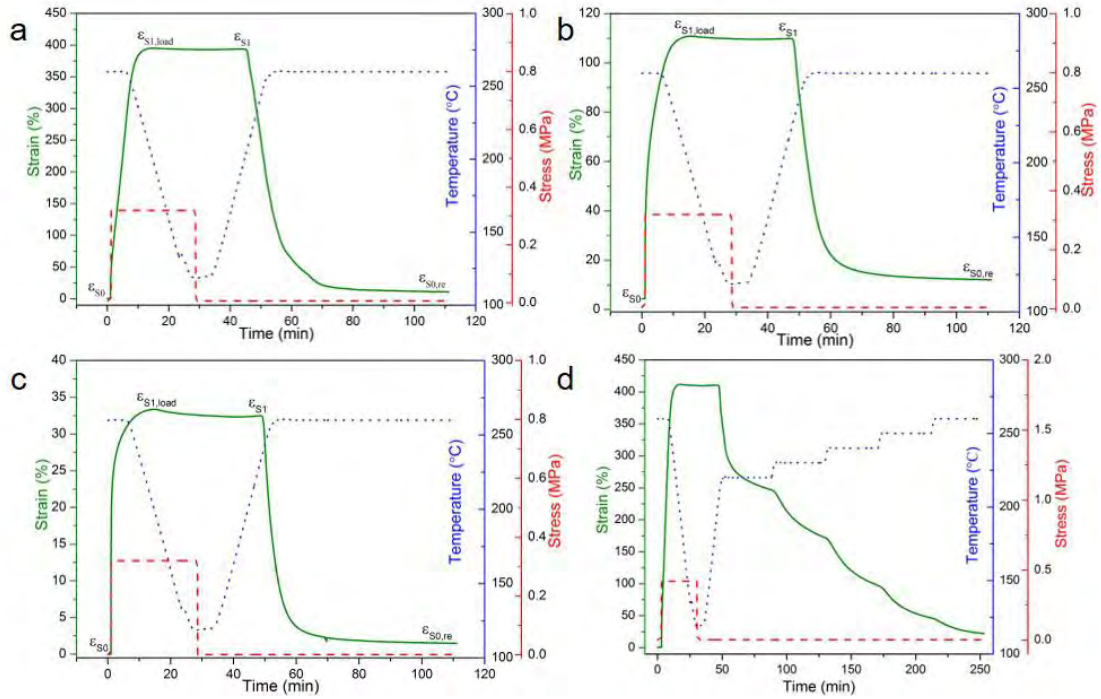


Figure 3. a) Dual shape memory cycle for PI-1 at T_d=T_r=260 ℃, T_f=120 ℃. R_f=99.6%, R_r=97.2%. b) Dual shape memory cycle for PI-2 at T_d=T_r=260 ℃, T_f=120 ℃. R_f=99.0%, R_r=92.3%. c) Dual shape memory cycle for PI-5 at T_d=T_r=260 ℃, T_f=120 ℃. R_f=97.6%, R_r=95.5%. d) Multi-stage shape recovery of PI-0.5 (T_d=260 ℃). Solid line: strain; dotted line: temperature; dashed line: stress.

The results of consecutive dual-shape memory cycling experiments are shown in Figure 4a,b. Four cycles were performed to investigate the effect of the deformation strain on the shape memory properties of PI-0.5. Each cycle exhibited the high R_f > 98%, and with the increasing of thermo-mechanical cycles, the R_r are increased from 85.5% to 94.9%. It should point out that the shape memory strain increases with the increasing number of cycles. It is inferred that some macromolecular chain have disentangled in the stretching process. For the comparison of the effect of two different crosslink, PI-5 with the higher crosslinker also be investigated. We found that with the increasing of number cycles, the strain of PI-5 has little change compared to PI-0.5, but R_r of PI-5 higher than PI-0.5. This should attribute to the chemical crosslink which are more stable than physical crosslink.

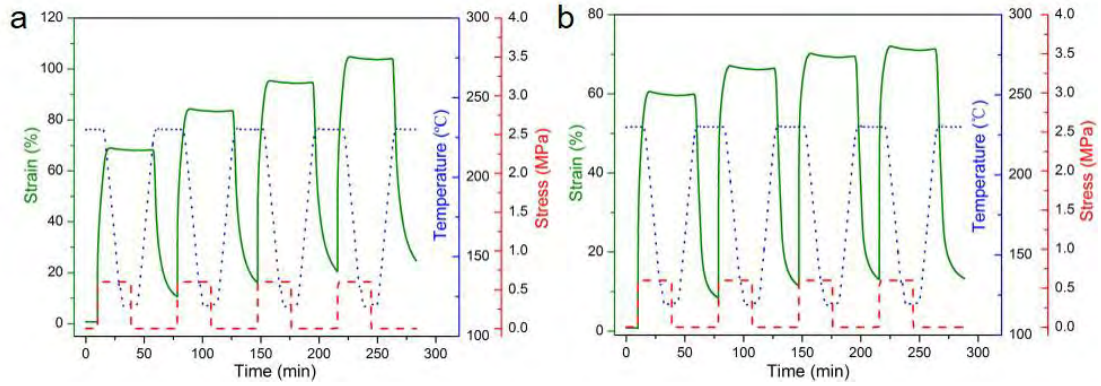


Figure 4. a) Consecutive dual-shape memory cycles of PI-0.5 with T_d=T_r=230 °C, T_f=120 ℃. b) Consecutive dual-shape memory cycles of PI-5 with T_d=T_r=230 °C, T_f=120 ℃.

4. CONCLUSIONS

In summary, we have prepared a series of high strain multi-shape memory polyimides with low crosslink density via a traditional polycondensation. Thanks to the synergistic effect of long repeating units and kinky structure, the polyimides have massive macromolecular chain entanglements, hence to obtain a high strain in the deformation process. The presence of $–CF_3$ can reduce the CT to some extent, and it also is an efficient way to obtain high strain of multiple-shape memory polyimides. Moreover, low density non-coplanar cross-linking also provides a good shape recovery of polyimides. The ease and tunable with which this preparation can be scaled to the industrial level, as the shape memory polyimides are commercially available for application in aviation and aerospace fields.

(continued from p10)

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