Fabrication of a kind of polyimides possess shape memory properties by using non-coplanar triamine as crosslinker

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ABSTRACT: A series of polyimide films with low cross-link density (TAPE=0%, 0.5%, 1%, 2%, 5%) were synthesized by a kind of non-coplanar triamine monomer via polycondensation. Polyimides with low cross-link density showed good shape memory effect. Meanwhile all these polyimides exhibited good thermal stability and high glass-transition temperature (T_g>260℃).
Keywords: Polyimides; Shape memory effect: Non-copolar crosslinker

1. INTRODUCTION

Shape memory polymers (SMPs) are intelligent polymer materials that can change their shape to the initial shape when controlled by external stimulus [1-3]. The macroscopic change of SMPs can be trigger by thermal, electric, light, magnetic, pH value or solution stimulus, and the most common type of SMPs is thermal induced shape memory polymers.

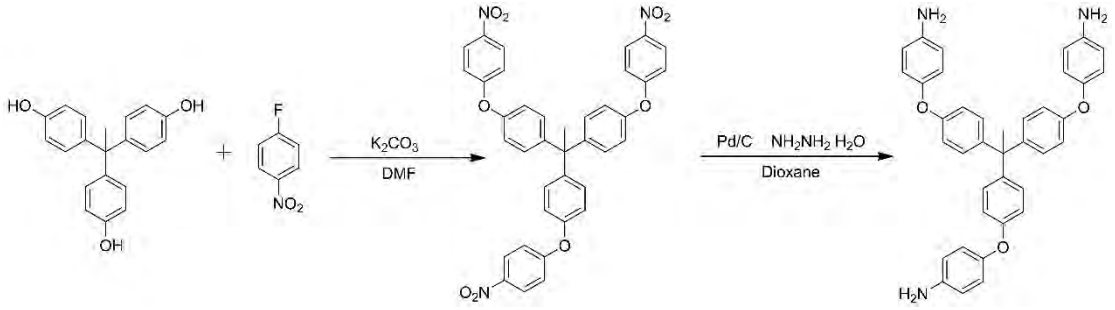
Polyimides (PIs) have good thermal stability, excellent mechanical properties, corrosion resistance and radiation resistance [4].

Shape memory polyimides (SMPIs) tailored the thermal stability of polyimides and the shape memory effect, and in so doing, it have attracted much attention in various fields, such as deployable space structures, shape morphing structures, smart jet propulsion system, and high-temperature sensors and actuators [5].

2. EXPERIMENTAL

Triamine (TAPE) monomer synthesis

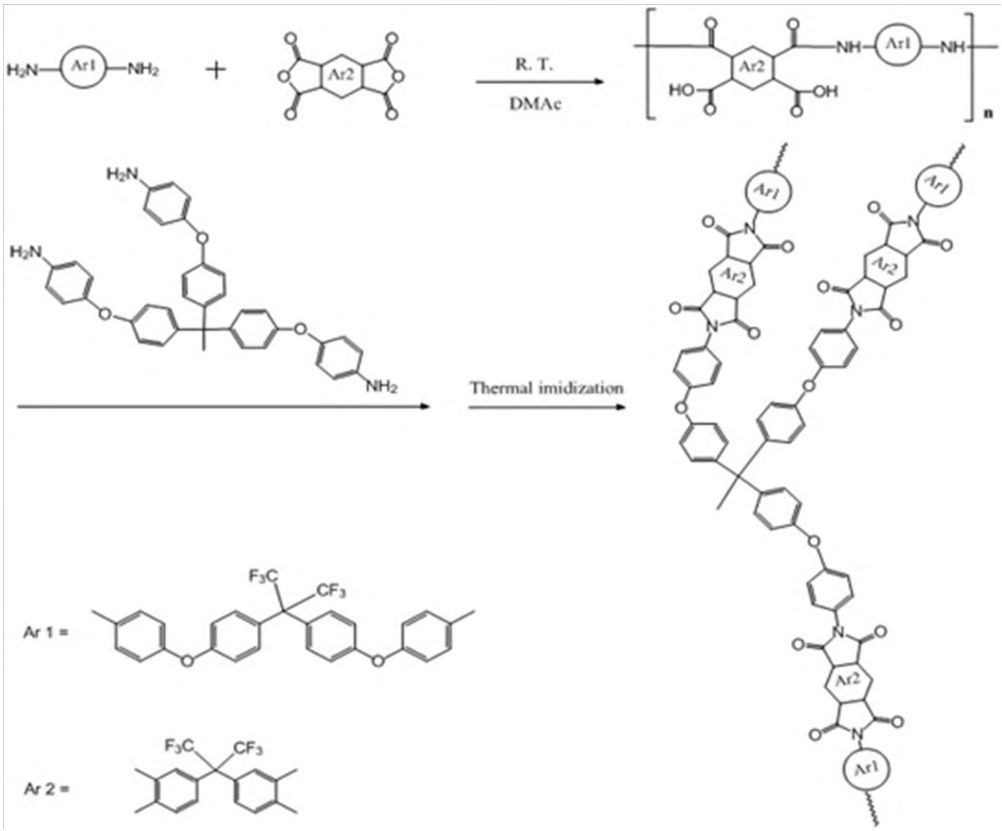
Triamine monomer 1,1,1-Tris(4-(aminophenoxy)phenyl)ethane was synthesis as **Scheme 1**.



Scheme 1 Synthesis of 1,1,1-Tris(4-(aminophenoxy)phenyl)ethane (TAPE)

Polymer synthesis

Different crosslink density of polyimides using TAPE as the cross-linker were fabricated via a traditional two-step polymerization process according to **Scheme 2**. PI-a (6FBAPP-6FDA), PI-b (6FBAPP-6FDA-0.5%TAPE), PI-c(6FBAPP-6FDA-1%TAPE), PI-d (6FBAPP-6FDA-2%TAPE), PI-e (6FBAPP-6FDA-5%TAPE).



Scheme 2 Synthesis of polyimides

3. RESULTS AND DISCUSSION

Thermal properties of polyimide films

The thermal properties of PIs were obtained by DSC, DMA and TGA. Glass-transition temperature (T_g) of the polyimide films were detected by DSC (**Figure 1**) .As **Figure 1** depicts, glass transition is found in the range of 263℃ to 277℃.The drop of storage modulus curves were obtained by DMA (**Figure 2**). According to **Figure 2** all samples exhibited a decrease in their storage modulus, by about three orders of magnitude, thereby suggesting that all PI films possess shape memory effect. All films shown excellent thermal stabilities in nitrogen atmosphere, for their 5% weight loss temperature and 10% weight loss temperature were recorded in the range of 529℃ to 531° C and 545℃ to 547℃, respectively, both these results were shown in **Table 1**.

Table 1 Thermal properties of polyimides

	T_g(℃)		T_{d5}[c](℃)		T_{d10}[c](℃)	
	DSC[a]	DMA[b]	N_2	Air	N_2	Air
PI-a	263	267	531	526	547	543
PI-b	267	267	531	526	547	543
PI-c	269	268	531	524	547	542
PI-d	269	267	529	522	545	540
PI-e	277	270	529	521	546	541

[a] Baseline shift in the second heating DSC traces, at 10 ℃/min under nitrogen atmosphere.

[b] T_g was regarded as the peak temperature of the tan δ.

[c] Decomposition temperature at which 5% and 10% weight loss recorded by TGA at a heating rate of 10 ℃/min under nitrogen and air atmosphere, respectively.

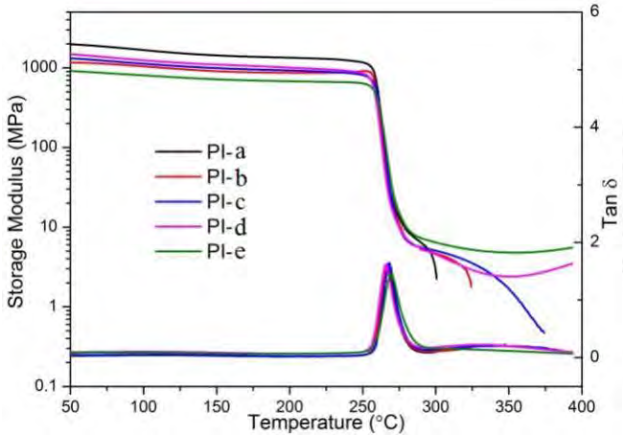


Figure 1 DSC curves of polyimides

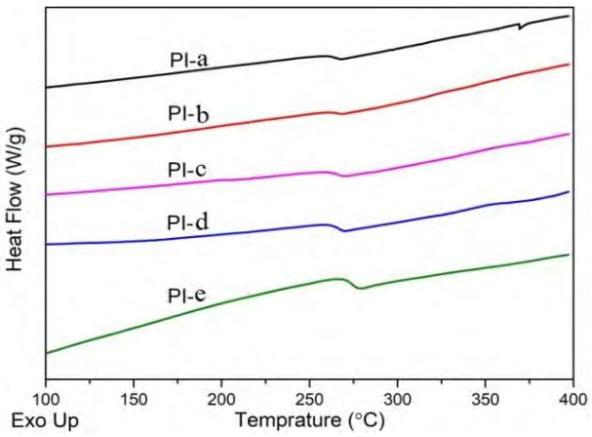


Figure 2 DMA curves of polyimides

Shape memory properties of polyimide films

We ues DMA stretch the film under 350℃ and then cooling to 120℃ . Laterly the external force was withdrawn and samples were heating to 350℃ to trigger the shape memory effect.

The shape memory properties are quantified by the determination of the strain-fixity (R_f) and the strain-recovery (R_r) as the following Equation (a) and (b). The R_f and the R_r of PI films were listed on **Table 2**.

$$R_f = \frac{\varepsilon_{(N)} - \varepsilon_{(N-1)}}{\varepsilon_{load(N)} - \varepsilon_{(N-1)}} \times 100\% \quad \text{(a)}$$

$$R_r = \frac{\varepsilon_{(N)} - \varepsilon_{re,(N-1)}}{\varepsilon_{(N)} - \varepsilon_{(N-1)}} \times 100\% \quad \text{(b)}$$

The shape memory properties of PIs were detected by DMA and the shape memory properties of PI-a was shown in **Figure 3** and others were shown in **Figure 4**. PI-a film show themaximum value of strain and the minimum strain-recovery for 394% and 65.4% comparing to others, due to this film don't have crosslink structure to fix the polymer chain. PI films (b-d) with low cross-link density shown great shape memory properties in strain-recovery value ranged from 80% to 70.9% due to the introduce of cross-link agent. With increasing the content of crosslinking agents, the strain-fixity rate (R_f) and the maximum strain (ε_{max}) decreased in the range of 98.8% to 92% and 150% to 15%, respectively, partly because too much crosslinking point limiting the movement of polymer chain segments.

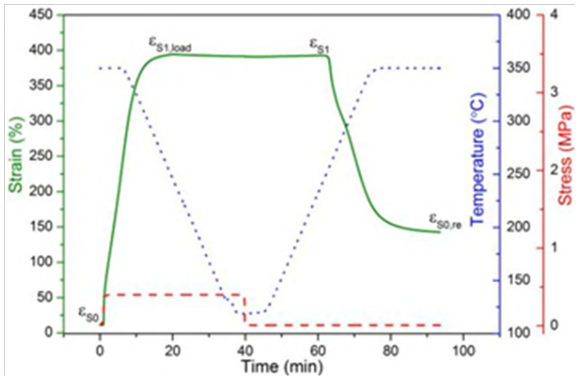


Figure 3 Dual shape memory property of PI-a

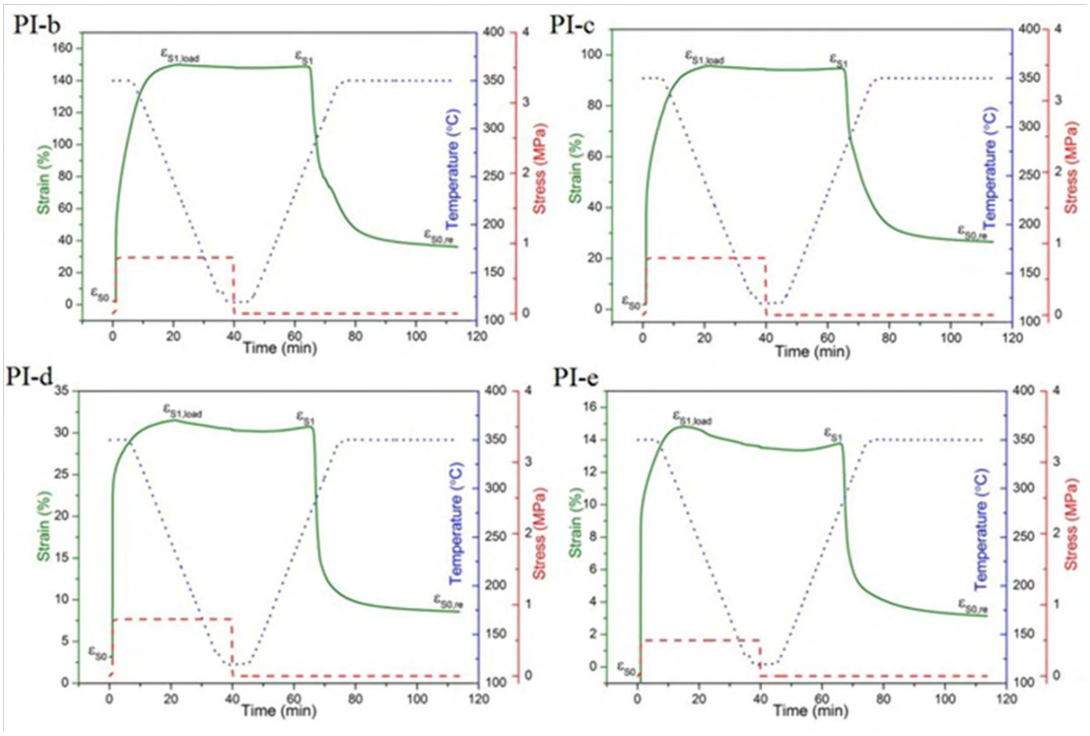


Figure 4 Dual shape memory properties of polyimides

Table 2 Dual shape memory properties of polyimides

	ε_{max}(%)	R_f(%)	R_r(%)
PI-a	394	99.2	65.4
PI-b	150	98.8	76.8
PI-c	96	98.4	73.4
PI-d	32	95.8	80.0
PI-e	15	92.0	70.9

4. CONCLUSIONS

A series of PI films with different content of crosslinking agents (TAPE) were prepared successfully. All these polyimides revealed good thermal stability with high glass-transition temperature and high decomposition temperature. Besides, these films possess shape memory effect in high temperature. The ease and tunable of these materials might be scaled to the industrial level, given that shape memory polyimides are commercially available for application in aerospace filed.

References

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