

Electronic Supplementary Information

Optically Transparent High Temperature Shape Memory Polymer

Xinli Xiao^{1,2}, Xueying Qiu¹, Deyan Kong¹, Wenbo Zhang¹, Yanju Liu³, Jinsong Leng^{2}*

1. Department of Chemistry, Harbin Institute of Technology, No. 92 West Dazhi Street, Harbin 150001, People's Republic of China.

2. Centre for Composite Materials and Structures, Harbin Institute of Technology, No. 2 YiKuang Street, Harbin 150080, People's Republic of China.

3. Department of Astronautical Science and Mechanics, Harbin Institute of Technology, No. 92 West Dazhi Street, Harbin 150001, People's Republic of China.

To whom correspondence should be addressed. J. S. Leng (lengjs@hit.edu.cn).

The shape memory polyimides (SMPI) with different molar ratios of BAB/BPADA are labeled as SMPI1, SMPI2, SMPI3, SMPI4 and TSMPI, as shown in Table 1. SMPI1 with the stoichiometric ratio achieves the highest M_n of 52.2 kg/mol, and stoichiometric imbalances cause the decrease of M_n . The observed critical lowest M_n is 21.7 kg/mol, below which the sample does not possess shape memory effect. The polyimide with M_n of 20.3 kg/mol ($M_w=40.1$ kg/mol) can form continuous film, but it is unable to fix the temporary shape or recover to the original shape very well. For the polyimides with much lower M_n , such as 13.9 kg/mol ($M_w=24.8$ kg/mol), 10.3 kg/mol ($M_w=21.1$ kg/mol) and 8.5 kg/mol ($M_w=17.8$ kg/mol), they formed fragments instead of continuous films.

Table 1. Physical properties of the transparent shape memory polyimide

BAB/BPADA	Title	M_n^a	M_w^a	T_g^b	E' at T_g-20 °C ^{c,e}	E' at T_g+20 °C ^{c,e}	T_d^b	R_f^d	R_r^d
1	SMPI1	52.2	119.2	183	1916±72	5.1±0.4	503	99.6	98.6
0.9850	SMPI2	42.6	77.9	180	1919±66	5.2±0.5	498	99.4	99.1
0.970	SMPI3	37.9	73.3	178	1827±58	4.7±0.3	486	99.5	98.2
0.940	SMPI4	26.8	47.1	174	1605±43	4.2±0.4	487	99.2	97.8
0.910	SMTPI	21.7	42.5	171	1671±51	3.9±0.2	485	99.3	97.6

Samples with lower M_n do not possess shape memory effects

a. kg/mol, b. °C, c. MPa, d. %. e. Average values and standard deviations.

The shape memory polyimide was prepared by thermal curing of the precursor PAA, and the FTIR spectra of PAA and SMTPI are shown in Figure S1. In the spectra of PAA, stretching vibration peaks of N-H at 3263 cm^{-1} and O-H (-COOH) at 2939 cm^{-1} appear, together with the obvious broad hydrogen-bonded O-H stretching vibrations. In addition, stretching vibration peaks of C=O (-COOH) and C=O (-CONH) appear at 1721 and 1660 cm^{-1} , respectively. In the spectra of PI, the peaks at 1782 (C=O, asymmetric stretching) and 1719 cm^{-1} (C=O, symmetric stretching) are the typical frequencies of imides. Besides, the C-N-C absorption at 1373 (stretching vibration) and 729 cm^{-1} (bending vibration) also confirm the formation of imides. However, the absorption peak attributed to N-H and O-H (-COOH) bonds does not appear in the spectra of PI.

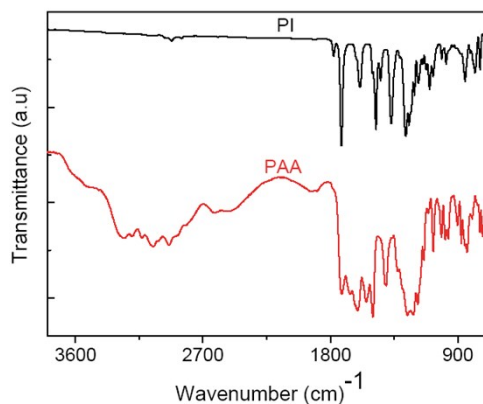


Figure S1. FTIR of the precursor poly(amic acid)(PAA) and shape memory polyimide (SMTI1).

The intensity ratio of symmetric stretching of C=O (1718 cm^{-1}) to stretching vibration of C-N-C (1373 cm^{-1}) increases with the decrease of M_n . From SMPI1 to TSMPI, the ratio is 1.35, 1.37, 1.40, 1.42 and 1.45, respectively. The increase of absorption intensity is consistent with the increase of molar ratio of dianhydride/diamine, as the percentage of C-N-C gets lower with the decrease of diamine.

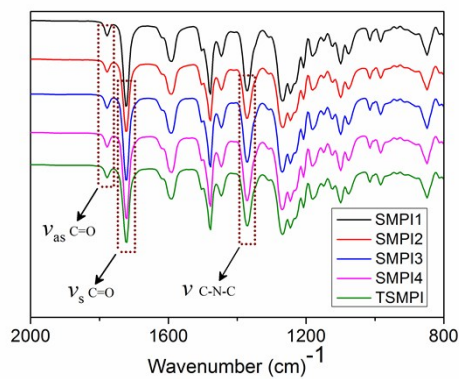


Figure S2. FT-IR spectra of the shape memory polyimides.

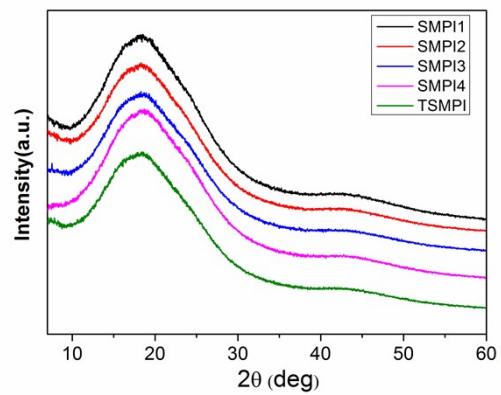


Figure S3. XRD spectra of the shape memory polyimide films.

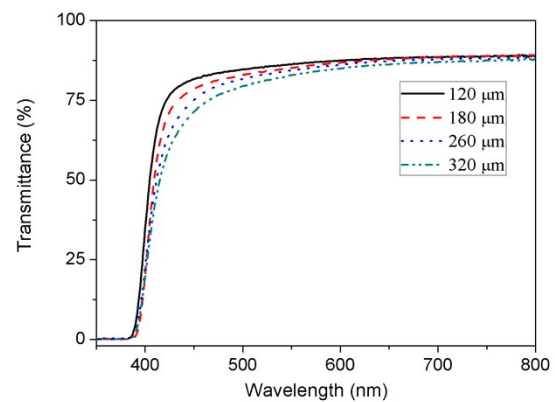


Figure S4. UV-vis spectra of TSMPI films with thickness of 120, 180, 260 and 320 μm.

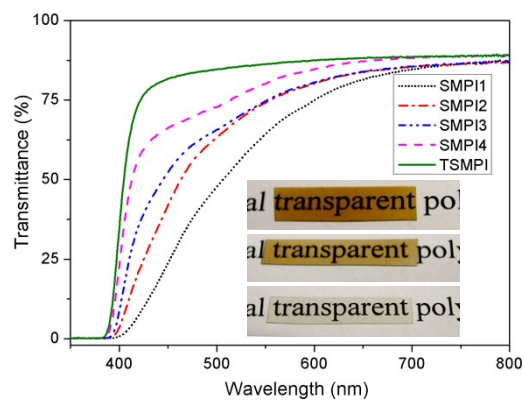


Figure S5. Transmittance of 120 μm thick shape memory polyimides. The inset shows images of SMPI1、SMPI3 and TSMPI.

Table S2. Optical properties of the 120 μm thick shape memory polyimides.

Titles	λ_0 (nm) ^a	T ₄₀₀ (%) ^{a, b}	T ₄₅₀ (%) ^{a, c}	T ₅₀₀ (%) ^{a, d}
SMPI1	396 \pm 5	0.7 \pm 0.1	23.8 \pm 0.2	47.7 \pm 0.3
SMPI2	390 \pm 3	3.5 \pm 0.2	41.9 \pm 0.3	63.2 \pm 0.2
SMPI3	388 \pm 4	8.4 \pm 0.3	52.4 \pm 0.2	65.6 \pm 0.3
SMPI4	384 \pm 3	22.7 \pm 0.2	66.3 \pm 0.4	72.8 \pm 0.4
TSMPI	381 \pm 2	34.5 \pm 0.4	81.7 \pm 0.3	84.7 \pm 0.3

a. Average values and standard deviations. b, c, and d are transmittance at 400, 450 and 500 nm, respectively.

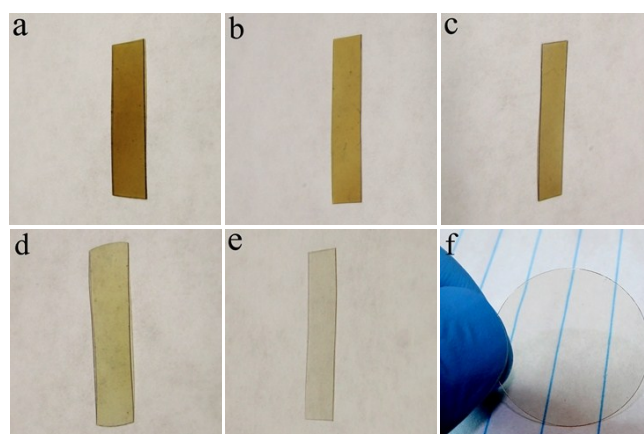


Figure S6. Photographs of (a) SMPI1, (b) SMPI2, (c) SMPI3, (d) SMPI4 and (e) TSMPI in slab shape; (f) TSMPI in round shape.

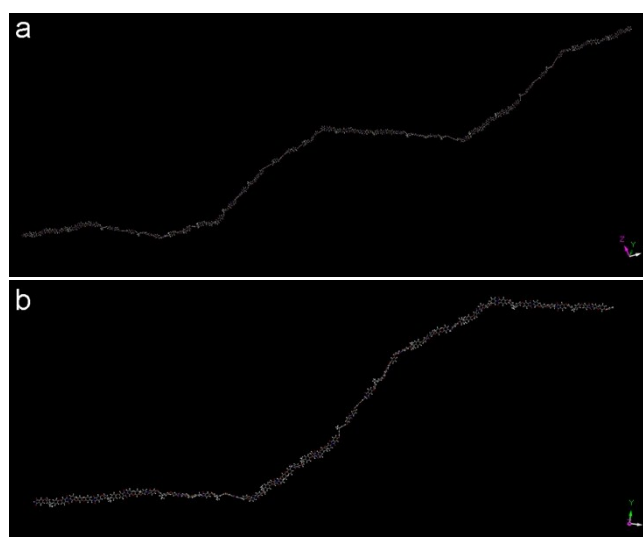


Figure S7. Three-dimensional structures of the polyimide chains with M_n of 16.1 kg/mol (a) and 9.7 kg/mol (b).

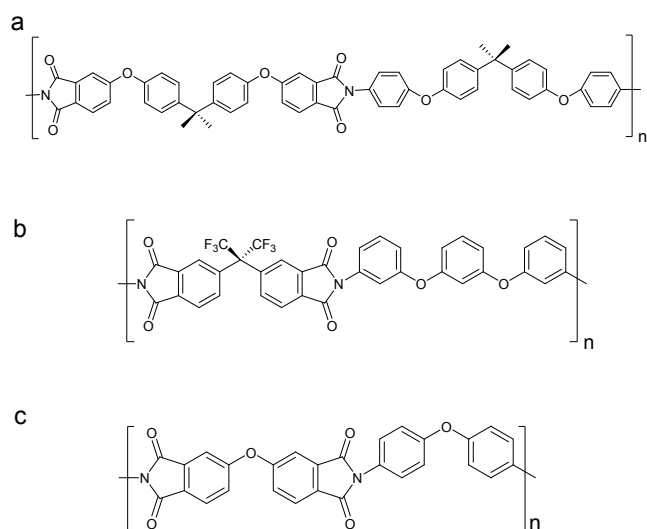


Figure S8. Molecular structures of the typical shape memory polyimide samples with different glass transition temperatures. (a) Polyimide based on BPADA/BAPP,¹ (b) polyimide based on 6FDA/BAB,² and (c) polyimide based on ODPA/ODA.³

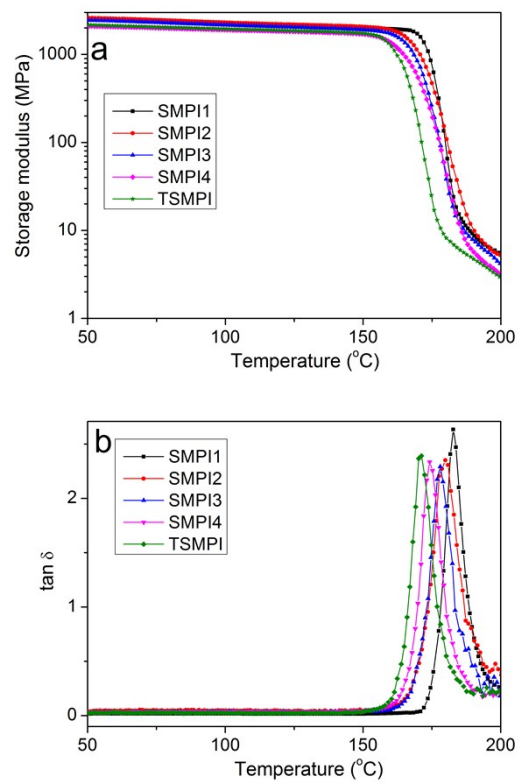


Figure S9. Thermomechanical properties of the shape memory polyimides. (a) tensile storage modulus and (b) loss factor ($\tan \delta$) versus temperature of the shape memory polyimides.

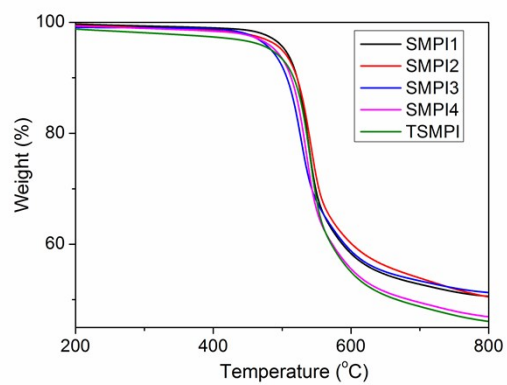


Figure S10. TGA spectra of the transparent shape memory polyimides.



Shape recovery process of TSMPI on hot stage.mov

Movie S1. The video showing deployable shape memory application pattern of SMTPI5.

REFERENCES:

- (1) Yoonessi, M.; Shi, Y.; Scheiman, D. A.; Lebron-Colon, M.; Tigelaar, D. M.; Weiss, R. A.; Meador, M. A. Graphene Polyimide Nanocomposites; Thermal, Mechanical, and High-Temperature Shape Memory Effects. *Acs Nano* **2012**, *6*, 7644–7655.
- (2) Koerner, H.; Strong, R. J.; Smith, M. L.; Wang, D. H.; Tan, L. S.; Lee, K. M.; White, T. J.; Vaia, R. A. Polymer Design for High Temperature Shape Memory: Low Crosslink Density Polyimides. *Polymer* **2013**, *54*, 391–402.
- (3) Wang, Q. H.; Bai, Y. K.; Chen, Y.; Ju, J. P.; Zheng, F.; Wang, T. M. High Performance Shape Memory Polyimides Based on π - π Interactions. *J. Mater. Chem. A*, **2015**, *3*, 352-359.