

Measurements

¹H NMR spectrum was obtained on a Bruker AN 600 spectrometer at 25 °C with deuterated chloroform as the solvent.

Fourier transform infrared (FT-IR) spectra were measured on a Nicolet 560 spectrophotometer using KBr pellets in the range from 4000 to 400 cm⁻¹ under a resolution of 4 cm⁻¹ at ambient temperature.

SEM analysis employed by a Quanta 250 scanning electron microscope (FEI, USA) to analyze the cross-section morphologies of films.

All fully expanded samples in deionized (DI) water were measured by differential scanning calorimetry (DSC) with a Q20 TA instrument at a heating or cooling rate of 1 K/min in a nitrogen atmosphere with a temperature range of 0-100 °C.

Stress-strain curves were measured for quantitatively evaluating the mechanical properties of all samples by an Instron 4465 testing machine. The elongation rate was set to 50 mm/min. The dimensions of dumbbell-shaped specimens were 20 mm (length) × 4 mm (width) × 0.5 mm (thickness).

TGA was carried out with a TGAQ50 TA instrument under nitrogen and air atmosphere from 50 to 700 °C with a heating rate of 10 K/min, respectively. Differential scanning calorimetry (DSC) measurements of all samples were performed on a Q20 TA instrument with a heating or cooling rate of 5 K/min under nitrogen atmosphere.

The optical images of these samples were obtained using a Nikon D5200 camera.

The transmittance spectra in the wavelength range of 200-2800 nm were collected using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu, Japan) at normal incidence and equipped with a heating and cooling stage (PE120, Linkam, UK).

The integral luminous transmittance T_{lum} (380-780 nm), IR transmittance T_{IR} (780-2500 nm) and solar transmittance T_{sol} (280-2500 nm) were calculated by Equation as follow: ¹

$$T_{lum / IR / solar} = \frac{\int \phi_{lum/IR/solar}(\lambda) T(\lambda) d\lambda}{\int \phi_{lum/IR/solar}(\lambda) d\lambda} \quad (1)$$

where $T(\lambda)$ denotes the recorded transmittance at a particular wavelength, $\phi_{lum}(\lambda)$ is the standard luminous efficiency function for the photopic vision² of human eyes in the wavelength range of 380-780 nm, $\phi_{IR}(\lambda)$ and $\phi_{sol}(\lambda)$ is the IR/solar irradiance spectrum for air mass 1.5 (corresponding to the sun standing 37° above the horizon with 1.5 atmosphere thickness, corresponds to a solar zenith angle of =48.2)³.

$$\Delta T_{lum/IR/sol} \text{ was obtained by } \Delta T_{lum/IR/sol} = T_{lum/IR/sol, 20^\circ\text{C}} - T_{lum/IR/sol, 40^\circ\text{C}} \cdot^{-1}$$

Table S1 Thermochromic Performance (Solar Transmittance Modulation, ΔT_{sol} , after Phase Transition, and Luminous Transmittance, T_{lum} , before Phase Transition) in Some of the Best Reported PNIPAm-based Films.

ΔT_{sol}	T_{lum}	Thickness	Ref.
73.5%	80%	400 μm	[4]
81.3%	87.2%	380 μm	[5]
68.1%	90%	1 cm	[6]
49.6%	85.8%	78 μm	[7]
86.15%	82.75%	100 μm	[8]
67.1%	94.5%	100 μm	[9]
63.24%	59.53%	100 μm	This work

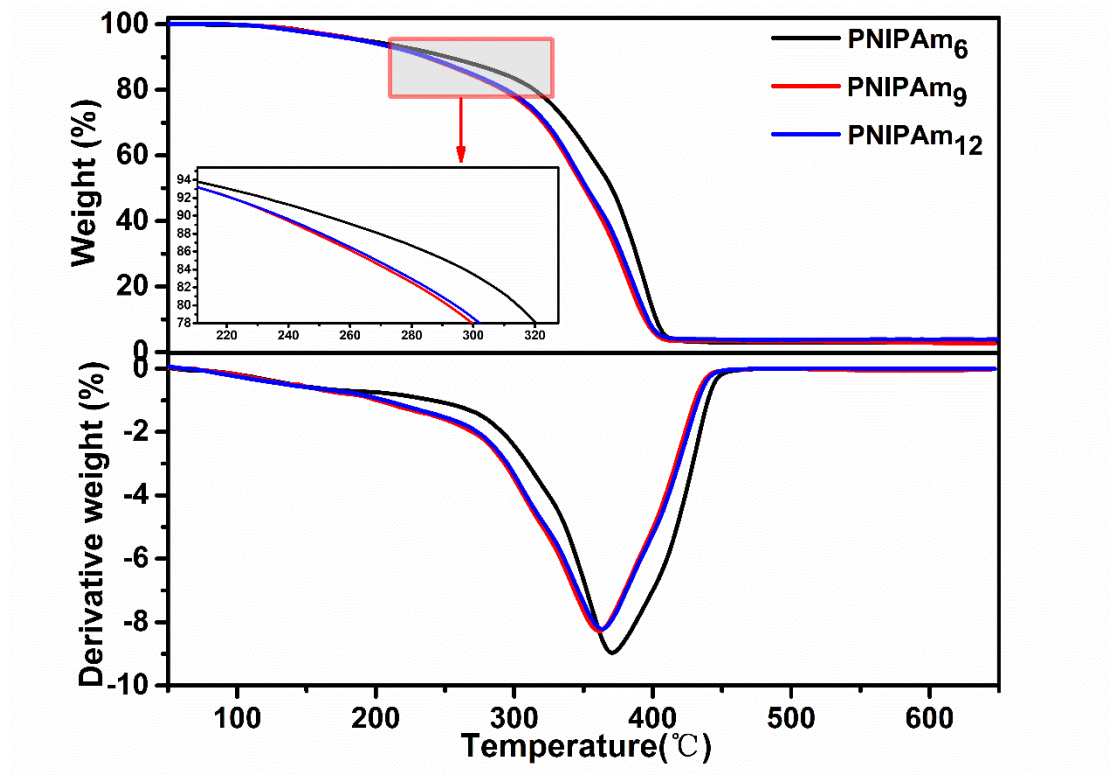


Fig.S1. The thermal stabilities of the PNIPAm_n: (up) TGA and (down) DTG curves.

Table S2 Thermal stabilities of the PNIPAm_n.

Sample	$T_{-5wt\%}$ (°C)	T_{max1} (°C)	Residual mass (%)
PNIPAm ₆	193.49	370.77	2.96
PNIPAm ₉	191.68	361.34	3.35
PNIPAm ₁₂	190.71	363.09	3.85

2. G. Wyszecki and W. S. Stiles, *Color science: concepts and methods, quantitative data and formulae*, John Wiley & Sons New York, NY, 1982.
3. S. Astm, G173 standard tables of reference solar spectral irradiances: direct normal and hemispherical on a 37 degree tilted surface, in: American Society for Testing and Materials.
4. Y. Zhou, M. Layani, S. Wang, P. Hu, Y. Ke, S. Magdassi and Y. Long, *Adv Funct Mater*, 2018, **28**, 1705365.
5. X. H. Li, C. Liu, S. P. Feng and N. X. Fang, *Joule*, 2019, **3**, 290-302.
6. Y. Zhou, S. Wang, J. Peng, Y. Tan, C. Li, F. Y. C. Boey and Y. Long, *Joule*, 2020, **4**, 1-17.
7. Y. Zhou, Y. Cai, X. Hu and Y. Long, *J. Mater. Chem. A*, 2014, **2**, 13550-13555.
8. J. Tian, J. Gu, H. Peng, H. Wang, Z. Du, X. Cheng and X. Du, *Composites Part A: Applied Science and Manufacturing*, 2021, **149**.
9. J. Tian, J. Xu, H. Peng, X. Du, H. Wang, Z. Du and X. Cheng, *Progress in Organic Coatings*, 2021, **160**.