Supporting Information

Synthesis of monolithic shape-stabilized phase change materials with high mechanical stability via a porogen-assisted *in situ* sol-gel process

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- Fig. S1 to S11
- Table S1
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Other Supplementary Materials for this manuscript include:

- Movie S1 to S4

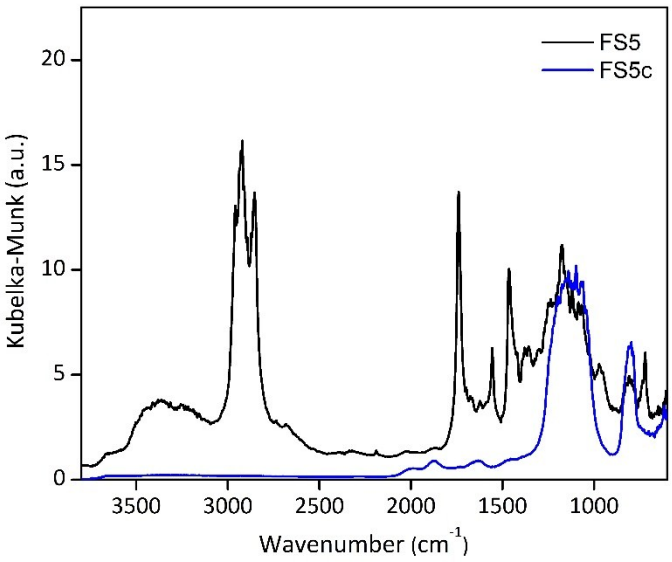

Fig. S1 Infrared spectrum of FS5 after drying and calcination at 600 °C (FS5c). The spectrum was measured via diffuse reflectance infrared fourier transform spectroscopy on a *Vector 22* spectrometer by *Bruker* at 100 °C in a nitrogen atmosphere (50 scans). For preparation, 30 mg of the ss-PCM sample were mixed and grinded with approximately 100 mg potassium bromide.

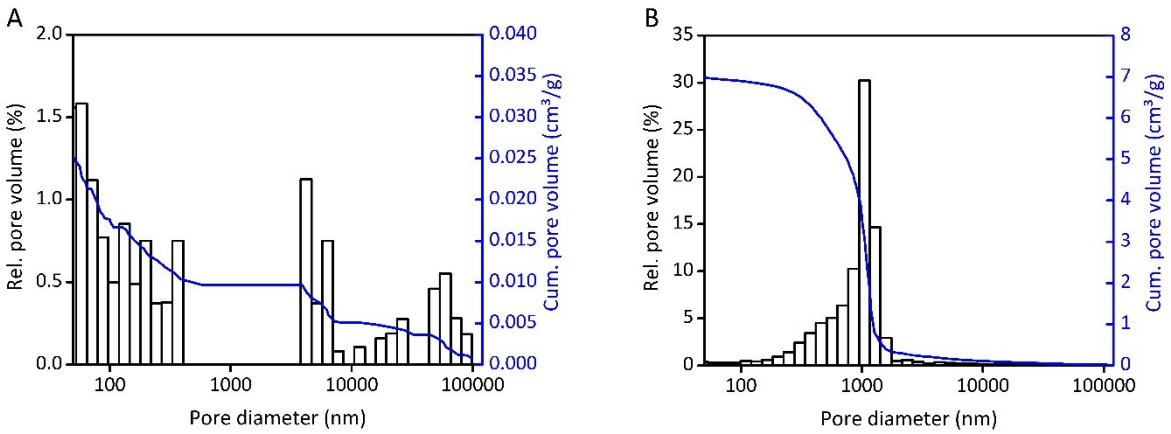

Fig. S2 Mercury intrusion measurements of FS4 (A) and FS4c (B).

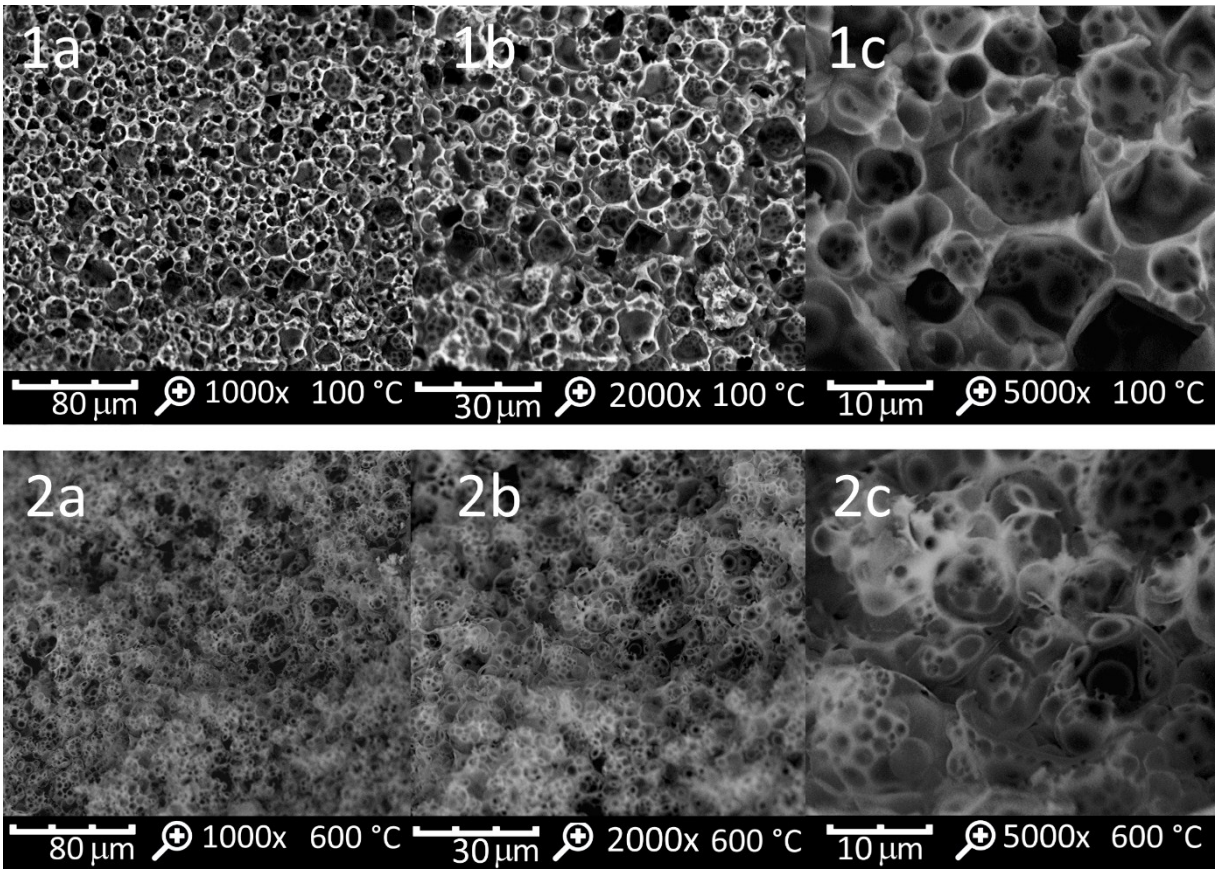

Fig. S3 SEM images of FS4 (1) and FS4c (2) with magnifications of 1000x (a), 2000x (b) and 5000x (c).

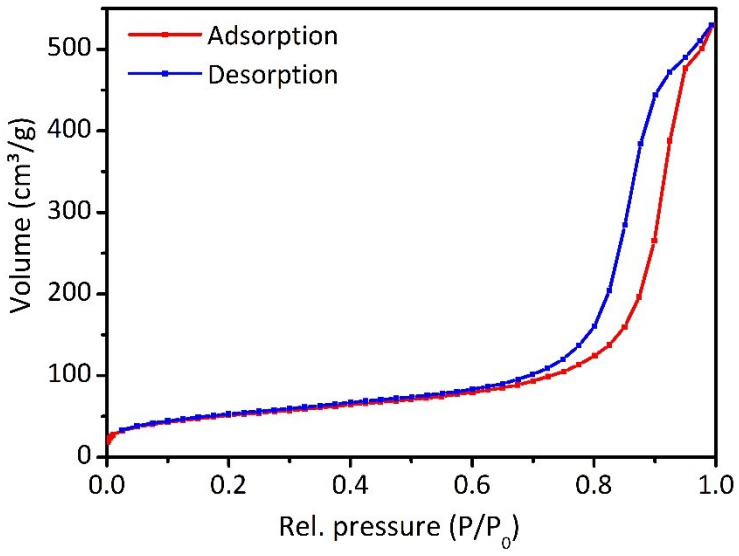

Fig. S4 Nitrogen adsorption isotherms of FS4c.

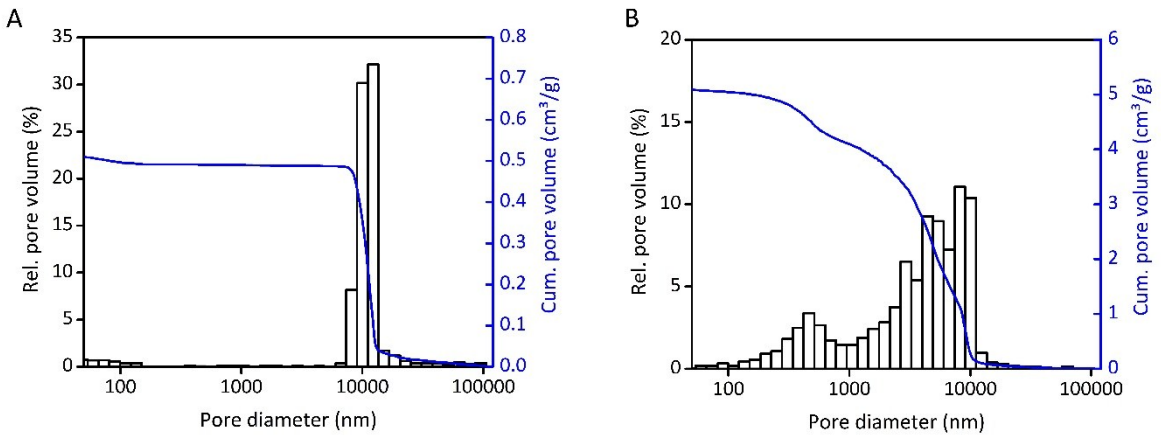

Fig. S5 Mercury intrusion measurements of $FS5_{125}$ (A) and $FS5c_{125}$ (B).

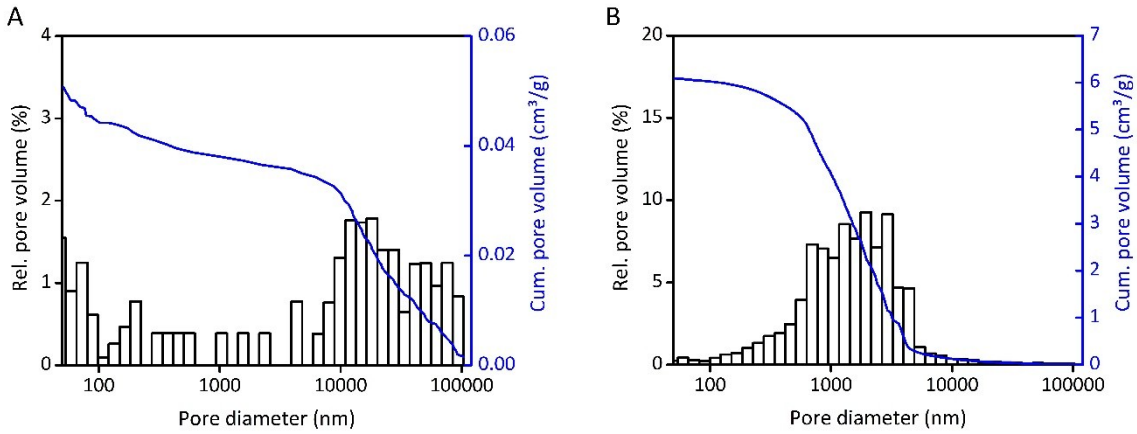

Fig. S6 Mercury intrusion measurements of $FS5_{175}$ (A) and $FS5c_{175}$ (B).

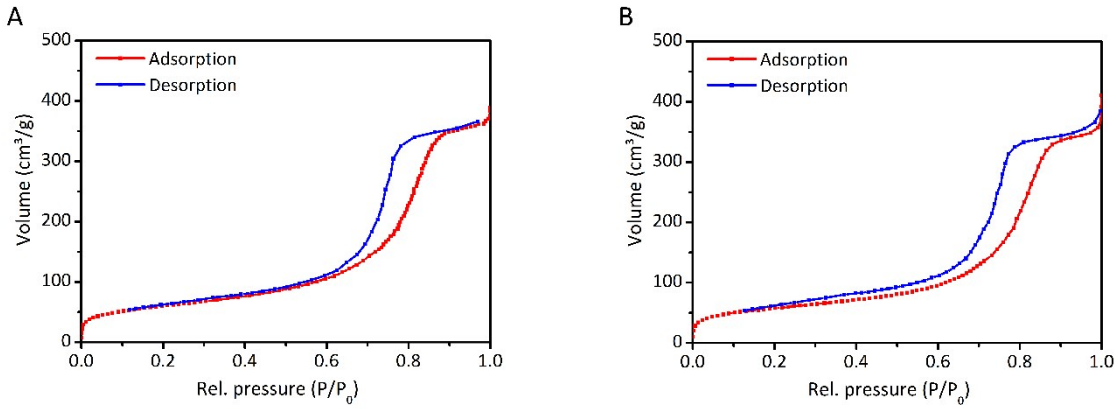

Fig. S7 Nitrogen adsorption isotherms of $FS5c_{125}$ (A) and $FS5c_{175}$ (B).

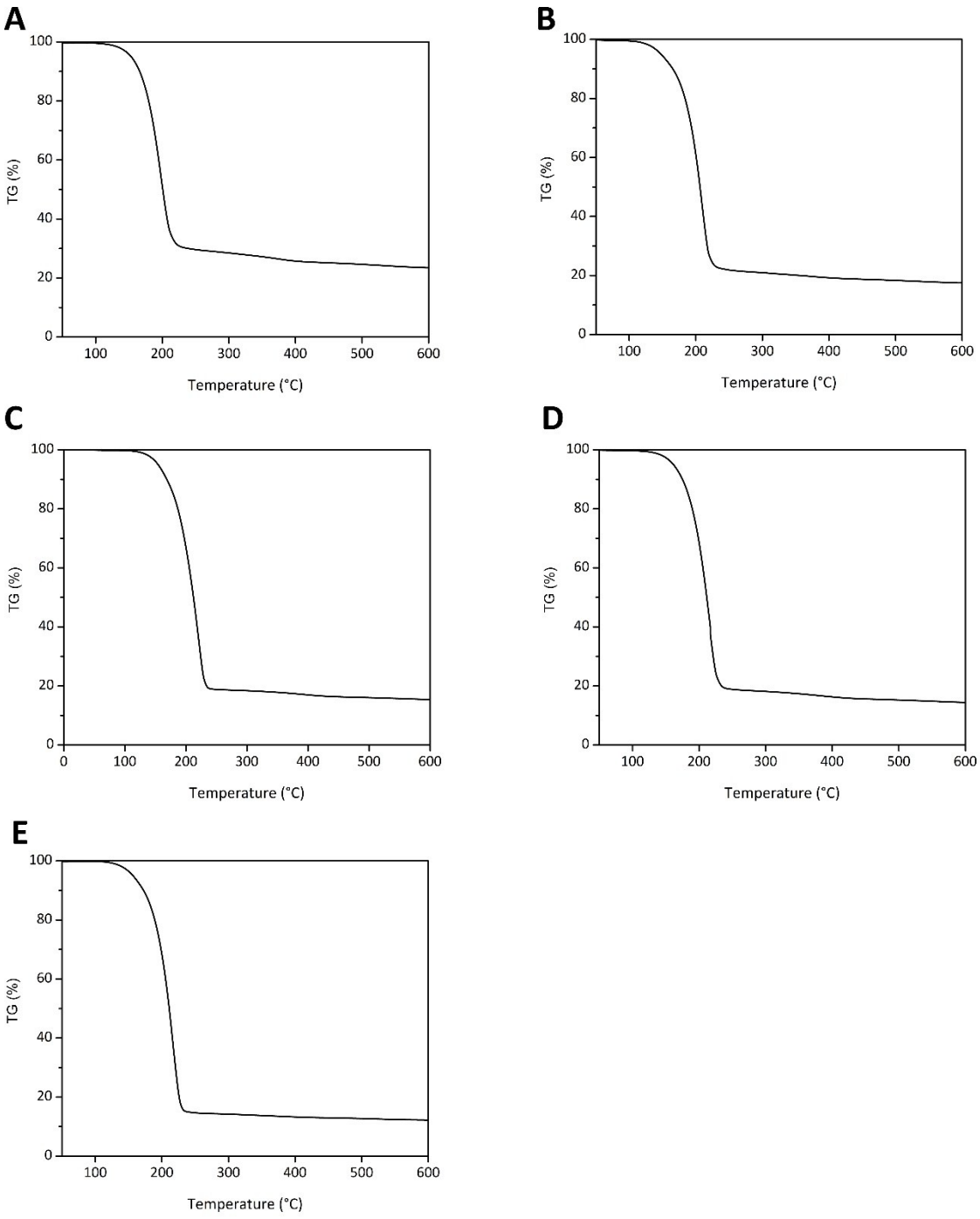

Fig. S8 TG curves of samples $FS5_{100}$ (A), $FS5_{125}$ (B), $FS5_{150}$ (C), $FS5_{175}$ (D) and $FS5_{200}$ (E) measured with a heating rate of 1 °C/min.

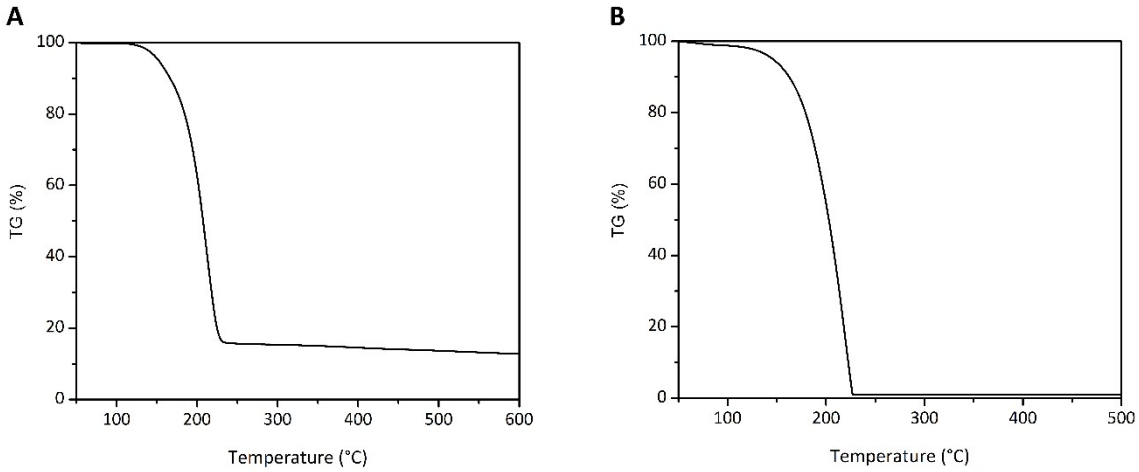

Fig. S9 TG curves of sample FS4 (A) and butyl stearate (B) measured with a heating rate of 1 °C/min.

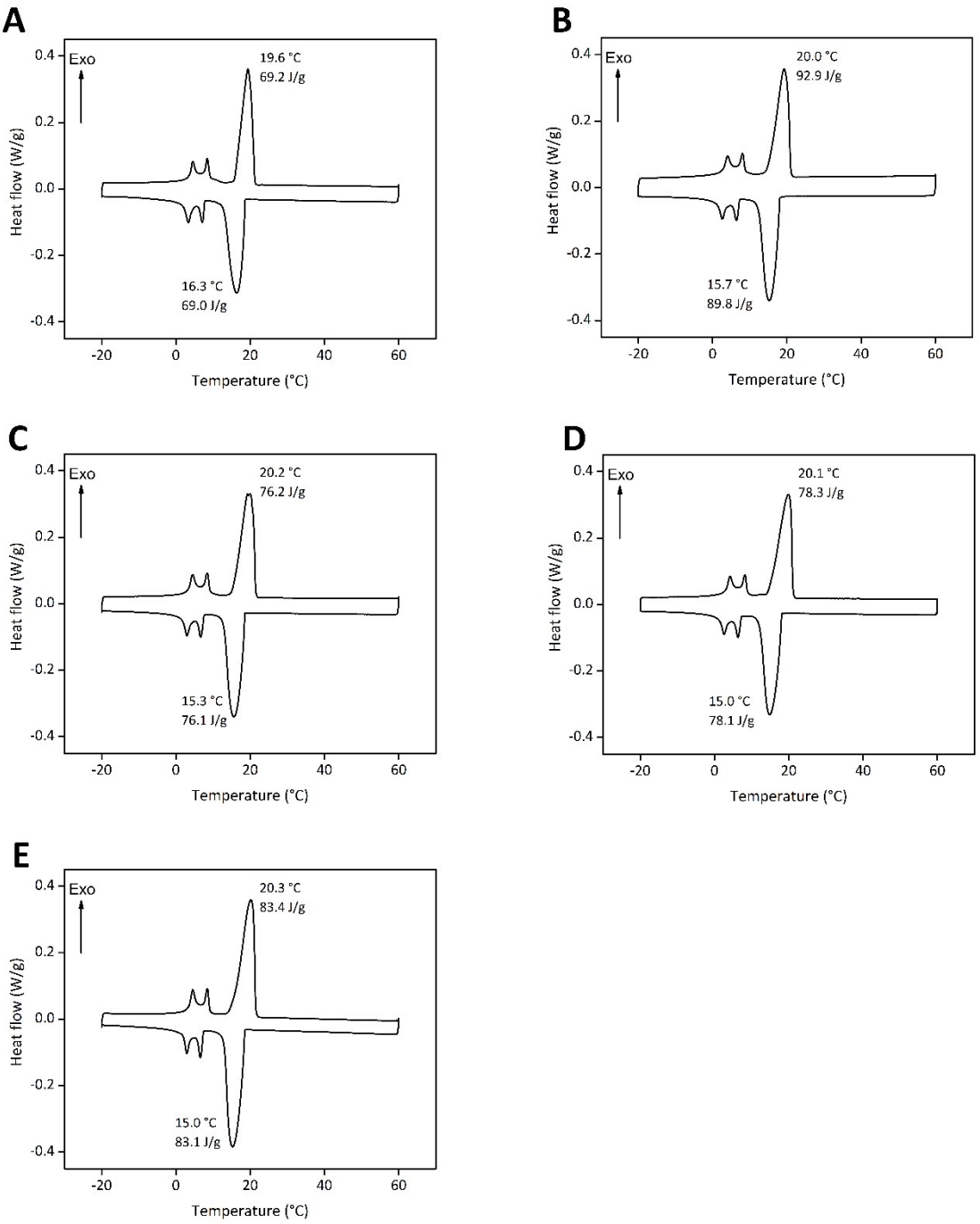

Fig. S10 DSC curves of ss-PCMs $FS5_{100}$ (A), $FS5_{125}$ (B), $FS5_{150}$ (C), $FS5_{175}$ (D) and $FS5_{200}$ (E) (heating rate: 1 °C/min).

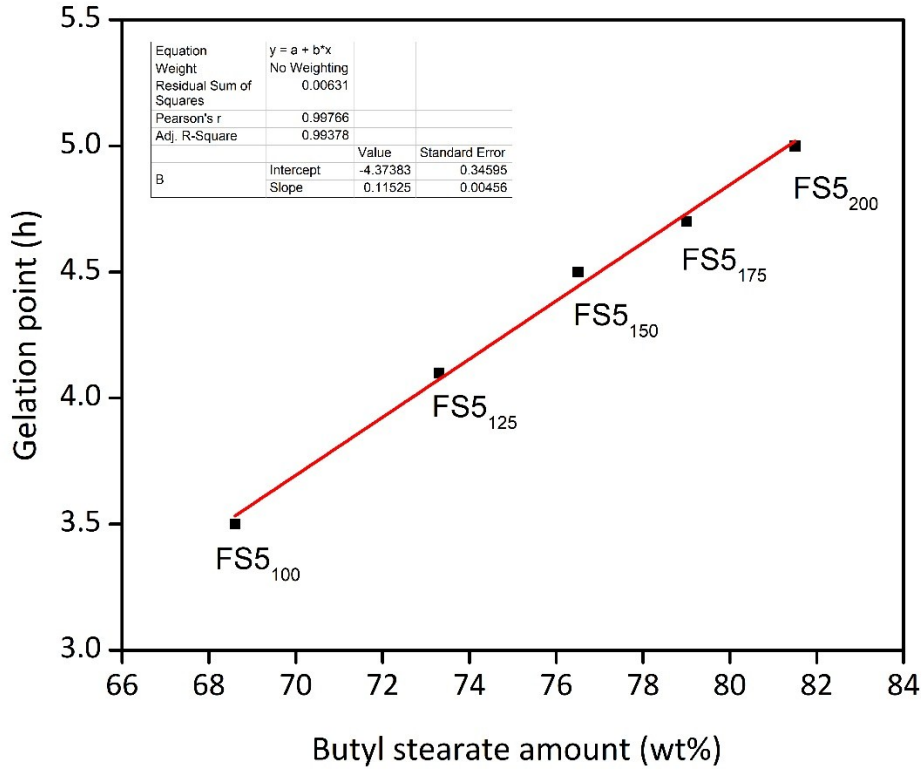

Fig. S11 Gelation points of samples $FS5_{100}$, $FS5_{125}$, $FS5_{150}$, $FS5_{175}$ and $FS5_{200}$.

Table S1 Thermal properties[1] of samples $FS5_{100}$–$FS5_{200}$ and FS4 calculated via weighing and DSC measurements.

Sample	ΔH_{BS} (J/g)	ΔH_{total} (J/g)	T_m (°C)	ΔT_s (°C)	$Ma(PCM)_{DSC}$ (wt%)	$Ma(PCM)_{mass}$ (wt%)	$Ma(PCM)_{max}$ (wt%)	E_{DSC} (%)	E_{mass} (%)
FS5100	69	88	19.6	3.3	69.8	68.6	69.0	101	99
FS5125	73	93	20.0	4.3	73.8	73.3	73.5	100	100
FS5150	76	97	20.2	4.9	77.0	76.5	77.0	100	99
FS5175	78	100	20.1	5.1	79.6	79.0	79.5	100	99
FS5200	83	104	20.3	5.3	82.5	81.5	81.6	101	100
FS4	85	105	20.0	4.7	83.3	82.6	83.0	100	100

1: Melding enthalpy of BS signal ΔH_{BS}, melting enthalpy of whole ss-PCM ΔH_{total}, melting point of BS signal T_m, supercooling ΔT_s, mean value for effective mass fraction of PCM $Ma(PCM)_{DSC}$ (equation 1) and $Ma(PCM)_{mass}$ (equation 2), highest value for effective mass fraction of PCM $Ma(PCM)_{max}$ (equation 3) and corresponding PCM immobilization efficiencies E_{DSC} (equation 4) and E_{DSC} (equation 5).

Movie S1

Different views of FS4.

Movie S2

Schematic presentation of each step to synthesize ss-PCMs via the *in situ* sol-gel process in this work.

Movie S3

X-ray nanotomographic imaging of sample FS4 and visualization of sequential tomograms, showing the pores distribution from bottom to top.

Movie S4

Three-dimensional visualization of sample FS4. Segmentation of the silica framework is shown in yellow, while the filled pores are randomly coloured.