Supplementary Material (ESI) for *Soft Matter*


# Fast responsive and morphologically robust thermo-responsive hydrogel nanofibres from poly(N-isopropylacrylamide) and POSS crosslinker

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Electronic Supplementary Information

**Figure S1**. Visible transmittance spectra of the cured nanofibre membrane at temperatures below and above the LCST (31.8 ºC). (PNIPAM 12.5 wt/vol%, PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt)

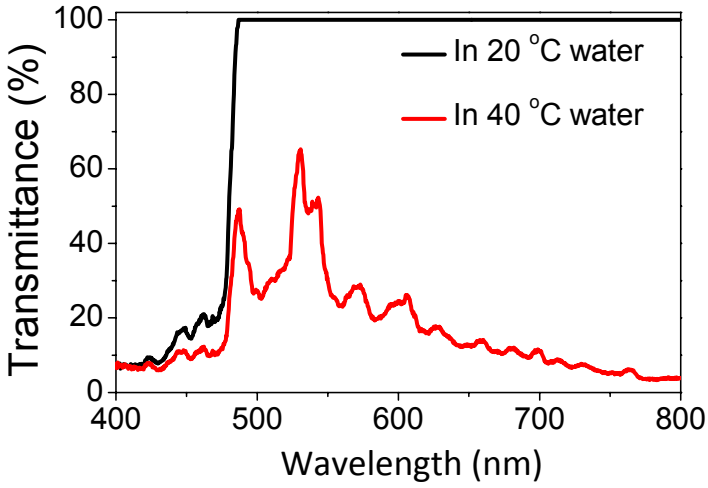


**Figure S2**. Photos of **a)** and **c)** water-swollen nanofibre mats, after dropping **b)** ethanol and **d)** acetone on the surface, respectively. (PNIPAM 12.5 wt/vol%, PNIPAM 10 wt%, PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt)

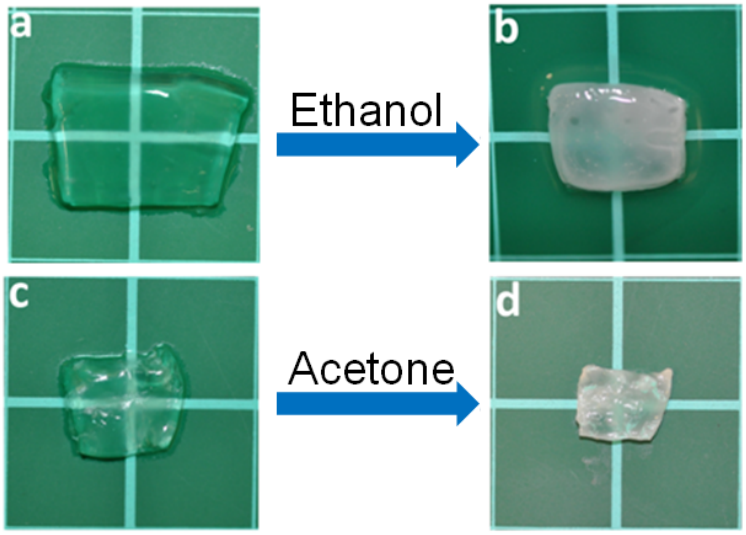
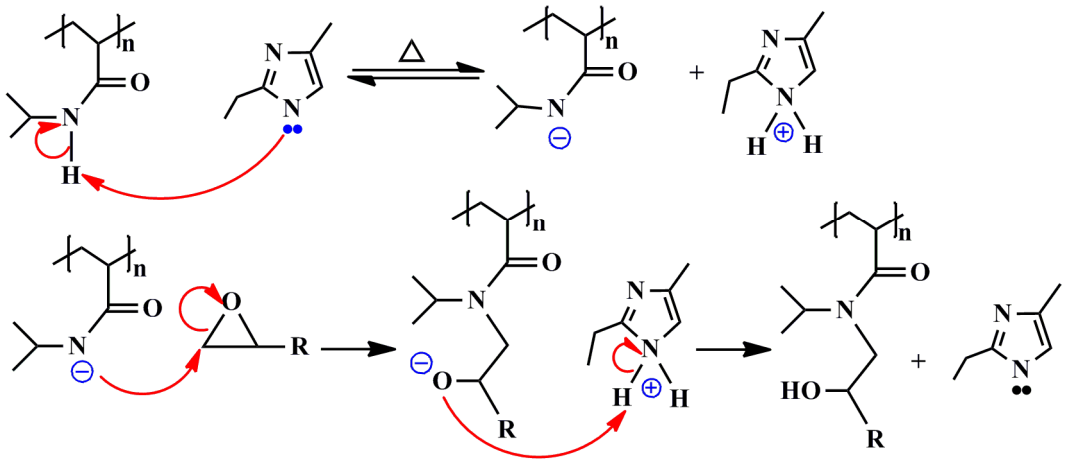


**Figure S3**. Suggested reaction mechanism between the NIPAM unit and OpePOSS catalysed by EMI.

Main Reaction:



Side Reaction:

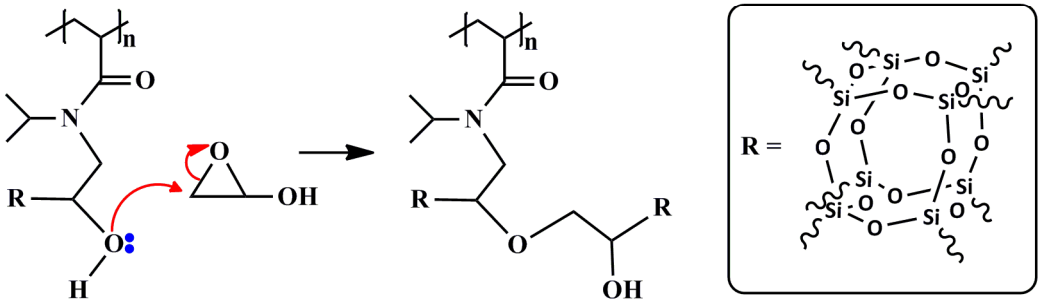


**Figure S4**. FTIR spectra of PNIPAM/OpePOSS nanofibres before and after curing treatment.

(PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt)

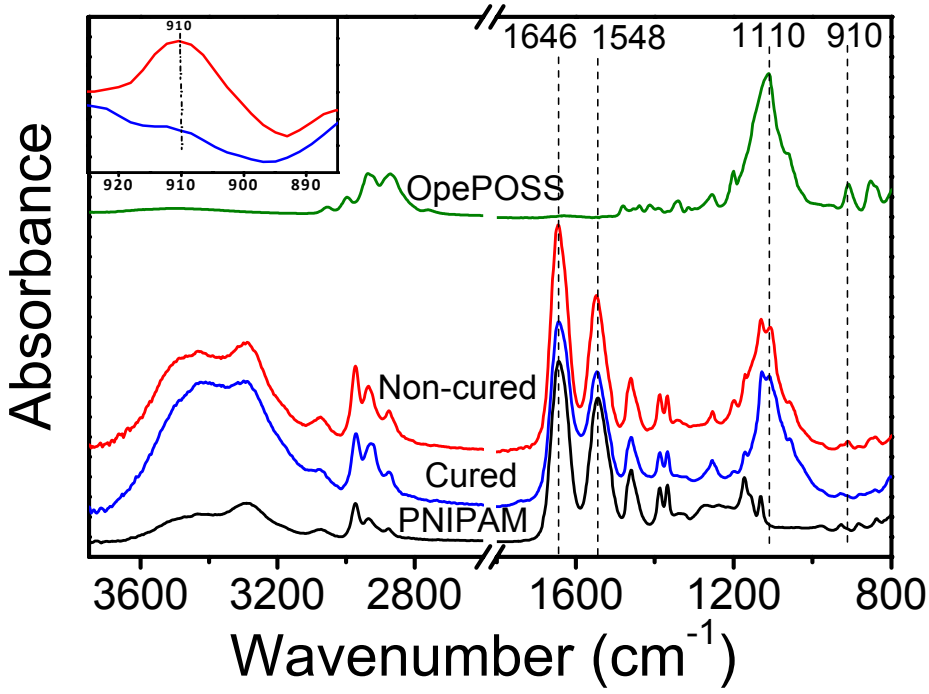


**Figure S5.** XPS survey spectra of electrospun PNIPAM/OpePOSS nanofibres. (PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt)

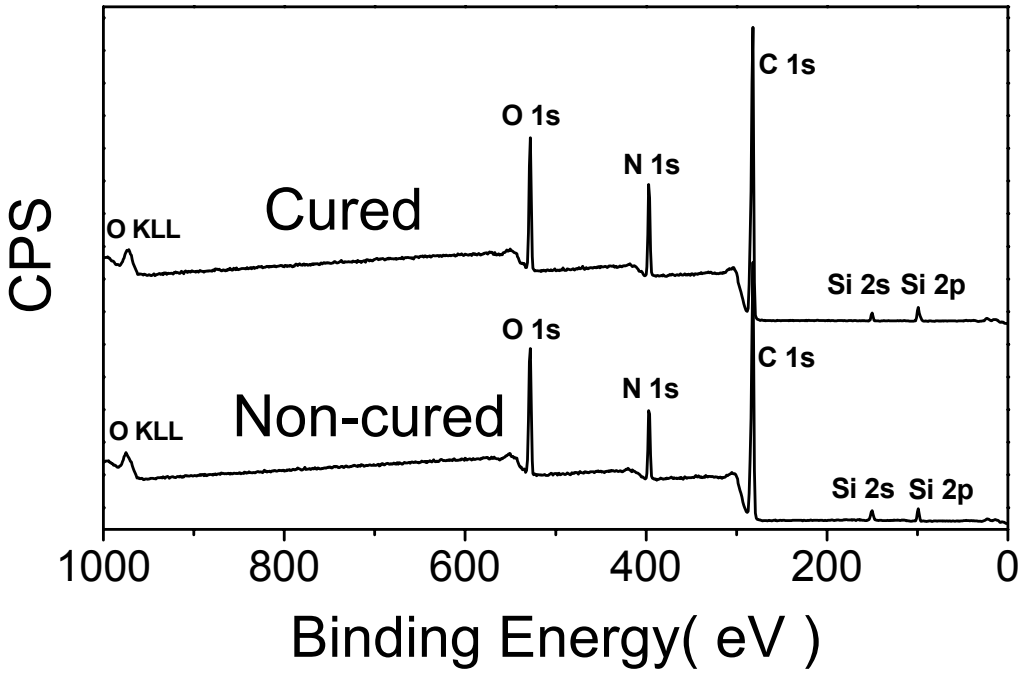


**Figure S6.** XRD patterns of pure PNIPAM and PNIPAM/OpePOSS nanofibres (PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt) before and after curing treatment.

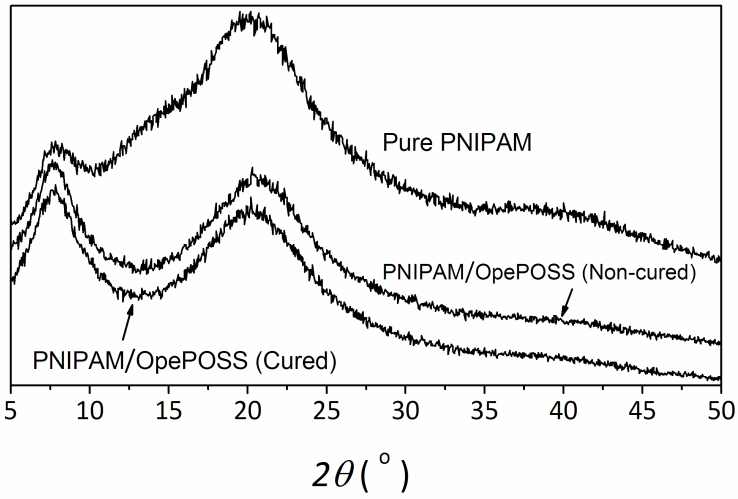


**Figure S7.** TGA curves of PNIPAM/OpePOSS nanofibres.

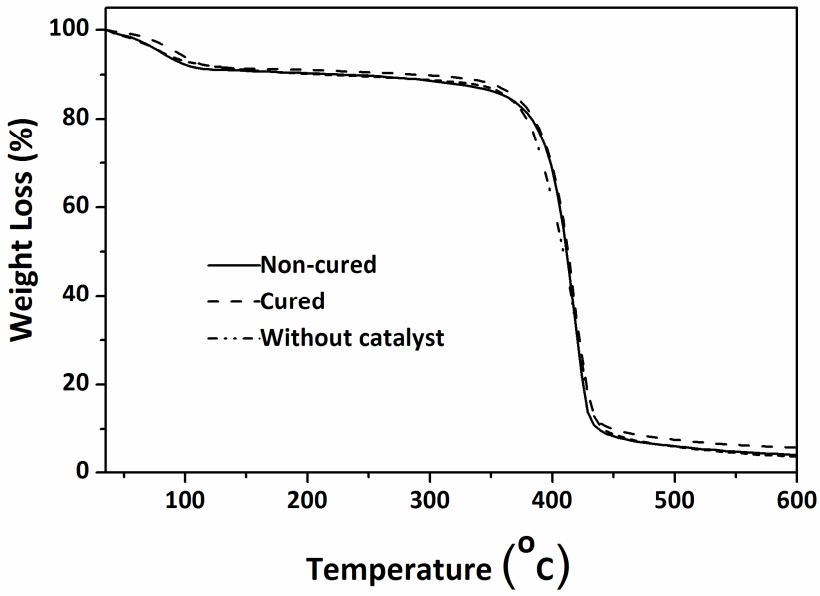


**Figure S8**. SEM images of the non-cured PNIPAM/OpePOSS nanofibres with the OpePOSS composition (based on the weight of PNIPAM) of **a**) 5%, **b**) 10%, **c**) 15%, **d**) 20%, and **e**) 25%. (PNIPAM 12.5 wt/vol%, OpePOSS: EMI =100:2 wt/wt for all conditions, scale bar is 5 μm)

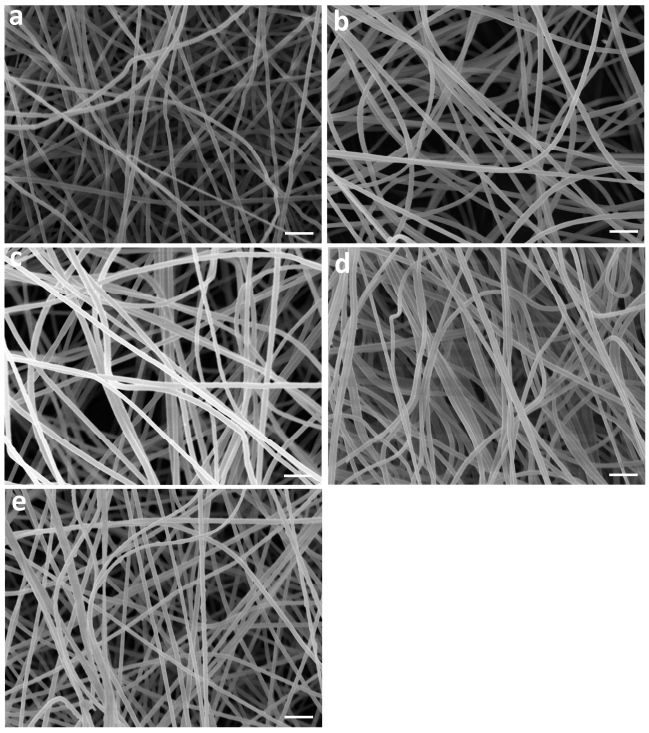


**Figure S9.** SEM images of cured PNIPAM/OpePOSS nanofibres with the OpePOSS composition (based on the weight of PNIPAM) of **a**) 5%, **b**) 10%, **c**) 15%, **d**) 20%, and **e**) 25%. (PNIPAM 12.5 wt/vol%, OpePOSS: EMI =100:2 wt/wt for all conditions, scale bar is 5 μm)

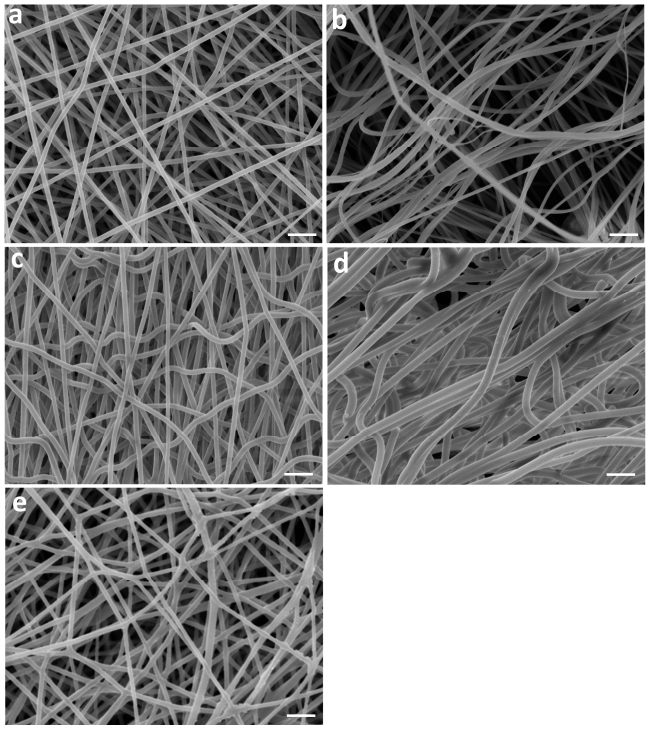


**Figure S10. a~e**) Swollen PNIPAM nanofibre mats at different elongations. **a**) 0%, **b**) 100%, **c**) 150%, **d**) 200%, and **e**) more than 800%, respectively. **1~5**) Respective SEM images of the fibres (Scale bar: 5 μm). **1′~5′**) Schematic illustration of the change in the nanofibre arrangements (●: bonded points, ○: non-bonded points). (PNIPAM 12.5 wt/vol%, PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt)

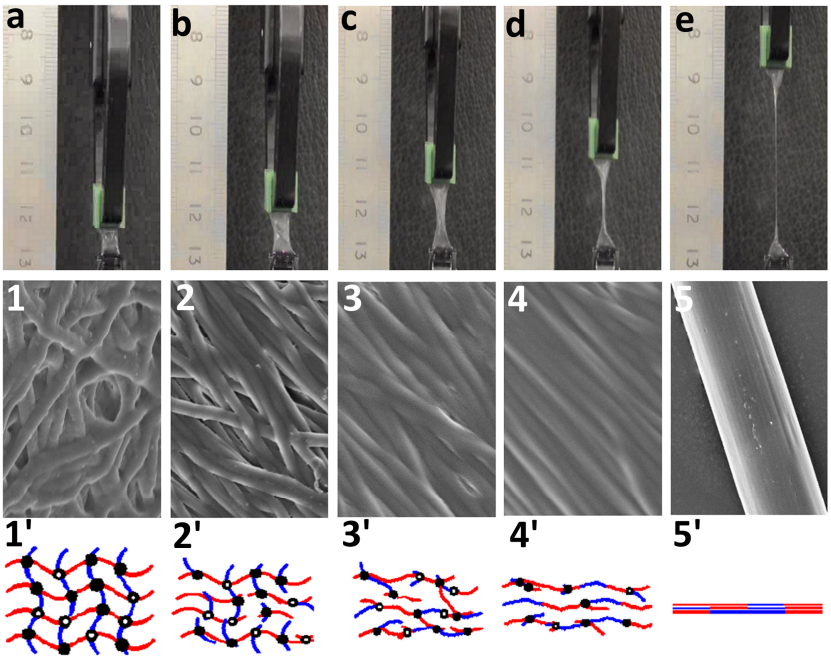
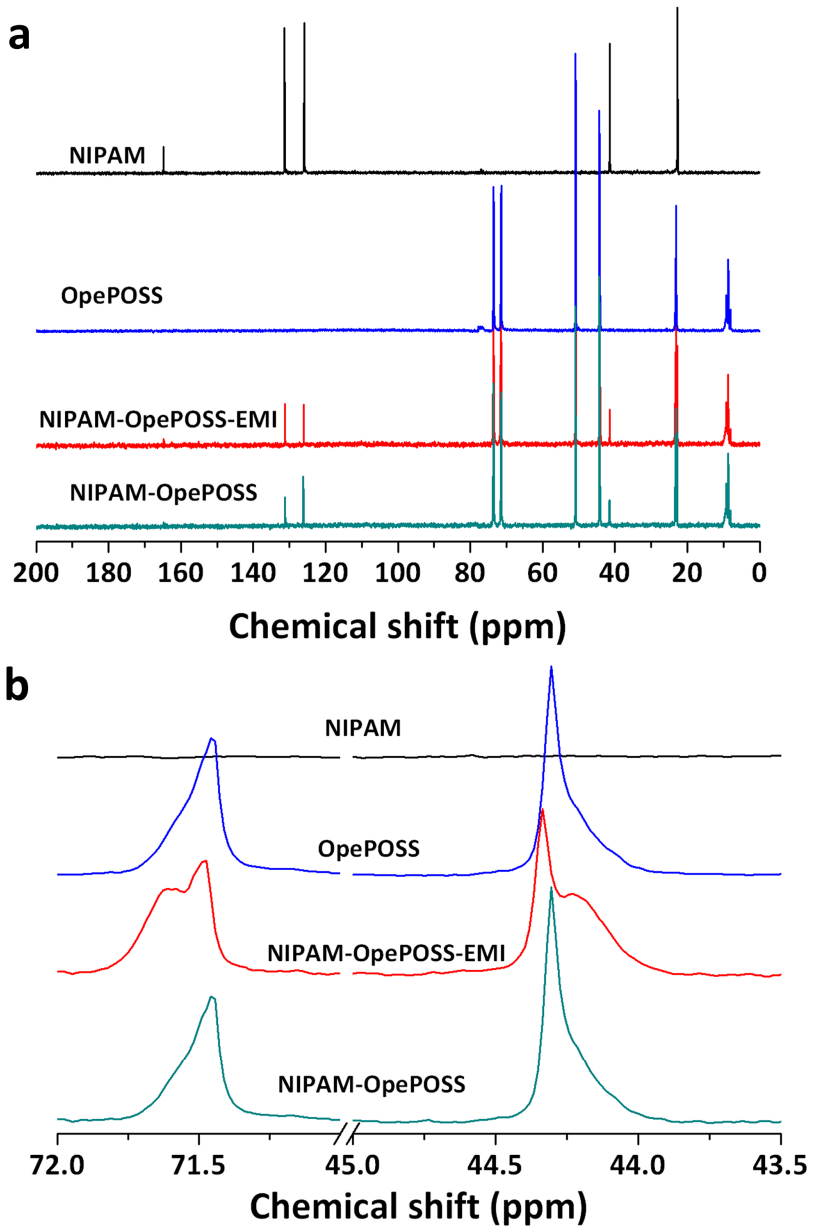


**Figure S11.** $^{13}$C-NMR spectra for: N-isopropylacrylamide (NIPAM), OpePOSS, the products of the reaction between OpePOSS and NIPAM with and without presence of trace-amounts of EMI (NIPAM-OpePOSS-EMI). (Reaction condition: 140 ºC, 2 hours with Nitrogen protection).




In the spectrum of NIPAM-OpePOSS-EMI, two new peaks are identified with resonance at: 44.3 ppm and 71.6ppm. These are respectively consistent with the C-N bond and the –OH carrying carbon resulting from the ring-opening of the epoxide group. The two new peaks for the NIPAM-OpePOSS under the same reaction condition are almost unnoticeable.

**Figure S12.** Temperature dependences of the optical transmittance and the relative volume (based on the fully swollen state) (PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt).

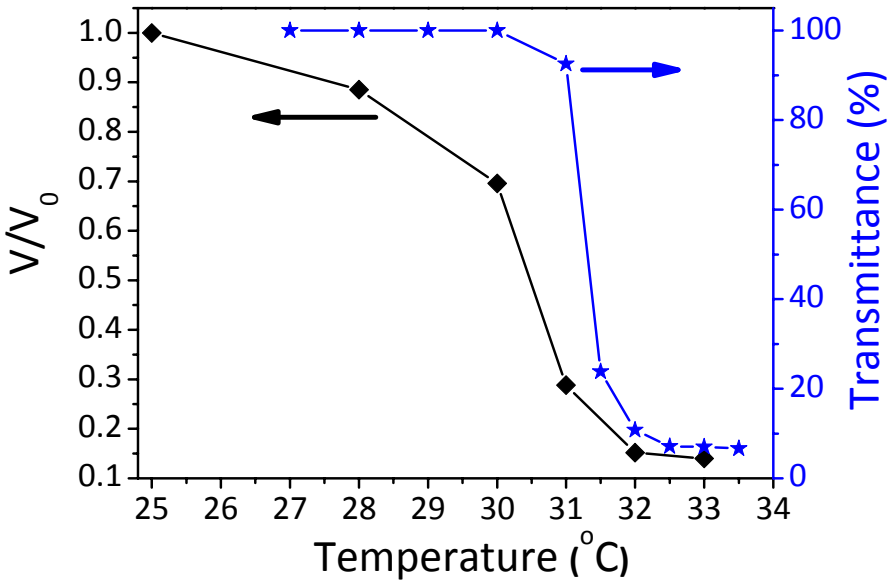


**Figure S13**. The influrence of OpePOSS content on the LCST.

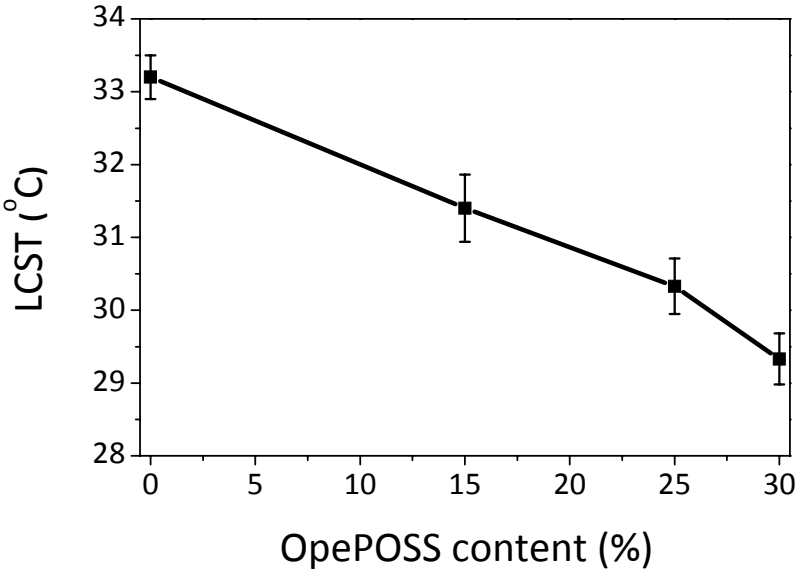


**Table S1.** C, H, N, Si Elemental analysis results of the cured PNIPAM/OpePOSS/EMI nanofibres after severe leaching with ethanol and water and the control.

| **Samples** | C | H | N | Si |
|---|---|---|---|---|
| **Non-cured without leaching treatment** | 55.73% | 9.27% | 9.54% | 2.78% |
| **Cured after leach treatment** | 56.97% | 9.16% | 9.37% | 2.90% |

(PNIPAM 10 wt%, PNIPAM: OpePOSS: EMI = 100:15:0.3, wt/wt)