

*Electronic Supplementary Information (ESI)*

**Closed-cell, emulsion-templated hydrogels for latent heat storage  
applications**

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## 1. Experimental Section

### 1.1 Materials

Block copolymer (BCP), poly(4-vinylpyridine)-*block*-poly(ethylene glycol)-*block*-poly(4-vinylpyridine) (P4VP-PEG-P4VP), was synthesized by atom transfer radical dispersed polymerization according to our previous work.<sup>1,2</sup> Sodium acrylate (NaA), *N,N'*-methylenebisacrylamide (MBAAm), 2-hydroxy-2-methyl propiophenone (Darocur 1173) and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methyl propiophenone, (Irgacure 2959) were purchased from Sigma-Aldrich. Other chemicals, such as hexane, octadecane and *N,N'*-dimethylformamide (DMF), were analytical grade and used without further purification. Deionized water was used throughout the experiments.

### 1.2 Preparation of HIPEs

BCP was dissolved in DMF, and then the solutions were slowly dropped to water (solution: water = 1:9) to obtain assembled BCP dispersions with the concentration of 0.5, 1 or 2 *w/v* %, respectively. HIPEs were formed by shearing hexane and the BCP colloid dispersion *via* a vortex mixer at 3700 rpm. HIPEs with 75.0, 83.3, 87.5 and 90.0 *vol* % of the internal phase were obtained.

### 1.3 Preparation of hydrogel polyHIPEs (HG-PHs)

The formulation of the HG-PHs are listed in Table S1, and the resultant HG-PHs were denoted HG-*X*-*Y*, where *X* (0.5, 1 and 2) and *Y* (I and D) represent BCP concentration in the aqueous continuous phase and the type of photoinitiators (I for the water-bone Irgacure 2959, and D for the oil-soluble Darocur 1173), respectively. For all HG-PHs, the volume fractions of dispersed hexane phase were fixed at 75 *vol* %. The typical procedure for the preparation of a HG-*X*-*Y*, is described below. An aqueous solution, containing 3.92 mol/L NaA, 0.08 mol/L MBAAm and 0.04 mol/L Irgacure 2959, was prepared. Then DMF solutions of BCP was slowly dropped to the aqueous solution until the concentration of BCP colloids reached to 1 *w/v* %, and the mixture was applied as the continuous phase of HIPEs. Hexane was dropped in to the aqueous phase under continuous shearing on a Vortex mixer to form a HIPE. The HIPE was

placed in a standard UV curing chamber (ELC-500) for 18 mins' irradiation, and monoliths were formed. The unreacted monomers were removed through Soxhlet extraction with acetone and then ethanol for 24 h, respectively. The solvent was finally removed by freezing drier. For HG-1-D-OD, water was carefully removed in a convection oven after polymerization, leaving OD stay in voids.

Table S1. Recipes of HG-X-Y

	HG-0.5-I	HG-1-I	HG-2-I	HG-1-D	HG-1-D-OD
Aqueous continuous phase ( <i>wt %</i> )					
Water	27.35	27.31	27.22	27.23	24.37
NaA	8.79	8.78	8.75	8.76	8.71
MBAAm	0.36	0.36	0.36	0.36	0.36
Irgacure 2959	0.24	0.24	0.24	--	--
BCP	0.15	0.30	0.60	0.30	0.27
DMF	3.03	3.02	3.01	3.01	2.69
Total	39.92	40.02	40.20	39.65	36.40
Organic dispersed phase ( <i>wt %</i> )					
Hexane	60.08	59.98	59.80	59.81	--
OD	--	--	--	--	63.12
Darocur 1173	--	--	--	0.54	0.48
Total	60.08	59.98	59.80	60.35	63.60

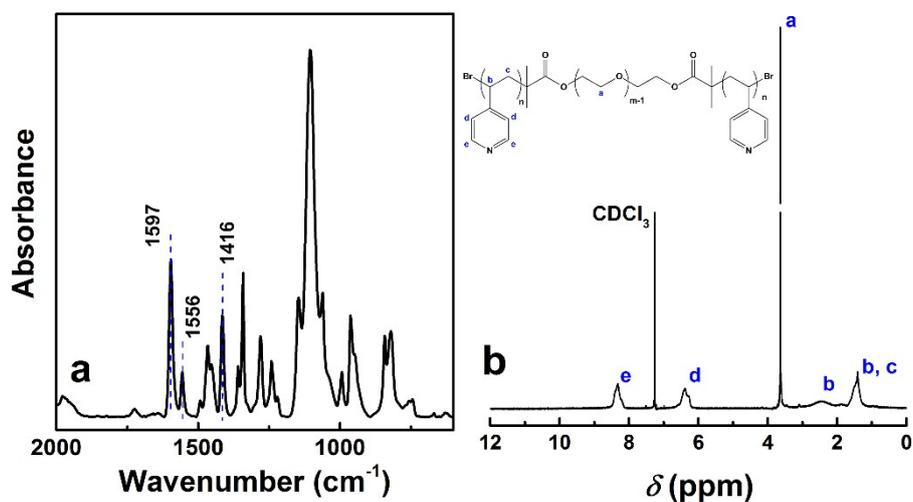
#### 1.4 Characterization

A Bruker Vertex 70 FTIR spectrometer and a JEOL ECS 400 NMR spectrometer were utilized to identify the chemical structures of P4VP-PEG-P4VP. Self-assembled BCP particles were characterized by the JEOL 2100 TEM and Malvern Zetasizer Nano ZS. The water-in-oil contact angles  $\theta_{ow}$  were measured at 25 °C using a contact angle meter (KSV Model CAM 101) setup by the captive drop method. BCP particles was coated on microscopic slides. About 3  $\mu$ L water droplets were deposited on the slides

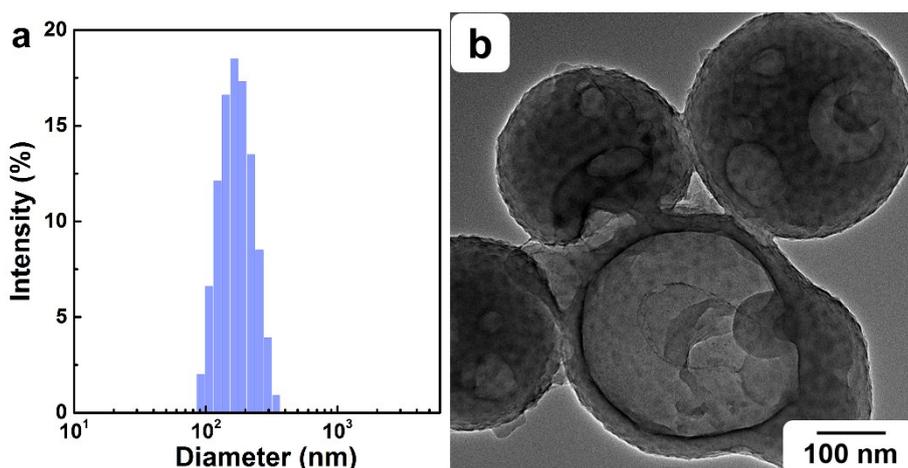
which were immersed in hexane. And the contact angle value was the average of 6 measurements. Structures of HIPEs were investigated by optical microscopy (Nikon Eclipse-80i). Morphology of HG-*X-Y* was observed with a Zeiss Supra 55VP SEM at an accelerating voltage of 5 kV, and fracture surfaces of HG-*X-Y* were coated with gold before observation. The void size and its distribution were statistically analyzed from SEM micrographs using ImageJ software, with around one hundred voids analyzed for every sample. Thermal properties of HG-1-D-OD were determined with the TA Q50 thermogravimetric analysis (TGA) and TA Q200 differential scanning calorimeter (DSC), with at least three parallel samples measured. TGA was operated in the range from 30 °C to 800 °C with an increase of 10 °C·min<sup>-1</sup> under nitrogen. During DSC measurements, nitrogen has been blowing. Firstly, preliminary crystallization of samples was conducted by cooling samples at most to -40 °C and held there for one hour. For the first cycle, the temperature was raised to 60 °C at 2 °C·min<sup>-1</sup>. After holding for 30 min, samples were cooled to -40 °C with a cooling rate at 2 °C·min<sup>-1</sup> too. The second cycle would start after samples keep at -40 °C for half an hour. Totally, 11 cycles were scanned with the same heating and cooling rate, 2 °C·min<sup>-1</sup>. The exotherm and endotherm curves of each cycle were recorded.

## 2. Results and Discussion

### 2.1 Synthesis and solvent-driven assembly of P4VP-PEG-P4VP



**Fig. S1** (a) FTIR spectra and (b) <sup>1</sup>H-NMR spectra of P4VP-PEG-P4VP.



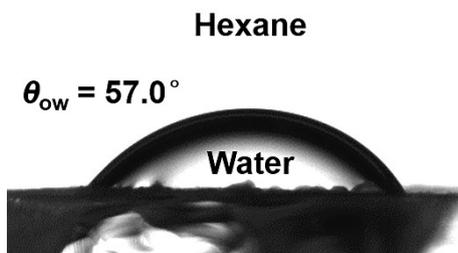
**Fig. S2** (a) size distribution of assembled BCP colloids from DLS; (b) TEM morphology of BCP colloids.

Chemical structures of P4VP-PEG-P4VP were confirmed by fourier-transform infrared (FTIR) spectrascopy and nuclear magnetic resonance (<sup>1</sup>H-NMR) (Fig. S1). The pyridines IR spectrum exhibited characteristic bands of ring skeletal vibrations 1610 ~ 1360 cm<sup>-1</sup>. <sup>1</sup>H-NMR signals were assigned as follows:  $\delta = 7.25$  ppm: CDCl<sub>3</sub>;  $\delta = 3.64$  ppm: -CH<sub>2</sub>-CH<sub>2</sub>-O- of PEG block;  $\delta = 1.42, 2.54$  ppm: -CH<sub>2</sub>-CH- of P4VP block;  $\delta = 6.38, 8.34$  ppm: H in pyridine ring. The number of repeat units for each P4VP block was calculated from <sup>1</sup>H-NMR to be 136 according to the method described in our

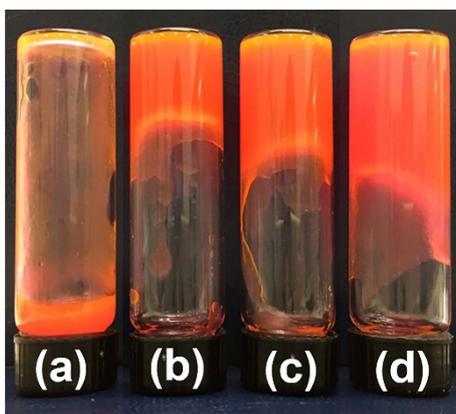
previous work.<sup>1,2</sup> The calculated  $M_{\text{copolymer}}$  was 12,700 and the BCP could be recorded as 4VP<sub>136</sub>-EG<sub>64</sub>-4VP<sub>136</sub>. The average size of the assembled BCP colloids was 177.1 nm based on Dynamic Light Scattering (DLS) (Fig. S2a). And the transmission electron microscope (TEM) morphology of the assembled BCP colloids were shown in Fig. S2b.

## 2.2 BCP colloids stabilized HIPEs

A wetting experiment was carried out to investigate the effect and to explore the ability of BCP colloids to stabilize emulsions. The water-in-oil contact angle,  $\theta_{\text{ow}}$ , of BCP colloids was 57.0° (Fig. S3), showing the BCP colloids can stabilize an o/w emulsions.<sup>3</sup>



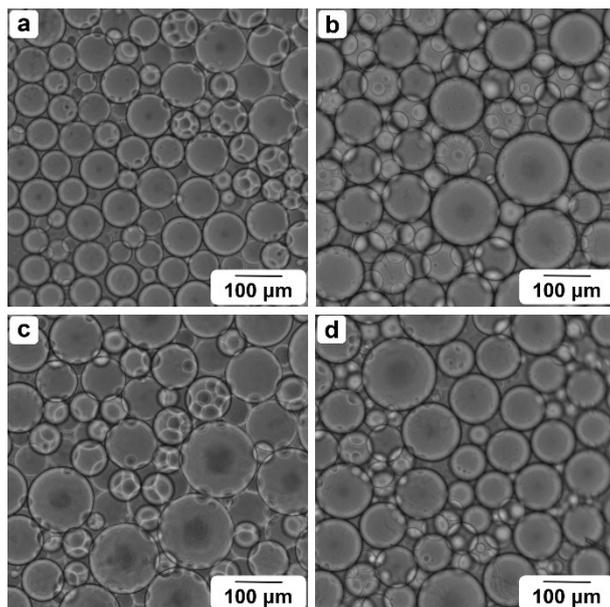
**Fig. S3** Water-in-oil contact angles  $\theta_{\text{ow}}$  of BCP colloids.



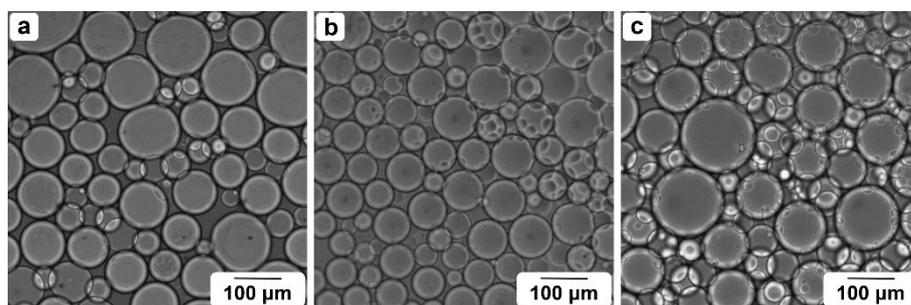
**Fig. S4** Photos of HIPEs with (a) 75.0, (b) 83.3, (c) 87.5 and (d) 90.0 *vol* % of hexane after 24 h storage (1.0 *w/v* % BCP colloid). Trace amount of Rhodamine B was added to mark the aqueous phases.

HIPEs with 75.0 *vol* % of hexane can flow, but HIPEs with flow-free behaviours were formed when their dispersed internal phase was increased to 80.0 or more. The morphology of these HIPEs was observed by optical microscope, and the oil droplets

were found to disperse in the aqueous phase. The average diameters of the dispersed droplets varied from tens micrometres to around 100  $\mu\text{m}$ , filling-in the size range of emulsions. Interestingly, the average diameters of the dispersed droplets increased with increasing volume fractions of the internal phase (Fig. S5). Polyhedral or polygonal droplets were observed, which agrees with theories postulation.<sup>4,5</sup> Interestingly, The droplet sizes were independent with BCP colloids content (Fig. S6).



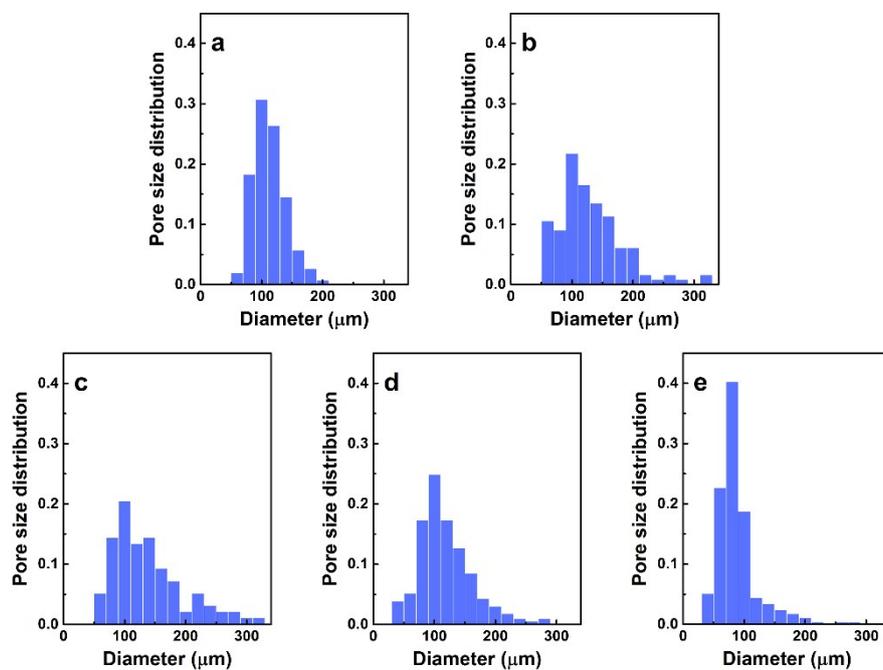
**Fig. S5** Optical micrographs of HIPEs with hexane fractions of (a) 75.0, (b) 83.3, (c) 87.5, and (d) 90.0 *vol %* as the internal phase (the BCP concentration in the continuous phase was fixed at 1.0 *w/v %*).



**Fig. S6** Optical micrographs of HIPEs with (a) 0.5, (b) 1.0 (the same graph as Fig. S5a) and (c) 2.0 *w/v %* BCP in the continuous aqueous phase (the volume fraction of hexane was fixed at 75 *vol %*).

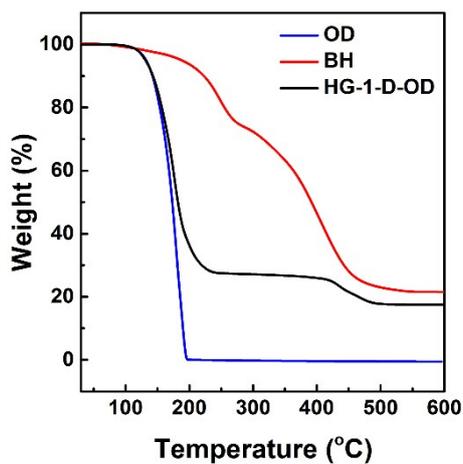
### 2.3 Void size dispersion of HG-PHs

Void size distributions (Fig. S6) of HG-0.5-I, HG-1-I, HG-2-I, HG-1-D and HG-1-D-OD (after extraction) were statistically analyzed from SEM micrographs using ImageJ software, with around one hundred voids analyzed.



**Fig. S7** Void size dispersion of HG-PHs: (a) HG-0.5-I, (b) HG-1-I, (c) HG-2-I, (d) HG-1-D, (e) HG-1-D-OD after extraction.

### 2.4 Thermal stability of HG-1-D-OD



**Fig. S8** TG curves of OD, BH and HG-1-D-OD.

Thermogravimetric decomposition of OD, BH (bulk hydrogel prepared with same composition of HG-1-D-OD, but without internal OD phase) and HG-1-D-OD was investigated by TG. There was almost no mass loss observed before 140 °C, showing that HG-1-D-OD was thermal stable before 80 °C. Two degradation steps were observed for HG-1-D-OD: the first stage occurred before 250 °C with about 73.1 % weight loss, which could be ascribed to the evaporation of OD from HG-1-D-OD. The second stage between 400-500 °C could be assigned to the degradation of the PH scaffold.

### 3. References

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