Electronic supplementary information

Phase change material nanocapsules for latent function thermal fluids with tuneable thermal energy storage profiles

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Table S1 Monomer and hexadecane quantities for the synthesis of crosslinked capsules

Reaction	Methacrylate Monomer		Trimethylolpropane trimethacrylate		Hexadecane	
	Mass/ g	Moles/ × 10^2	Mass/ g	Moles/ × 10^3	Mass/ g	Moles/ × 10^2
PMMA_HD	3.490	3.49	1.310	3.87	3.2	1.41
PBzMA_HD	3.796	2.67	1.004	2.97	3.2	1.41
PnBMA_HD	3.956	2.24	0.844	2.49	3.2	1.41
PIBMA_HD	4.106	1.85	0.694	2.05	3.2	1.41

Table S2 Molecular weight characteristics of ω-unsaturated macromonomers synthesised by CCTEP and seeded RAFT emulsion polymerisation.

	M_n[a] /g mol^{-1}	M_w /g mol^{-1}	$Đ$	DP_n (GPC)	DP_n (^{1}H NMR)
P(MAA-*co*-MMA)	2800	5900	2.03	29	31[b]
P(BMA-*b*-[MAA-*co*-MMA])	4100	5900	1.46	38	43[c]

[a]GPC measured in THF with 2 x PLgel Mixed C columns at 30 °C. [b]^{1}H NMR measured in DMSO-d_6. [c]^{1}H NMR measured in $CDCl_3$:DMSO-d_6 2:1 mixture.

Table S3 Transition onset temperature and enthalpy for crystallisation and fusion for hexadecane (HD) and crosslinked poly(methyl methacrylate), poly(benzyl methacrylate), poly(n-butyl methacrylate) and poly(isobornyl methacrylate) capsules. Measured using a TA instruments DSC 2500 under nitrogen atmosphere at 1 °C min^{-1}. The final heating and cooling scans of three cycles were analysed.

Sample	Crystallisation			Melting		
	$T_{c,i}$/ °C	$T_{c,ii}$/ °C	ΔH_c/ J g^{-1}	$T_{m,i}$/ °C	$T_{m,ii}$/ °C	ΔH_f/ J g^{-1}
HD	14.6	-	214.3	-	16.6	214.6
PMMA_HD	9.3[a]	3.2	74.0	-	12.2	71.1
PBzMA_HD	9.3[a]	2.9	63.9	-	11.9	62.7
PnBMA_HD	9.7	0.57	59.6	-	11.4	60.3
PIBMA_HD	10.8	-0.6	38.4	10.0	15.8	39.0

$T_{c,i}$ and $T_{c,ii}$ crystallisation onset temperatures, ΔH_c enthalpy of crystallisation, $T_{m,i}$, and $T_{m,ii}$ melting onset temperature, ΔH_f enthalpy of fusion. [a]Crystallisation phase transition onset at 9.3 °C is not present is first cooling scan for PMMA and PBzMA.

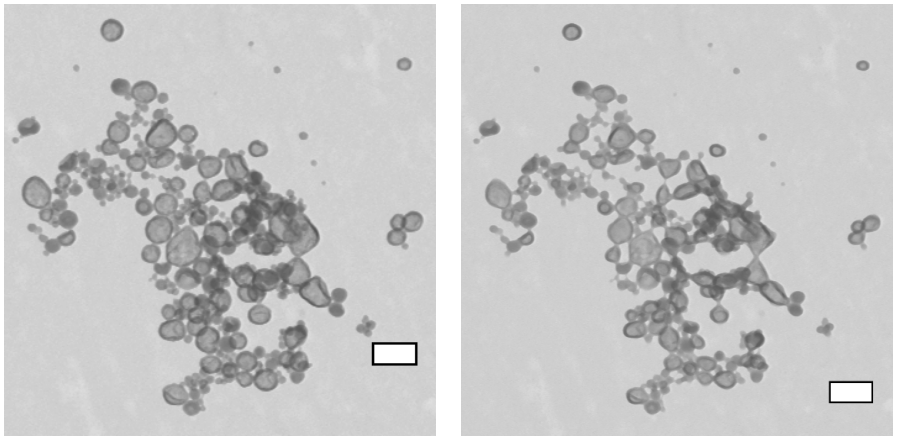

Figure S1 Scanning transmission electron microscope (STEM) images at 2 × 10^4 times magnification of the same crosslinked poly(methyl methacrylate) *n*-octadecane capsules (synthesised in section 4.2.3). Left image taken immediately, right image taken after approximated 60 seconds.

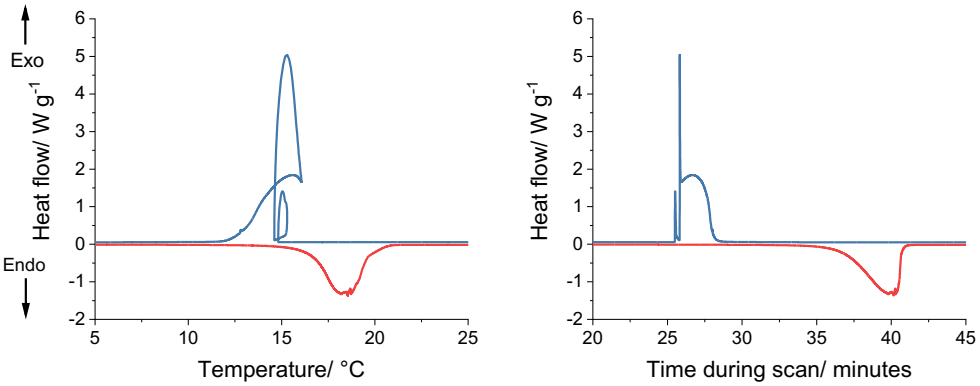

Figure S2 DSC curves with x-axes as temperature and time for bulk *n*-hexadecane cooled and heated at a scan rate of 1 °C min^{-1} under an atmosphere of nitrogen. The abnormal curve when heat flow is plotted against temperature is caused by the rapid solid-solid rotator transitions.

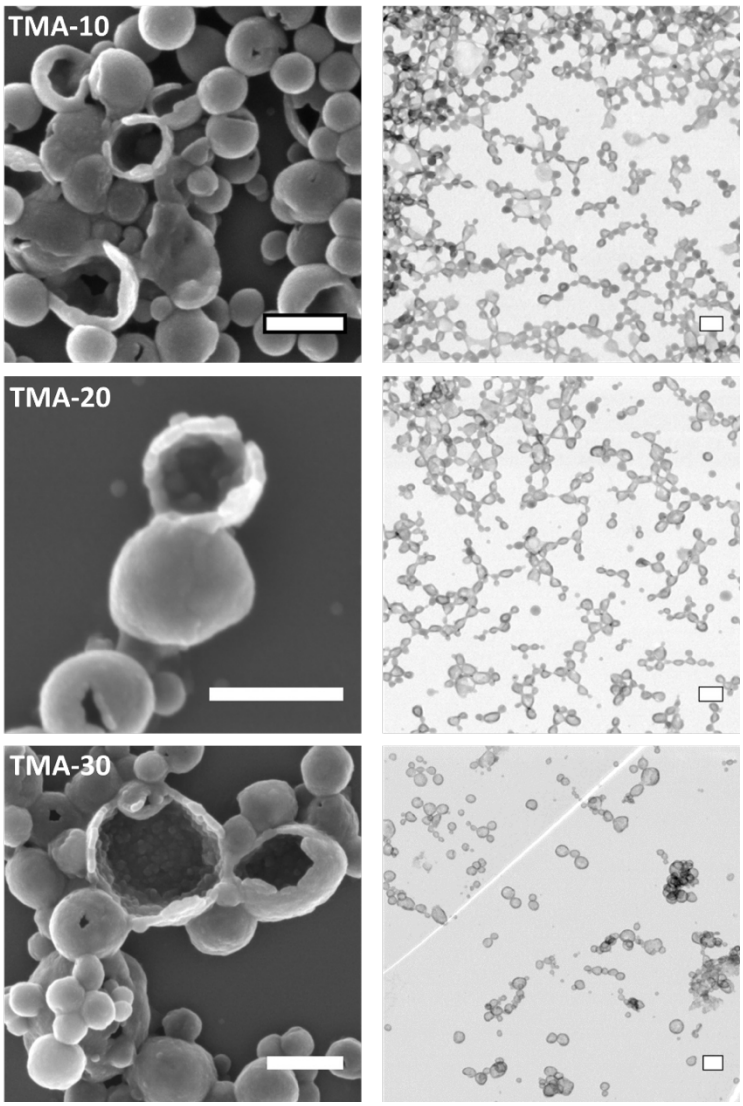

Figure S3 Electron microscope images of poly(benzyl methacrylate)-hexadecane capsules synthesised using different amounts of trimethylolpropane trimethacrylate (TMA) crosslinking monomer. Images from SEM (left) and STEM (right). Reactions TMA-10, TMA-20 and TMA-30 used 10, 20 and 30 % w/w crosslinking monomer to total dispersed phase. Scale bars are 200 nm for all images.

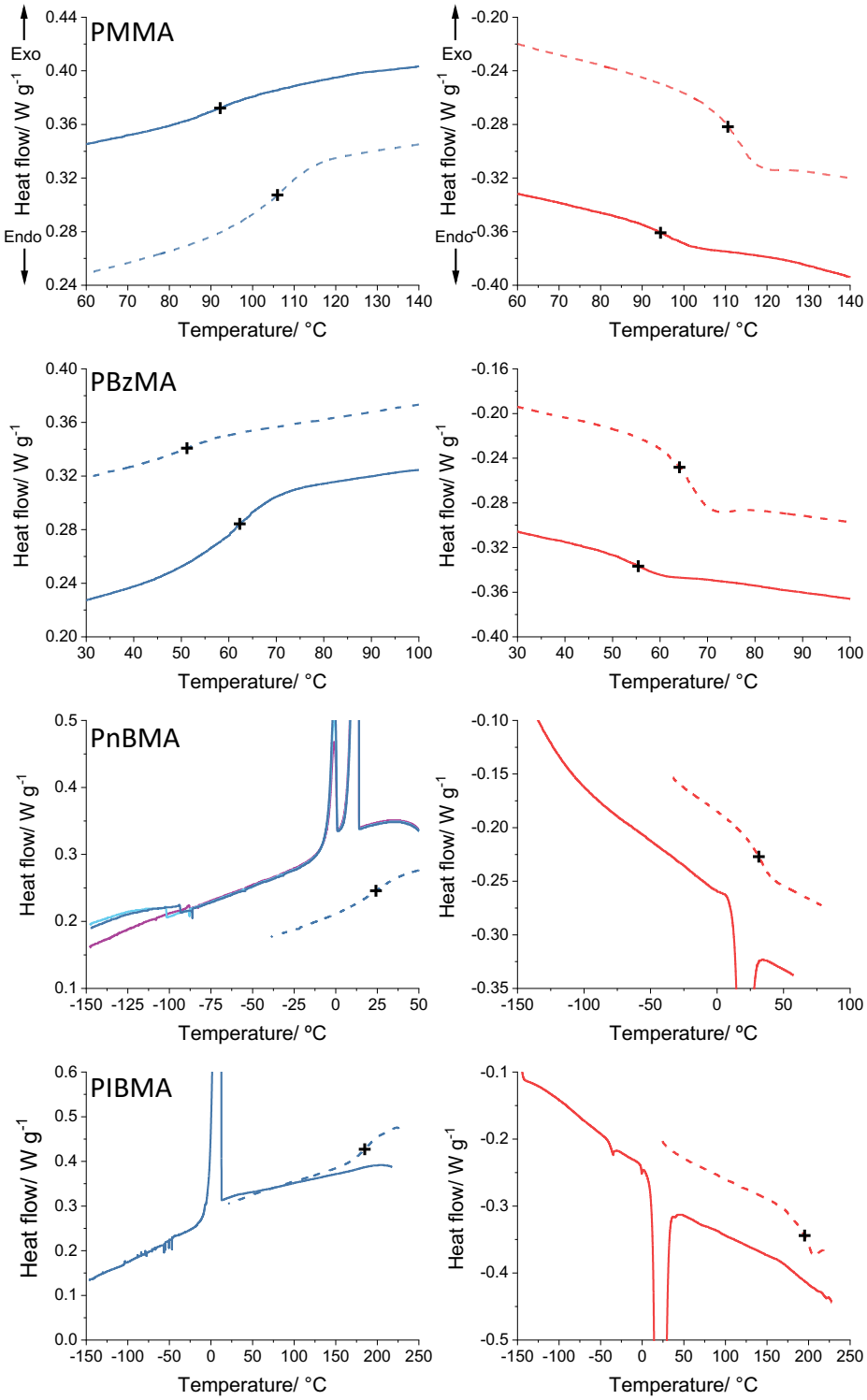

Figure S4 Dynamic scanning calorimetry spectra of poly(methyl methacrylate), poly(benzyl methacrylate), poly(*n*-butyl methacrylate) and poly(isobornyl methacrylate) showing the presence or absence of glass transitions. Measured using a TA Instruments DSC 2500, under nitrogen atmosphere, at 10 °C min^{-1}. Transitions on cooling shown on the left, transitions on heating on the right, midpoint T_g values have been added as crosses. The final scans of three temperature cycles are shown with the exception of PnBMA. Spectra for dry polymers (dashed lines) and polymers that were soaked in hexadecane for 48 hrs (solid lines) are shown.

Table S4 Temperature-dependent specific heat capacity data

Substance	$C_p(T)$ Equation	Temperature Range	Reference
Water	$A + BT + CT^2 + DT^3 + E/T^2$ A = -203.6060 B = 1523.290 C = -3196.413 D = 2474.455 E = 3.855326	298 – 500 K	Chase, M.W., Jr., NIST-JANAF Themochemical Tables, Fourth Edition, J. Phys. Chem. Ref. Data, Monograph 9, 1998, 1-1951.
n-Docosane	**High T** A + BT A = 2.106 B = 3.41E-3 **Low T** 1.48T	353 – 453 K 300 – 500 K	Atkinson, C.M.L.; Larkin, J.A.; Richardson, M.J., Enthalpy changes in molten n-alkanes and polyethylene, J. Chem. Thermodynam., 1969, 1, 435-445. Hoehne, G.W.H., Transitions of n-alkanes above the melting point, Polym. Bull. (Berlin), 1981, 6, 41-46.
n-Octadecane	**High T** 2.2T **Low T** 1.91T	300 – 500 K 12 – 380 K	Hoehne, G.W.H., Transitions of n-alkanes above the melting point, Polym. Bull. (Berlin), 1981, 6, 41-46. Messerly, J.F.; Guthrie, G.B.; Todd, S.S.; Finke, H.L., Low-temperature thermal data for n-pentane, n-heptadecane, and n-octadecane, J. Chem. Eng. Data, 1967, 12, 338-346.
PMMA	**High T** A + BT A = 0.265 B = 1.39E-3	298 – 463 K	Pavlinov, L.I.; Rabinovich, I.B.; Okladnov, N.A.; Arzhakov, S.A., Heat capacity of copolymers of methyl methacrylate with methacrylic acid in the region 25-190°C, Polymer Sci., 1967, USSR 9A, 539-544.