

Electronic Supplementary Information (ESI)

Synthesis and characterization of CO₂-sensitive temperature-responsive catalytic poly(ionic liquid) microgels

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SI 1. Experimental procedures

1.1. LLS study

Standard Laser Light Scattering (LLS) spectrometer (BI-200SM) equipped with a BI-9000 AT digital time correlator (Brookhaven Instruments, Inc.) and a Mini-L30 diode laser (30 mW, 637 nm) as the light source was used. The refractive indexes of different water/ DMAc mixtures and the refractive index increments (dn/dc) of microgels in different water/DMAc mixtures were determined by a deflection type differential refractometer (BI-DNDC). The very dilute microgel dispersions (10.0 $\mu\text{g/mL}$) were passed through Millipore Millex-HV filters (pore size 0.80 μm) to remove dust before LLS measurements. In Dynamic LLS (DLS), Laplace inversion of each measured intensity-intensity time correlation function in a dilute dispersion can lead to a line-width distribution $G(\Gamma)$. For a purely diffusive relaxation, Γ is related to translational diffusion coefficient D by $(\Gamma/q^2)_{C \rightarrow 0, q \rightarrow 0} = D$, so that $G(\Gamma)$ can be converted to a translational diffusion coefficient distribution and the average hydrodynamic diameter ($\langle D_h \rangle$; intensity contribution) distribution by using the Stokes-Einstein equation, $\langle D_h \rangle = (k_B T / 3\pi\eta) / D$, where k_B , T , and η are the Boltzmann constant, absolute temperature, and solvent viscosity, respectively.

1.2. Uptake of the compounds in the equilibrated microgels

The composition of DMAc and water of the uptaken medium in the equilibrated microgels were determined at a set constant temperature of 25.0 °C, 50 °C, and 90 °C, respectively. The dilute isotope solutions (9.25×10^4 Bq/mL $^3\text{H}_2\text{O}$ in water, and 3.19×10^3 Bq/mL ^{14}C labelled DMAc) were prepared and mixed in preset ratios as the donor solutions for partition studies. Radioactivities of the donor solutions of known water/DMAc mol ratios were measured by using a low background liquid scintillation counter (Hitachi ALOKA LSC-LB7), and used for model construction. The microgels were immersed in the donor solutions (the final concentration of the microgels was set to 10.0 $\mu\text{g/mL}$) and allowed to equilibrate for 48 h in vials, whose temperature was controlled by an oil bath of the set constant temperature. Then the microgels (20.0 mL) were separated by centrifugation, and soaked in vials containing DMAc (20.0 mL) to the elute radiolabeled DMAc and water in microgels. After 48 h, the radioactivities of solvents in vials were measured, and the uptake DMAc and water in the equilibrated microgels was calculated from the model that was constructed by using water/DMAc mixtures of known mol ratios. The uptake mol fraction (X_{uptake}) of DMAc is defined as a DMAc mol fraction in total solvents uptaken in the equilibrated microgels.

The adsorption of 1,2-epoxybutane and the produced cyclic carbonate (i.e., 4-ethyl-1,3-dioxolan-2-one) on the equilibrated CSM microgels in the presence of DMAc were determined at a set constant temperature by the same method, but with the donor solutions prepared by mixing those compounds with the dilute isotope solution of ^{14}C labelled DMAc.

1.3. Other characterizations

The pH value was measured on a EUTECH PH 700 instruments. All titrations were performed in triplicate using a pH meter. The pH values were measured on a METTLER TOLEDO SevenEasy pH meter. FTIR spectra were recorded with a Thermo Electron Corporation Nicolet 380 Fourier transform infrared spectrometer. NMR spectra were recorded on a Bruker AVIII 500MHz solution-state NMR

spectrometer. TEM images were taken on a JEM-2100 high resolution transmission electron microscopy operating at an accelerating voltage of 200 kV. SEM images were obtained on Hitachi S4800 scanning electron microscope with a field emission electron gun.

SI 2. Figures.

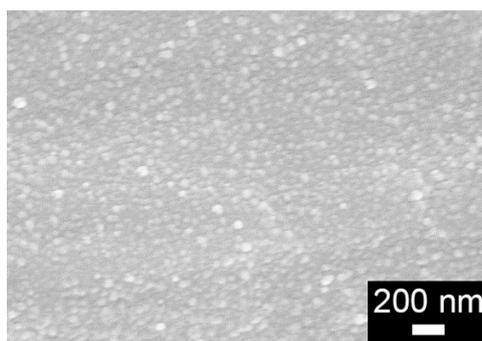


Fig. S1 A typical SEM image of the CSM microgels.

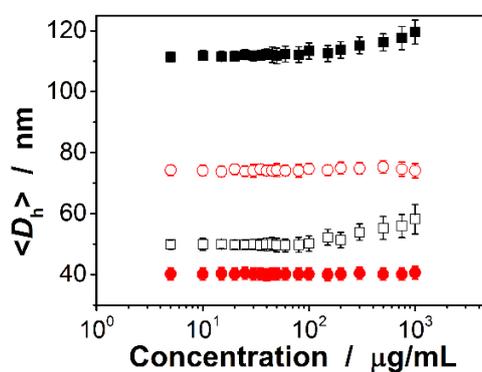


Fig. S2 The $\langle D_h \rangle$ values as a function of the concentration of the CSM microgels in water (■, □) or DMAc (●, ○), and measured at 25.0 °C (solid symbols) or 90.0 °C (open symbols) (upon bubbling of N_2 for 20 min).

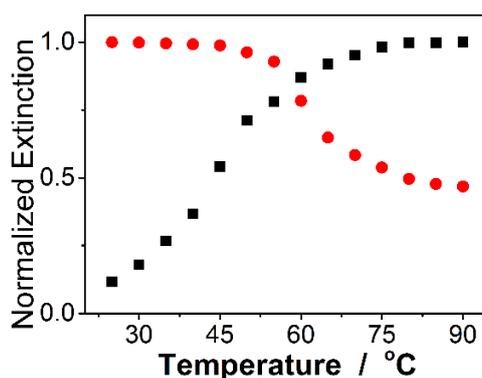


Fig. S3 Temperature-dependent turbidity (normalized extinction at 500 nm) of a CSM microgel dispersion in water (■) or DMAc (●). Because the extinction of the very dilute dispersion (10.0 $\mu\text{g/mL}$) might be too low for turbidity tests, the microgel dispersions of 100.0 $\mu\text{g/mL}$ were measured (upon bubbling of N_2 for 20 min).

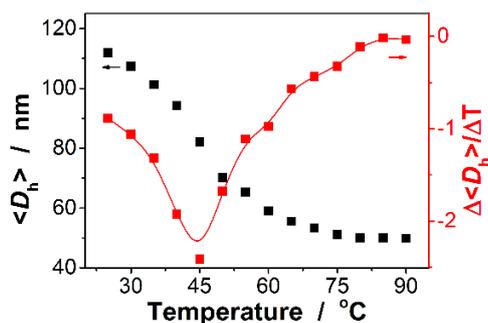


Fig. S4 Typical $\langle D_h \rangle - T$ and $\Delta \langle D_h \rangle / \Delta T - T$ plots of the CSM microgels in water. DLS measurements were made on 10.0 $\mu\text{g/mL}$ microgel dispersions (upon bubbling of N_2 for 20 min).

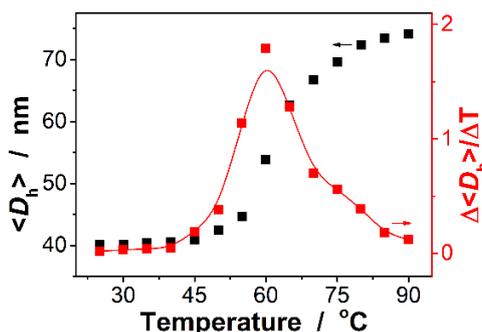


Fig. S5 Typical $\langle D_h \rangle - T$ and $\Delta \langle D_h \rangle / \Delta T - T$ plots of the CSM microgels in DMAc. DLS measurements were made on 10.0 $\mu\text{g/mL}$ microgel dispersions (upon bubbling of N_2 for 20 min).

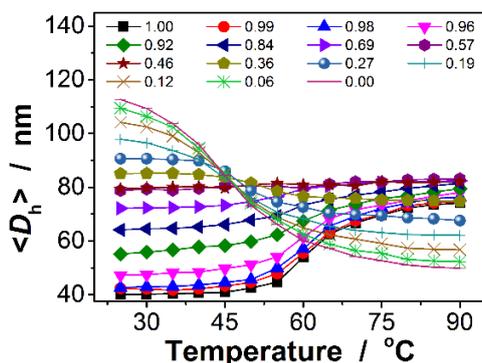


Fig. S6 Temperature-dependent $\langle D_h \rangle$ of the CSM microgels dispersed in the mixture of water/DMAc of different mol fractions of DMAc (X_{DMAc}). DLS measurements were made on 10.0 $\mu\text{g/mL}$ microgel dispersions (upon bubbling of N_2 for 20 min).

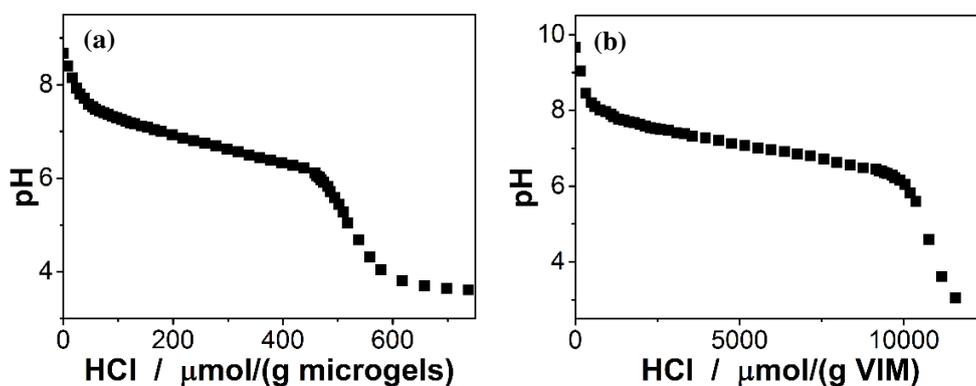


Fig. S7 pH titration of (a) CSM microgels (10.0 $\mu\text{g/mL}$) and (b) VIM dispersed in water against HCl at 25.0 $^\circ\text{C}$.

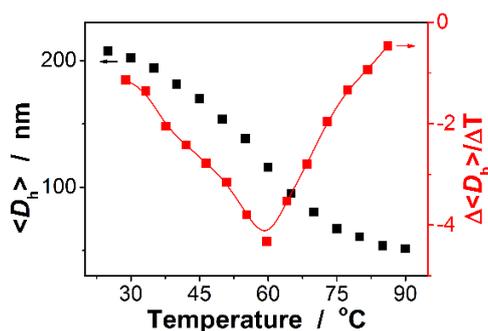


Fig. S8 Typical $\langle D_h \rangle - T$ and $\Delta \langle D_h \rangle / \Delta T - T$ plots of the CSM microgels in water. DLS measurements were made on 10.0 $\mu\text{g/mL}$ microgel dispersions (upon bubbling of CO_2 gas flow of 20 mL/min for 20 min under 1 atm).

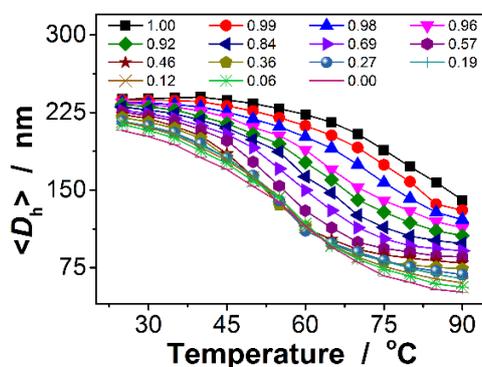


Fig. S9 Temperature-dependent $\langle D_h \rangle$ of the CSM microgels dispersed in the mixture of water/DMAc of different mol fractions of DMAc (X_{DMAc}). DLS measurements were made on 10.0 $\mu\text{g/mL}$ microgel dispersions (upon bubbling of CO_2 gas flow of 20 mL/min for 20 min under 1 atm).

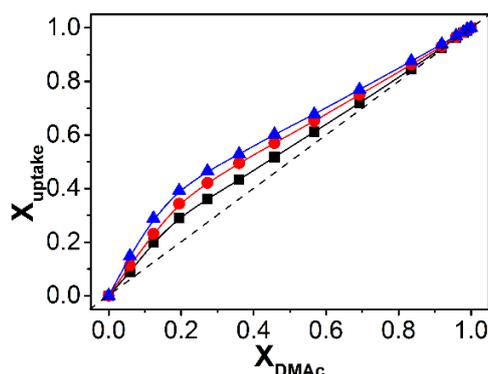


Fig. S10 A comparison of the X_{DMAc} and the X_{uptake} , the mol fraction of DMAc of the uptaken medium in the equilibrated CSM microgels, at 25.0 $^\circ\text{C}$ (■), 50.0 $^\circ\text{C}$ (●) and 90.0 $^\circ\text{C}$ (▲), respectively.

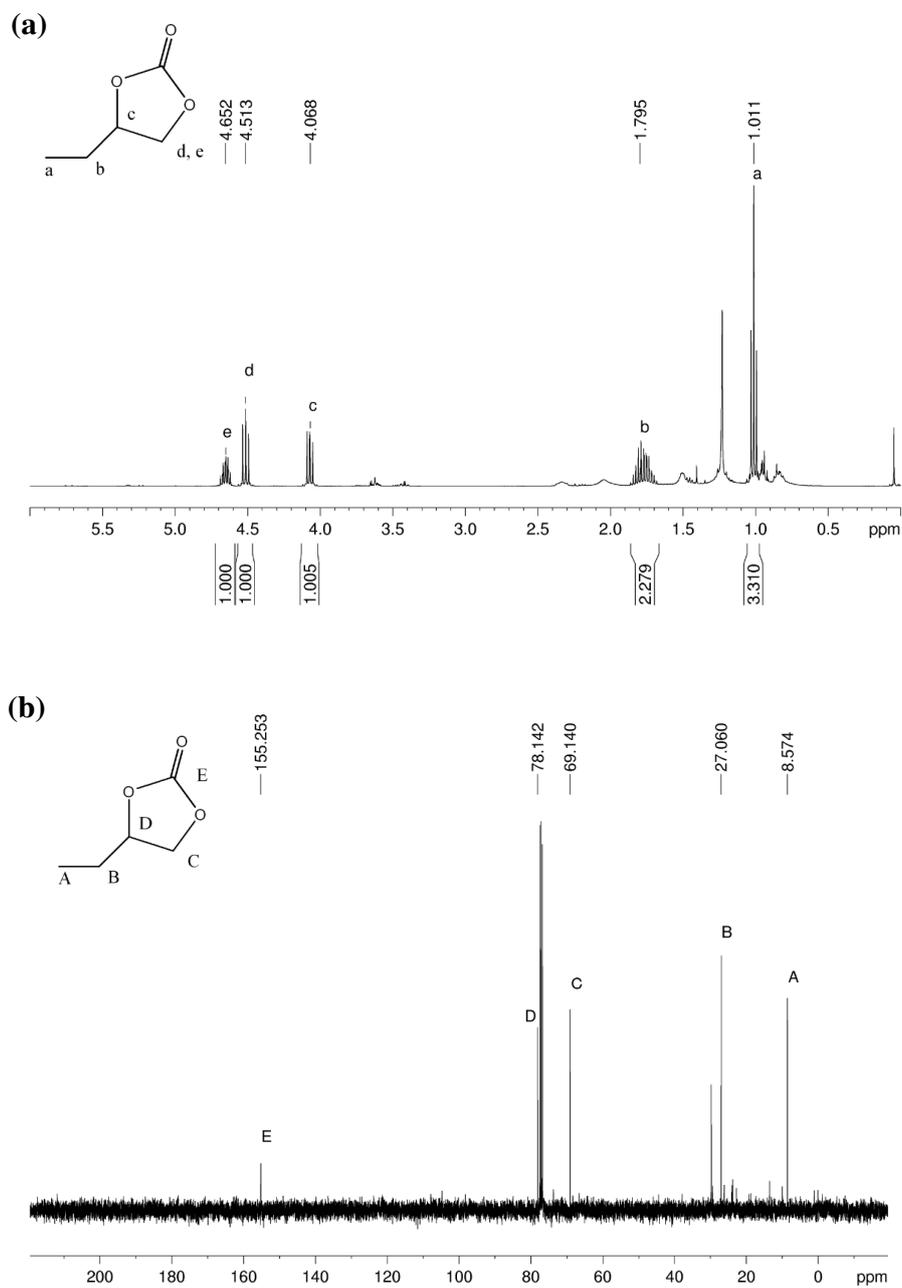


Fig. S11 (a) ^1H and (b) ^{13}C NMR spectra of 4-ethyl-1,3-dioxolan-2-one (in CDCl_3) yielded from the model reaction.

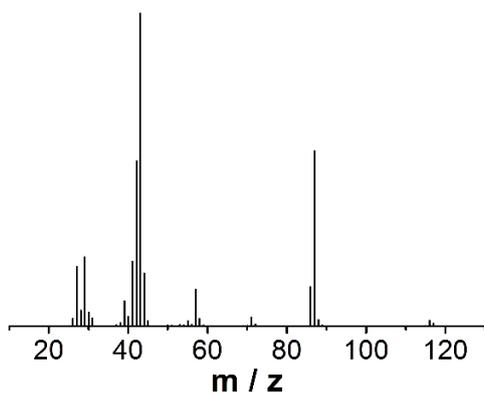


Fig. S12 Typical MS spectrum of 4-ethyl-1,3-dioxolan-2-one (corresponding to the GC peaks at 4.6 min) yielded from the model reaction.

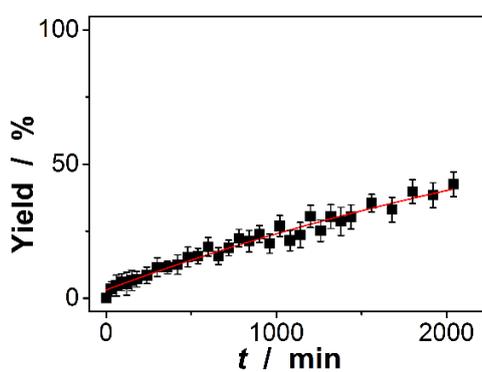


Fig. S13 Time trace of yield of 4-ethyl-1,3-dioxolan-2-one during the model reaction catalyzed by TPSS (containing 8.3×10^{-2} mmol phosphonium, with the amount close to that on 40.0 mg CSM microgels) at 90.0 °C. The line is an exponential fit.

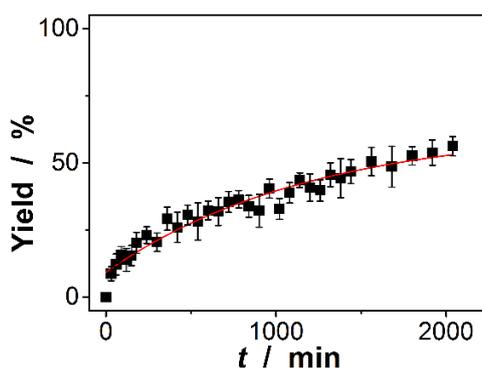


Fig. S14 Time trace of yield of 4-ethyl-1,3-dioxolan-2-one during the model reaction catalyzed by Bu₄PBr (containing 8.3×10^{-2} mmol phosphonium, with the amount close to that on 40.0 mg CSM microgels) at 90.0 °C. The line is an exponential fit.

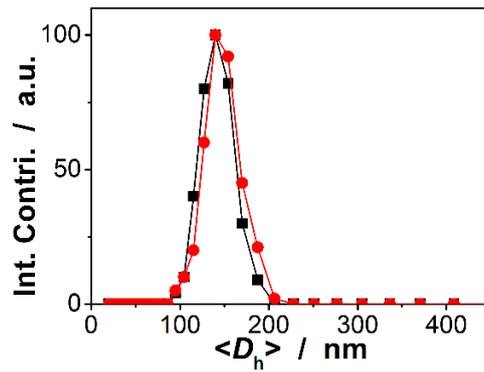


Fig. S15 DLS size distribution for the CSM microgels before (■) and after (●) six cycles' of use for the model reaction. DLS measurements were made in DMAc at 90.0 °C (upon bubbling of CO₂ gas flow of 20 mL/min for 20 min under 1 atm).

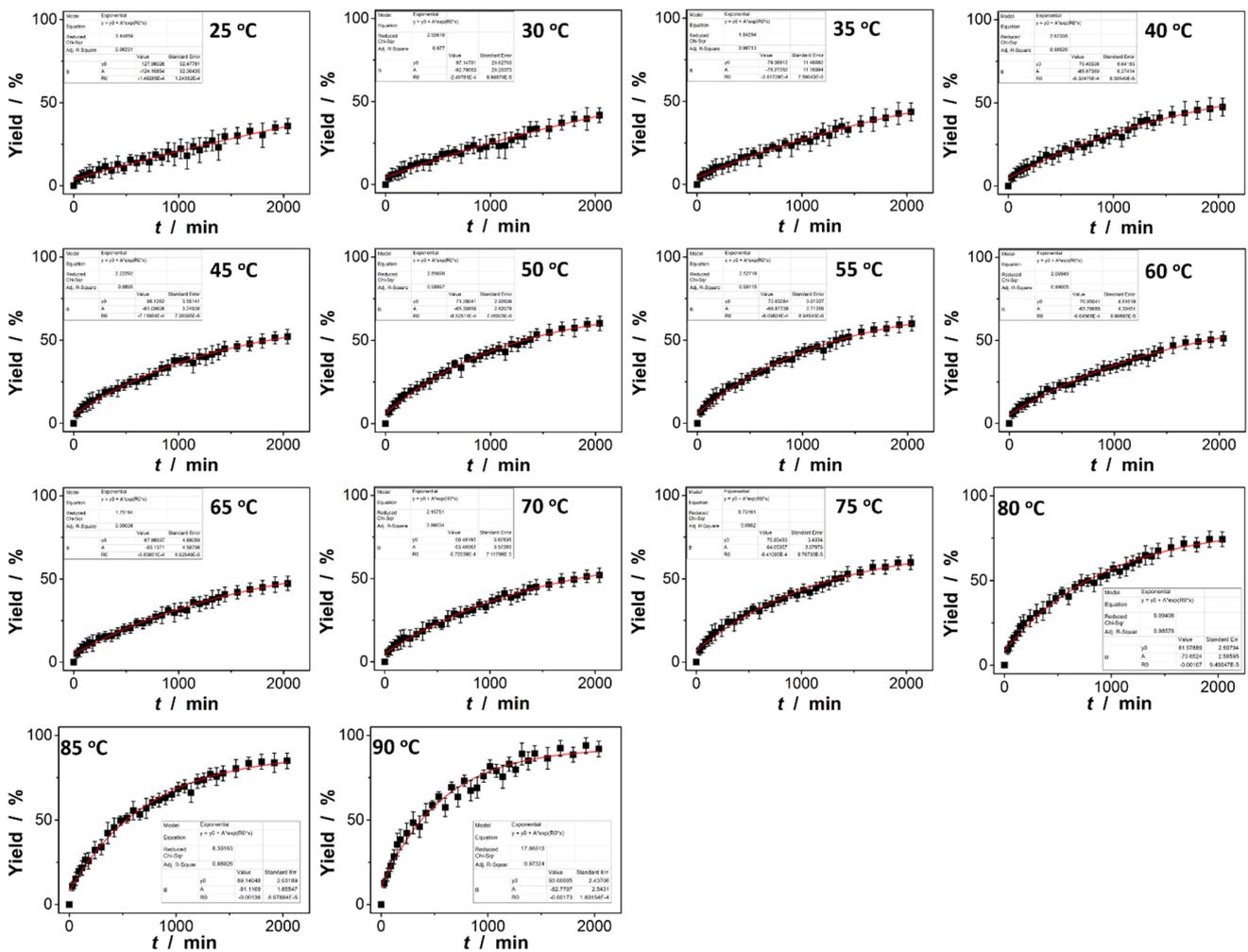


Fig. S16 Time trace of the yield during the model reaction catalyzed by the CSM microgels at different temperatures. Results are mean \pm SD ($n = 3$). The lines are exponential fits.

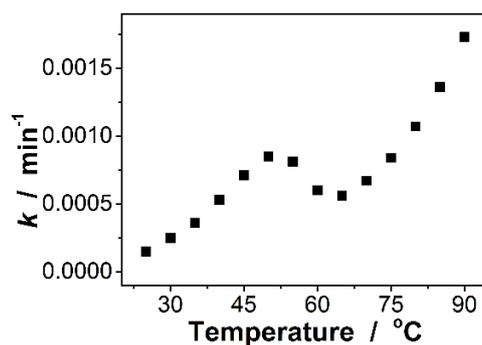


Fig. S17 Temperature-deepened k values for the model esterification reaction of PA catalyzed by IL-UM microgels.

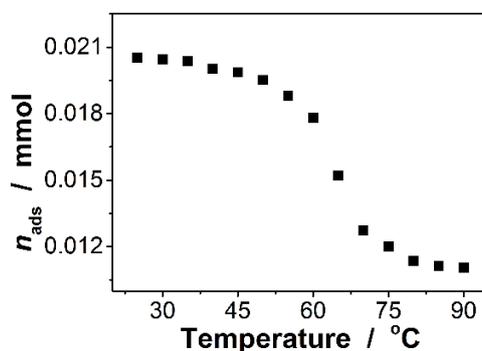


Fig. S18 Temperature-deepened n_{ads} values for the CSM microgels (40.0 mg) in a mixture of 1,2-epoxybutane (0.35 mL) and DMAc (1.0 mL) under the atmospheric pressure (1 atm CO_2). We measured the reduce amount n_{red} of CO_2 by GC after reacting for the first 10 min, which subtracted the reacted portion (calculated from the yield of the product 4-ethyl-1,3-dioxolan-2-one) to yield the adsorption amount n_{ads} .

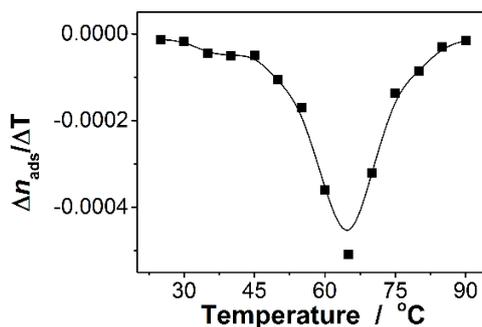


Fig. S19 Typical $\Delta n_{\text{ads}} / \Delta T - T$ plot of the CSM microgels.

Table S1. Additional results on the model cycloaddition reaction over CSM microgels.

entry	reaction conditions						yield						
	DMAC (mL)	1,2-epoxybutane (mL)	p(CO ₂) (atm)	CSM (mg)	temperature (°C)	time (h)							
1	1.00	0.35	1	40.0	90.0	24	89						
						12	64						
						3	38						
						0.5	13						
2^a	1.00	0.35	1	40.0	90.0	24	26						
3^b	1.00	0.35	1	40.0	90.0	24	6						
4^c	1.00	0.35	1	40.0	90.0	24	89						
5^d	1.00	0.35	1	40.0	90.0	24	88						
6^e	1.00	0.35	1	40.0	90.0	24	89						
7^f	1.00	0.35	1	40.0	90.0	24	86						
8^g	1.00	0.35	1	40.0	90.0	24	83						
9^h	1.00	0.35	1	40.0	90.0	24	71						
10ⁱ	1.00	0.35	1	40.0	90.0	24	30						
11^j	1.00	0.35	1	40.0	90.0	24	47						
						12	1.00	0.35	1	40.0	50.0	24	54
						12	34						
13	1.00	0.35	1	40.0	75.0	3	17						
						24	53						
						12	35						
						3	18						

^a By adding polyTPSS (containing 8.3×10^{-2} mmol phosphonium, with the amount close to that on 40.0 mg CSM microgels)

^b By adding polyVIM (containing 2.1×10^{-2} mmol imidazole, with the amount close to that on 40.0 mg CSM microgels)

^c Additionally adding water of 5.0 μ L in the solvent.

^d Additionally adding water of 10.0 μ L in the solvent.

^e Additionally adding water of 25.0 μ L in the solvent.

^f Additionally adding water of 50.0 μ L in the solvent.

^g Additionally adding water of 100.0 μ L in the solvent.

^h Additionally adding water of 200.0 μ L in the solvent.

ⁱ By adding TPSS (containing 8.3×10^{-2} mmol phosphonium, with the amount close to that on 40.0 mg CSM microgels)

^j By adding Bu₄PBr (containing 8.3×10^{-2} mmol phosphonium, with the amount close to that on 40.0 mg CSM microgels)