

Electronic Supplementary Information (ESI)

Synthesis and characterization of ureido-derivatized UCST-type poly(ionic liquid) microgels

Shoumin Chen,^{‡a} Aiping Chang,^{‡a} Xuezhen Lin,^a Zhenghao Zhai,^a Fan Lu,^a Shiming Zhou,^b Haoxin Guo,^a
and Weitai Wu^{*a}

^a State Key Laboratory for Physical Chemistry of Solid Surfaces, Collaborative Innovation Center of Chemistry for Energy Materials, The Key Laboratory for Chemical Biology of Fujian Province, and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, Fujian 361005, China. E-mail: wuwtxmu@xmu.edu.cn

^b Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei 230026, Anhui, China.

SI 1. Experimental procedures

1.1. Materials

All chemicals were purchased from Aldrich. Poly(ethylene glycol) dimethacrylate (PEGDMA, $M_n \approx 550$ g/mol) and propargyl acrylate (PGA) were purified with neutral Al_2O_3 . Sodium dodecyl sulfate (SDS), ammonium persulfate (APS), 3-chloro-1-propylamine hydrochloride, 2-azido-1-ethylamine, 2-azido-1-ethylcarbamide, NaN_3 , KOH, $MgSO_4$, $CuSO_4 \cdot 5H_2O$, KOCN, methyl iodide (CH_3I), ascorbic acid, methanol, ethanol, trifluoromethanesulfonic acid (HSO_3CF_3), palmitic acid (PA), diethyl ether, dimethylsulfoxide (DMSO), dimethylformamide (DMF), ethylene diamine tetraacetic acid (EDTA), and the certified reference standard dodecane were used as received without further purification. 3-azido propylamine and 3-azido-1-propylcarbamide were self-synthesized according to the methods reported in literature (see ESI). The water used in all experiments was of Millipore Milli-Q grade.

1.2. Synthesis of 3-azido propylamine

NaN_3 (7.500 g) was added to the solution of 3-chloro-1-propylamine hydrochloride (5.000 g) in water (100.0 mL), and the reaction mixture was heated to 80.0 °C for 15 h. The solution was

basified with KOH (ca. 22 g) and extracted with diethyl ether. The organic layer was dried over MgSO₄, filtered, and concentrated to give a volatile colorless oil (3.240 g, 85 % yield).

1.3. Synthesis of 3-azido-1-propylcarbamide

The concentrated HCl (1.1 mL) was added to 2-azido-1-ethylamine (1.000 g) at 0 °C, and the mixture was dissolved in hot ethanol (5.0 mL). This solution was added to a solution of KOCN (1.249 g) dissolved in distilled water (5.0 mL), and the reaction mixture was stirred at room temperature overnight. Most of the KCl was precipitated by the addition of ethanol (ca. 50 mL) and was filtered off. The filtrate was then concentrated under reduced pressure to give a pale yellow waxy solid (1.130 g, 79 % yield).

1.4. Synthesis of homogeneous ILs

Typically, PGA (containing ca. 8.0 mmol of alkynyl) was dispersed into DMSO (10.0 mL), and then the solutions of 2-azido-1-ethylcarbamide (3.436 g) in DMSO (10.0 mL) and ascorbic acid (0.352 g) in water (2.0 mL) were added. After N₂ bubbling for 15 min, CuSO₄·5H₂O (0.4 mmol) aqueous solution (1.0 mL) was added to initiate click reaction. The reaction was allowed to run for 5 days at 60 °C. The product mixture was purified by silica gel column chromatography. For quaternization, this purified product (containing ca. 8.0 mmol of triazole) were dispersed into DMF (20.0 mL). Then CH₃I (40.0 mmol; 2.5 mL) was added into microgel dispersion, and the reaction was allowed to proceed for 48 h at 45.0 °C in dark. The quaternized sample was also purified by silica gel column chromatography, and the purified product (containing ca. 8 mmol of iodide) was treated with a solution containing anhydrous DMF (20.0 mL) and HSO₃CF₃ (8.0 mmol; 703.0 μL) for 48 h at 45 °C, to yield the *homogeneous ILs* of structures similar to the IL-UM (containing ⁻SO₃CF₃ and -NH₃⁺).

1.5. 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/methanol mixtures

and the refractive index increments (dn/dC) of microgels in different water/methanol 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 ($\langle D_h \rangle$) 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.

1.6. Uptake of the compounds in the equilibrated microgels

The composition of methanol and water of the uptaken medium in the equilibrated microgels were determined at a set constant temperature of 20.0 $^{\circ}\text{C}$, 40.0 $^{\circ}\text{C}$, and 60.0 $^{\circ}\text{C}$, respectively. Typically, the dilute isotope solutions (9.25×10^4 Bq/mL $^3\text{H}_2\text{O}$ in water, and 1.30×10^4 Bq/mL $^{14}\text{CH}_3\text{OH}$ in methanol) were prepared and then mixed in preset ratios as the donor solutions for partition studies. Radioactivities of the donor solutions of known water/methanol mol ratios were measured by 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 methanol (20.0 mL) to elute radiolabeled methanol and water in microgels. After 48 h, the radioactivities of solvents in vials were measured, and the uptake methanol and water in the equilibrated microgels was calculated from the model that was constructed by using water/methanol mixtures

of known mol ratios. The uptake mol fraction (X_{uptake}) of methanol is defined as a methanol mol fraction in total solvents uptaken in the equilibrated microgels.

Adsorption of palmitic acid and methyl palmitate on the equilibrated microgels in the presence of methanol were determined at a set constant temperature (at 60.0 °C oil bath) by the same method, but with the donor solutions being prepared by mixing each compound with the dilute isotope solution of $^{14}\text{CH}_3\text{OH}$ in methanol.

1.7. 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.

SI 2. Figures.

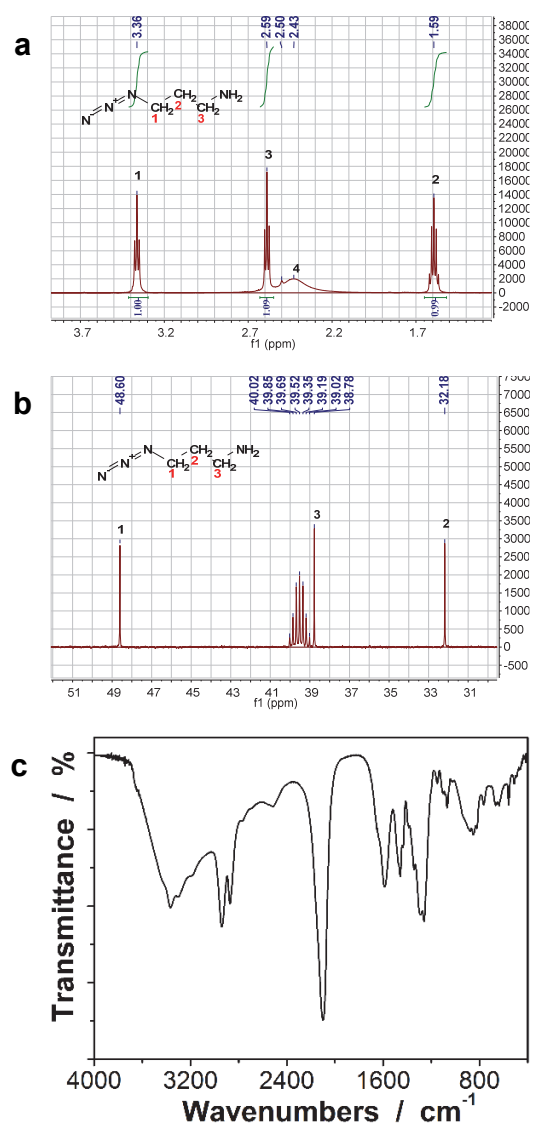


Fig. S1 (a) ¹H NMR, (b) ¹³C NMR and (c) IR spectra of 3-azido propylamine in DMSO-*d*₆.

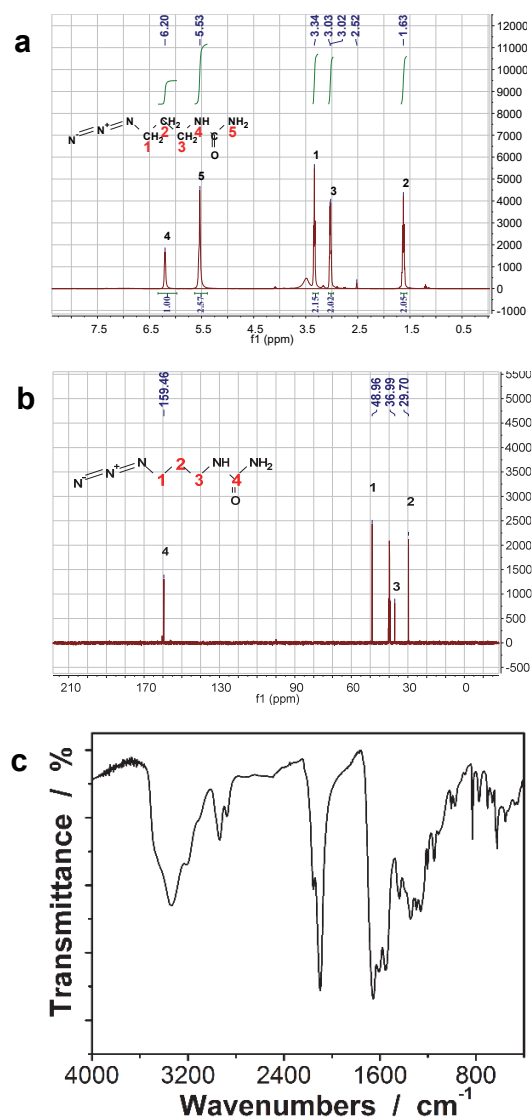


Fig. S2 (a) ^1H NMR, (b) ^{13}C NMR and (c) IR spectra of 3-azido-1-propylcarbamide in $\text{DMSO-}d_6$.

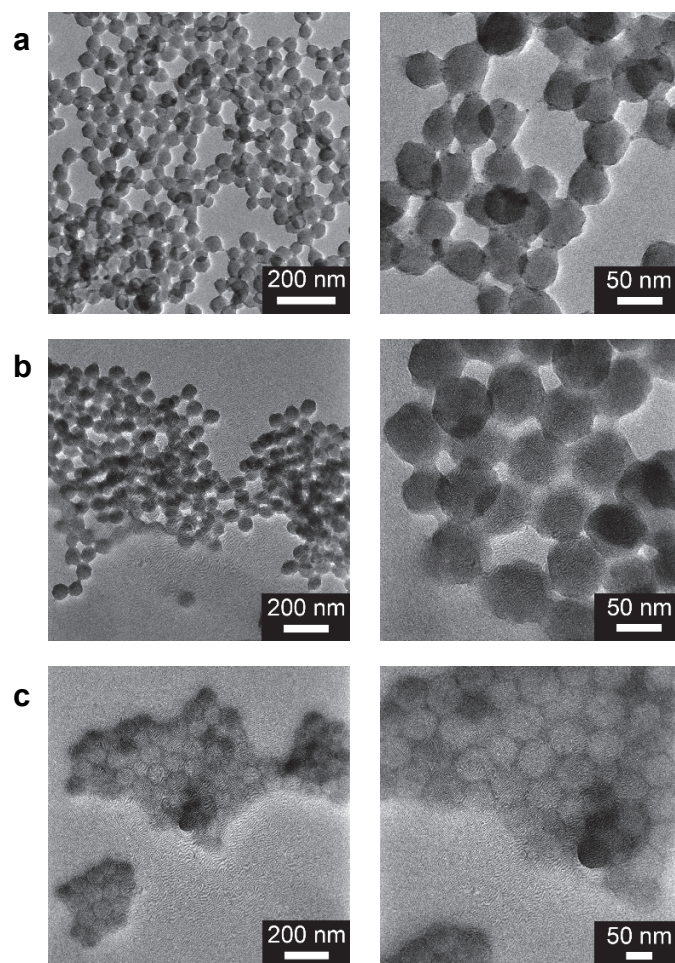


Fig. S3 TEM images of (a) the alkynyl-pendent microgels (microgel-1), (b) those after further click coupling reaction of alkynyl pendants with 3-azido-1-propylcarbamide (microgel-2), and (c) quaternary ammonization of triazole rings with methyl iodide (microgel-3).

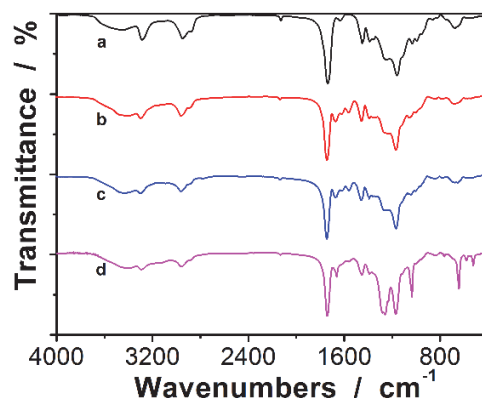


Fig. S4 FTIR spectra of (a) the alkynyl-pendent microgels (microgel-1), (b) those after further click coupling reaction of alkynyl pendants with 3-azido-1-propylcarbamide (microgel-2), (c) quaternary ammonization of triazole rings with methyl iodide (microgel-3), and (d) post synthetic modification via anion-exchange treatment (IL-UM microgels).

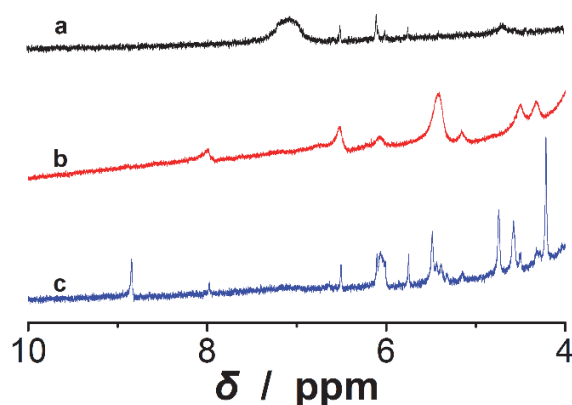


Fig. S5 ^1H NMR spectra of (a) the alkynyl-pendent microgels (microgel-1), (b) those after further click coupling reaction of alkynyl pendants with 3-azido-1-propylcarbamide (microgel-2), and (c) quaternary ammonization of triazole rings with methyl iodide (microgel-3), in $\text{DMSO-}d_6$.

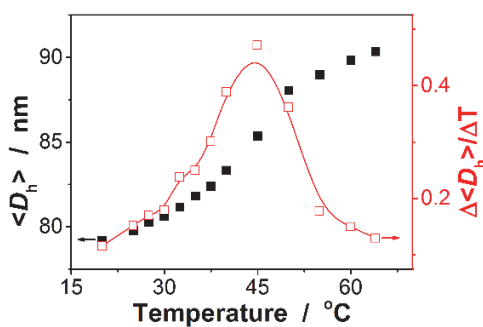


Fig. S6 Typical $\langle D_h \rangle - T$ and $\Delta \langle D_h \rangle / \Delta T - T$ plots of the IL-UM in water.

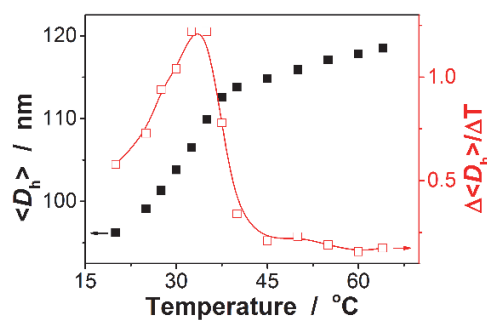


Fig. S7 Typical $\langle D_h \rangle$ - T and $\Delta \langle D_h \rangle / \Delta T$ - T plots of the IL-UM in methanol.

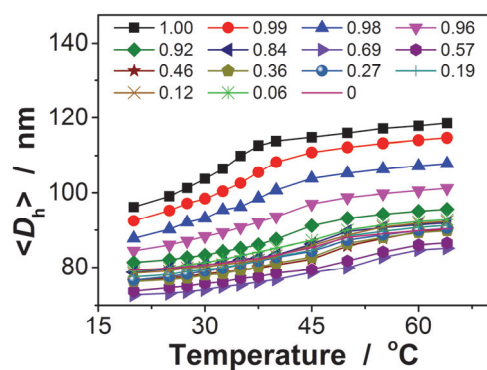


Fig. S8 Temperature-dependent $\langle D_h \rangle$ of IL-UM microgels dispersed in the mixture of water/methanol of different mol fractions of methanol (X_{methanol}). DLS measurements were made on 10.0 $\mu\text{g/mL}$ microgel dispersions.

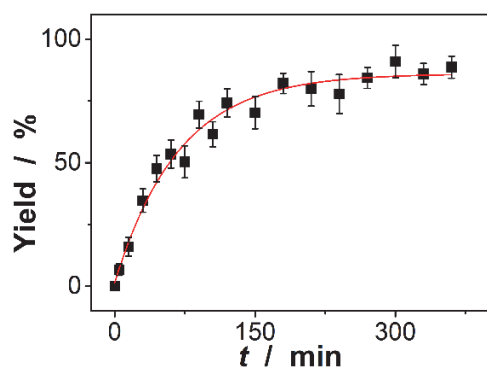


Fig. S9 Time trace of yield of FAME during the model reactions catalyzed by otherwise prepared homogeneous ILs of similar structures (containing 3.7×10^{-3} mmol $-\text{SO}_3\text{CF}_3$ and 2.2×10^{-3} mmol $-\text{NH}_3^+$, with the amounts close to those on 5.0 mg IL-UM microgels) at 60.0 $^\circ\text{C}$. The line is an exponential fit.

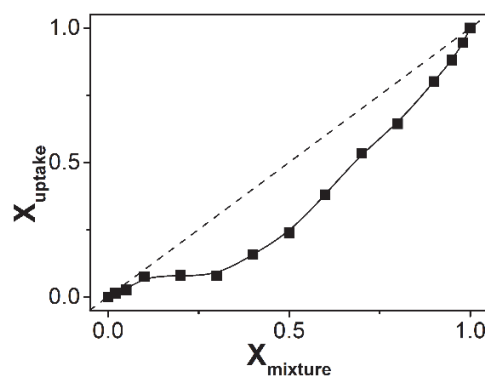


Fig. S10 A comparison of the uptaken mol fraction of methyl palmitate in the equilibrated IL-UM microgels in the presence of methanol at 60.0 °C, and the corresponding mol fractions in the initial bath mixtures.

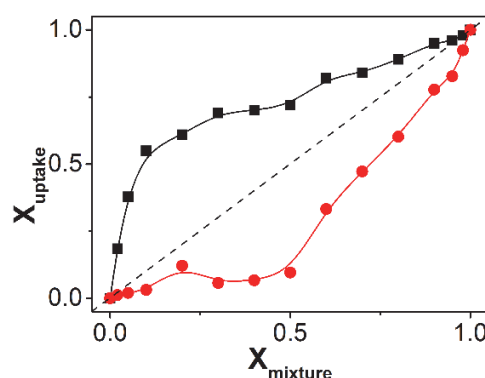


Fig. S11 Because of the difficulty in measuring the uptaken mol fraction of PA on IL-UM microgels in the presence of methanol, the uptaken mol fraction of PA (■) and methyl palmitate (●), respectively, on the equilibrated microgels (after quaternary ammonization of triazole rings with methyl iodide, i.e., without post synthetic modification via anion-exchange treatment; microgel-3) in the presence of methanol at 60.0 °C was measured and compared to the corresponding mol fractions in the initial bath mixtures, which provides an indirect but helpful information on the adsorption of these compounds on IL-UM microgels.

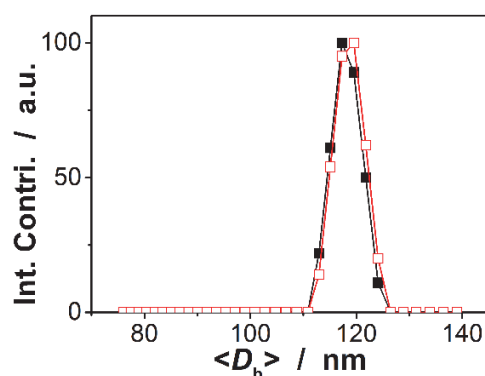


Fig. S12 DLS size distribution for IL-UM microgels before (■) and after (●) six cycles' of use for the model esterification reaction of PA. DLS measurements were made in methanol at 60.0 °C.

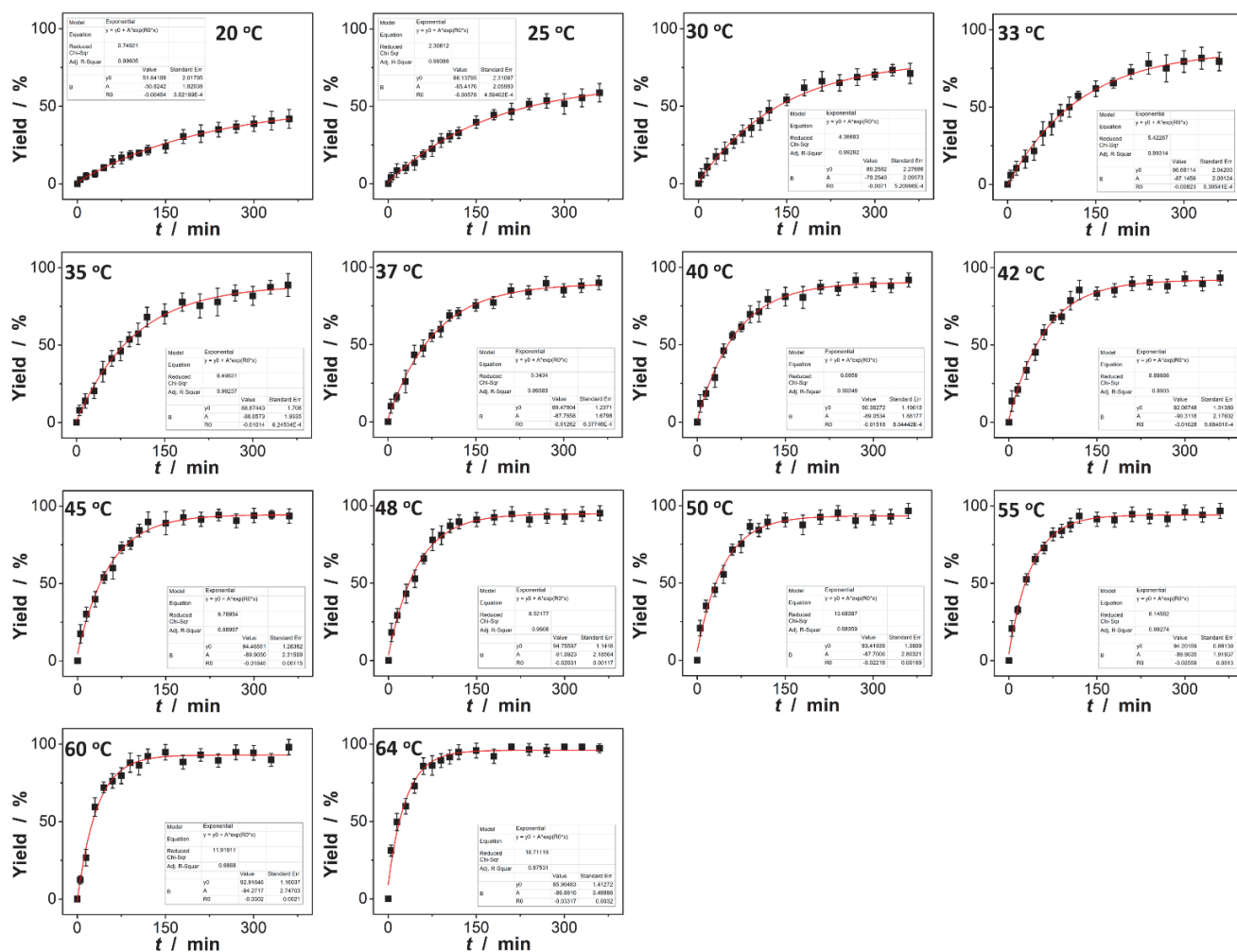


Fig. S13 Time trace of the yield of FAME during the model esterification reaction of PA catalyzed by IL-UM microgels at different temperatures. Results are mean $\pm$ SD ($n = 3$). The lines are exponential fits.

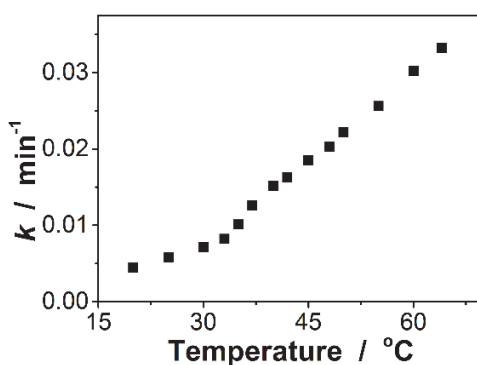


Fig. S14 Temperature-deepened k values for the model esterification reaction of PA catalyzed by IL-UM microgels.

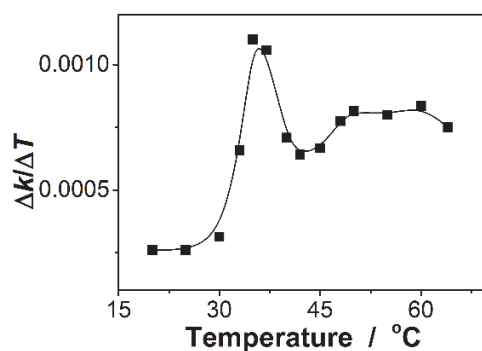


Fig. S15 A $\Delta k/\Delta T$ - T plot, showing the k change as a function of temperature for the model esterification reaction of PA catalyzed by IL-UM microgels.

Table S1. Additional results on the model esterification reaction over IL-UM microgels.

entry	reaction conditions					yield of FAME
	methanol / water (mL / mL)	PA (mg)	IL-UM (mg)	temperature (°C)	time (h)	
1	1.00 / 0.00	128.2	0.5	60.0	24	> 99
					6	98
					3	89
					1	76
2^a	1.00 / 0.00	128.2	0.5	60.0	24	95
3^b	1.00 / 0.00	128.2	0.5	60.0	24	91
4^c	1.00 / 0.00	128.2	0.5	60.0	24	89
5^d	1.00 / 0.00	128.2	0.5	60.0	24	81
6^e	1.00 / 0.00	128.2	0.5	60.0	6	88
					3	82
					1	53
7	0.95 / 0.05	128.2	0.5	60.0	24	89
8	0.90 / 0.10	128.2	0.5	60.0	24	76
9	0.85 / 0.15	128.2	0.5	60.0	24	64
10	0.80 / 0.20	128.2	0.5	60.0	24	18

^a By adding otherwise prepared microgels of similar structures but of lower 1,2,3-triazole/1,2,3-triazolium molar ratio of ca. 1.0:2.3

^b By adding otherwise prepared microgels of similar structures but of lower 1,2,3-triazole/1,2,3-triazolium molar ratio of ca. 1.0:2.5

^c By adding otherwise prepared microgels of similar structures but of lower 1,2,3-triazole/1,2,3-triazolium molar ratio of ca. 1.0:2.9

^d By adding otherwise prepared microgels of similar structures but of lower 1,2,3-triazole/1,2,3-triazolium molar ratio of ca. 1.0:3.2

^e By adding otherwise prepared homogeneous ILs (see above) of similar structures (containing 3.7×10^{-3} mmol $^{-}\text{SO}_3\text{CF}_3$ and 2.2×10^{-3} mmol $^{-}\text{NH}_3^{+}$, with the amounts close to those on 5.0 mg IL-UM microgels).