Thermo- and pH-Responsive Nanogel Particles Bearing Secondary Amine Functionalities for Reversible Carbon Dioxide Capture and Release

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Supporting Information

ABSTRACT: We report the synthesis of temperature- and pH-responsive nanogel particles (NPs) consisting of *N*-isopropylacrylamide (NIPAM) and *N*-(2,2,6,6-tetramethyl-piperidin-4-yl)methacrylamide (TMPMA). NPs can reversibly capture and release carbon dioxide via temperature-induced volume phase transition and changes in pH. These stimuli-responsive particles contain sterically hindered secondary amine functionalities and exhibit a volume phase transition temperature (VPTT) in aqueous solution. The fully reversible VPTT behavior involves a precise shrinkage to 40% of the



initial particle size along with a large change in pH from 10.25 to 7.65 upon increasing temperature. We could reversibly release 35 mL (1.4 mmol) of CO_2 per gram of polymer in very short heating times, thereby significantly increasing the amount of CO_2 with respect to the regeneration time. This behavior could be repeated for various cycles at moderate temperatures (85 °C).

INTRODUCTION

The carbon dioxide concentration in the atmosphere is steadily increasing because of industrial processes and has reached over 400 ppm.^{1,2} The growing CO_2 content in the atmosphere is widely accepted to be a major contributor to climate change and a huge challenge to mankind in the future.¹ Carbon capture and storage (CCS) is considered as one of the main options to reduce the CO₂ concentration in the athmosphere.³ Within CCS, postcombustion CO₂ separation is one of the most promising techniques because it can be applied to already existing fossil fuel power plants.4,5 Amine solutions such as monoethanolamine are mostly used in these wet-scrubbing processes; however, because of carbamate formation, the regeneration of the solvents is energy-consuming and decreases the overall power plant efficiency by at least 10%.⁶ Improvements could be made using mixtures of primary and tertiary amines or hindered amines.^{4,7} To reduce cost and design this process more economically, novel CO2 capture materials are required to decrease the temperature during sorbent regeneration. Various materials such as metal-organic frameworks,^{8,9} solid and porous polymer amines,^{10,11} ionic liquids,^{12,13} and stimuli-responsive polymers¹⁴ have been investigated for the low-temperature solvent regeneration of CO₂.

In particular, stimuli-responsive polymers have gained considerable interest in recent years,^{15–17} with CO₂-responsive polymers¹⁸ and hydrogels leading the way. Herein, CO₂ can act as a "green" trigger that switches polymer properties¹⁹ or capture CO₂ directly from air or exhaust gas.^{14,20,21} CO₂-responsive functionalities in these polymers can be categorized into amidine,^{22–24} amine,^{14,25,26} and carboxyl^{27,28} groups. Zhao

et al. discovered that LCST of poly(N,N-dimethylaminoethyl methacrylate) could be reversibly tuned by CO_2 and argon.²¹ Furthermore, they demonstrated that hydrogels can undergo a reversible volume transition upon treatment with CO2.27 Additional reports using volume transition as a reversible target capture-and-release mechanism have been published.^{29,30} Lyon and co-workers reported the thermally regulated uptake and release of the chemotherapeutic drug doxorubicin from microgel thin films by copolymerizing N-isopropylacrylamide (NIPAM) with acrylic acid (AAc) into microgel structures.³¹ Yu Hoshino adapted this approach to synthesize microgel particles (GPs) with NIPAM and the tertiary amine monomer *N*-[3-(dimethylamino)propyl]methacrylamide (DMAPM) and reported the reversible capture and release of CO₂ through a temperature-induced phase transition.²⁰ Hoshino's group then refined their system to form thermoresponsive microgel films to improve the capacity of CO₂ capture in wet environments.²¹ Huang combined the thermo- and CO2-responsive functionality in one monomer and demonstrated the ability to tune LCST by adjusting pH.³² Recently, we reported temperatureand CO_2 -responsive polyethylenimine polymers that can reversibly absorb and desorb CO_2 .¹⁴ Herein, branched polyethylenimine was acylated with butyric anhydride to introduce thermoresponsive behavior (LCST), and a significant increase in the desorption CO₂ flow was observed through the phase separation of the acylated polyethylenimine.

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Figure 1. (A) Reaction scheme for the synthesis of TMPMA. (B) Synthesis of nanogel latex particles via precipitation polymerization in H_2O at 70 °C for 3 h using monomers, cross-linker (BIS), and surfactant (CTABr). (C) SEM and (D) TEM images of dried NPs from an aqueous solution showing NP sizes based on DLS measurements along with a homogeneous size distribution. (E) Catalytic cycle of carbon dioxide capture and release through temperature-induced volume transition for P(NIPAM-*co*-TMPMA) nanogel particles (NPs).

RESULTS AND DISCUSSION

Here we report the synthesis of novel secondary aminecontaining nanogel particles (NPs) for the capture and release of CO_2 . We provide detailed information on the mechanism of the volume phase transition-induced release of CO_2 and present high desorption amounts in relation to regeneration times.

We synthesized the monomer *N*-(2,2,6,6-tetramethylpiperidin-4-yl)methacrylamide (TMPMA), which contains a sterically hindered secondary amine. This monomer was prepared following an adapted literature procedure³³ in which methacryloyl chloride was reacted with 4-amino-2,2,6,6tetramethylpiperidine, forming the corresponding methacrylamide (Figure 1A). This amine was chosen because of its higher basicity than the respective tertiary amines because tertiary amines are known to have significantly lower uptake kinetics for CO₂ than secondary or even primary amines.^{34,35}

Whereas primary and secondary amines react to form carbamates in the presence of CO_2 , tertiary amines follow a bicarbonate mechanism (Scheme 1).³⁴ To combine the positive effects of the higher basicity and the formation of bicarbonate upon reaction with CO_2 , TMPMA was synthesized because sterically hindered amines (e.g., 2-amino-2-methyl-1-propanol, AMP) are known to form bicarbonate instead of carbamates with CO_2 .³⁶ In our approach, following the bicarbonate route to absorb CO_2 into the liquid phase is crucial because bicarbonate decomposes to water and CO_2 upon the addition of acid, whereas carbamates do not. To lower the temperature for regeneration, which is the most energy-consuming part of the process, temperature- and pH-responsive NPs containing different contents of TMPMA (0%, 5%, 10%, 20%, and 30%) and *N*-isopropylacrylamide (NIPAM) were synthesized. With

Scheme 1. Reaction Pathways for CO_2 in Water and in the Presence of Primary, Secondary, or Tertiary Amines (Reproduced with Permission from ref 34)



the addition of 2% of N,N'-methylenebis(acrylamide) (BIS) as a cross-linker along with a surfactant, the stimuli-responsive NPs were synthesized via precipitation polymerization in water (Figure 1B). The pH responsiveness of NPs enables them to reversibly produce protons upon mild increases in temperature.

In summary, CO_2 is absorbed by the sterically hindered secondary amines in NPs, forming bicarbonate and the corresponding ammonium salt. Heating the system above its volume phase transition temperature (VPTT) an entropically induced contraction occurs in which NPs decrease in size. The shrinkage leaves NPs in a less-hydrated state and releases protons from the ammonium salt, forming the corresponding amine. The released protons conclusively react with bicarbonate to form carbonic acid, which then decomposes to water and CO_2 (Figure 1E).

To demonstrate that the absorption of CO_2 follows the bicarbonate mechanism, a sample of NPs was charged with CO_2 , and ¹³C NMR spectra of this sample, NPs without CO_2 , and a sodium bicarbonate solution were measured. The NMR

spectra provide clear evidence of bicarbonate, and the lack of any shift in the carbamate signals confirms the suggested mechanism (Figure S3).

To determine VPTT of NPs, the diameter of a sample was measured with increasing temperature until no further particle contraction could be observed. The inflection point of the curve marks VPTT. The particles continued to shrink until the temperature reached 85 $^{\circ}$ C; therefore, this temperature was chosen for regeneration experiments because higher temperatures have no effect on the volume phase transition of NPs.



Figure 2. Determination of the volume phase transition temperature (VPTT) of NP30s.

The sizes of NPs in aqueous solution were determined via dynamic light scattering (DLS). The particle diameter increases from 134 nm for pure PNIPAM particles (NP0s) to 212 nm for particles containing 5% of TMPMA (NP5s). The diameter then reaches a relatively constant size distribution of around 400–425 nm for the particles containing 10%–30% TMPMA (NP10s, NP20s, and NP30s). The size distribution and diameter of NP30s were additionally measured using SEM/TEM. These values were in good accordance with those determined by DLS and indicate a homogeneous particle distribution (Figures S4–S6).

VPTT was studied over four cycles using DLS measurements (Figure 3). The hydrodynamic diameter was continuously recorded over the heating (85 °C) and cooling (30 °C) loops. The initial hydrodynamic diameter of NP30s was 425 nm. The diameter then shrinks steadily to a size of around 180 nm upon heating to 85 °C. In cycles 2-4, the NP diameter oscillates between 340 and 135 nm during the heating/cooling loops and corresponds over all cycles to a value of 40% in comparison with the expanded state. Upon leaving the sample for a few hours after measurement, the diameter returns to 425 nm. The measurement results demonstrate a fully reversible process of NP swelling and shrinking upon temperature changes and demonstrate the extremely precise NP behavior over various cycles (Figure 3). Bergbreiter et al. previously synthesized and reported the thermo- and pH-responsive behavior of a TMPMA analogue monomer copolymerized to statistically linear polymers with NIPAM.33 We synthesized novel TMPMA-containing NPs that exhibit even stronger thermo-



Figure 3. Heating of a nanogel solution (NP30s) induces a volume phase transition that reversibly alters NP diameter to 40% of the original hydrodynamic diameter.

and pH-responsive properties (Figure 4), which are most likely due to an ion-imprinted polymerization process.³⁷



Figure 4. pH (blue circles) of an NP30s solution reversibly changes between 10.25 and 7.65 upon heating and cooling.

The pH of an NP30s solution was continuously recorded (blue circles) and plotted against temperature. Upon heating and cooling the solution for 12 min each, pH was reversibly changed from 10.25 to 7.65. At room temperature, NPs are in their expanded state, and the secondary amines act as a base. Heating the system above its volume phase transition temperature induces an entropically driven contraction of the PNIPAM particles.^{38,39} For cross-linked gels such as NPs in this study, this leads to swelling and shrinking behavior. In this collapsed state, NPs are in less-hydrated, and amphoteric groups such as the ammonium salts undergo a significant change in basicity and release their protons to form the corresponding amines. This leads to a general neutralization of the NP solution, and it reverts to its basic state after cooling (Figure 4).

Even more interesting is the shapes of the titration curves. While the curves of both TMPMA and NPs at room temperature exhibit shapes of a standard weak base/strong acid, the shape of the titration curve of NPs at elevated

10,5 10,5 initial pH 100 L 100 initial pH 10.0 10.0 A on 9.5 9.5 80 9.0 9.0 temperature [°C] ΰ 8,5 8,5 emperature Hd Hd 8,0 8,0 60 60 7,5 7,5 50 50 7,0 7,0 40 40 6,5 6.5 30 30 6,0 6.0 20 20 140 40 60 100 20 40 80 100 120 20 80 60 time [min] time [min]

Figure 5. (left) CO_2 release measured through pH recovery of a CO_2 -saturated solution of NP30s via temperature swing. pH could be raised to 10.0 after six heating cycles. (right) CO_2 release measured through pH recovery of NP30s via temperature swing and pressure swing (bubbling argon, red boxes, 2 × 10 min). pH could be raised to value over 10.0 after only two heating cycles.

temperatures is clearly different. Although there is no slight decrease upon added HCl, all acid is buffered at neutral pH until the equivalence point is reached (Figure 6, \bigcirc). This is because of the fact that at elevated temperatures, nearly all of the amines are in nonprotonated states being in their less-hydrated, contracted state. By adding acid, the amines are then protonated, and pH remains constant at around 7. All amines in NPs are being protonated until the equivalence point is reached.

All titration curves show only one equivalence point, and no difference on accessibility of amine functionality. Based on the amount of titrated NP30s and the equivalence point, the amine content was determined to be 22.5% (compared with 30% in TMPMA) during the polymerization process. This could indicate that the polymerization only led to 22.5% TMPMA and an increased incorporation of NIPAM. However, a more probable explanation is that polymerization led to the desired ratio of 30/70, but not all amines were accessible on the inside of the nanogel particles.

After CO₂ saturation, pH of the solution drops to around 5.70 (Figure 5). The release of CO₂ was indirectly measured by recording pH. The solution was regenerated following several heating/cooling cycles, while pH increased in a linear fashion (Figure 5, left) to approximately 10. When we performed the same heating/cooling cycles while also bubbling argon during heating (Figure 5, right, red boxes), pH rose above 10 in just two cycles. However, bubbling argon into the CO₂-saturated NPs solution at room temperature for 100 min resulted in a pH value of just 8.5 (Figure S7). Thus, even purging the solution over a long time with argon at room temperature could not release all of the CO₂; however, CO₂ rapidly desorbs at elevated temperature.

We then constructed titration curves to determine the pK_A values for the TMPMA monomer and the corresponding NPs at room temperature as well as at 85 °C. The pK_A values were then estimated from the half volumes of the equivalence points (Figures S8–S15). The pK_A values of monomer TMPMA were determined to be 9.72 at room temperature and 8.37 at 85 °C, corresponding to ΔpK_A of 1.35. The calculated pK_A values of NP30s at room temperature and 85 °C were 8.81 and 6.72, respectively (Figure 6), corresponding to a large ΔpK_A of 1.89.

Both TMPMA and NPs have a significant $\Delta p K_A$, although it is notably higher for the nanogel particles ($\Delta \Delta p K_A = 0.54$).

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Figure 6. (•) Titration curve of NP30s at room temperature, resulting in pK_A of 8.61. (O) Titration curve of NP30s at 85 °C, resulting in pK_A of 6.72. (•) Titration curve of TMPMA monomer at room temperature, resulting in pK_A of 9.72. (□) Titration curve of TMPMA at 85 °C, resulting in pK_A of 8.37.

As expected from the previous measurements, NPs exhibited a large difference in pK_A of nearly two units, and the difference in basicity is stronger in the contracted NP state than in the monomer. The titration curves show only one equivalence point, whereas Hoshino et al. reported two-stage titration curves indicative of different amine environments in their GPs.²⁰ Interestingly, this effect seems to increase with increasing temperature.

To quantify the amounts of released CO_2 , we used a microGC setup. The CO_2 -saturated sample was placed in a calibrated ~200 mL Schlenk tube, which was then closed with a rubber septum. Samples (50 μ L) were drawn from the gaseous

volume above the solution at 0 min and after each heating cycle.

After only two 15 min heating cycles, the CO_2 content in the gaseous phase was nearly constant (32 mL/g), and it only increased in small amounts during the next three cycles (35 mL/g; Figure 7, blue). In comparison, a sample of NIPAM and



Figure 7. (blue) Amount of CO_2 released from NP30s (170 mg polymer, 1.4 mmol g⁻¹) as a result of temperature change and measured via microGC in the gas volume above the solution. (black) Measured CO_2 volume from an equivalent mixture of TMPMA/NIPAM monomers in water. (inset) Reversible capture and release of carbon dioxide over various cycles.

TMPMA with the same concentration was saturated with CO_2 and identically desorbed. The released CO_2 amounts were significantly lower for the monomers (9 mL) because no VPTT and no subsequent proton release produced CO_2 (Figure 7, black).

Pure water showed no relevant CO_2 absorption or desorption. The complete desorption amounts and relevant data for the NPs can be found in Table 1. As mentioned before, the CO_2 content after two 15 min heating cycles is only increasing in small steps, resulting in 35 mL (1.4 mmol) of CO_2 per gram of polymer (Table 2). This value is significantly higher than that we achieved previously and equivalent to that reported in the literature on stimuli-responsive polymers for CO_2 capture in aqueous solution (Table 2).

 Table 2. Desorption Amounts, Amine Contents, and

 Regeneration Temperatures

absorb	$\begin{array}{c} \text{desorbed } \text{CO}_2 \\ [\text{mL/g}] \end{array}$	desorbed CO ₂ [mmol/g]	amine content [%]	reg temp [°C]
NP30s	~35	~1.4	23	85
b-PEI ¹⁴	19	0.8		95
GP30s ²¹	~38	~1.7	30	75

CONCLUSION

In summary, we present an approach to synthesize nanogel particles via the precipitation polymerization of NIPAM and TMPMA. Titration experiments show that accessibility ranges from 75% to 92% depending on the amine content. The sterically hindered secondary amines in TMPMA follow a bicarbonate mechanism upon treatment with CO₂, as demonstrated by ¹³C NMR experiments. The sizes of the nanogel particles were determined using DLS measurements. The particles showed almost no swelling behavior upon CO₂ treatment. We demonstrated that the volume phase transition temperature and the resulting phase transition of the nanogel particles (NPs) are crucial for a fast and complete regeneration of the bicarbonate solution. Herein, protons are released because of the phase transition of NPs, forming carbonic acid with bicarbonate, which then decomposes to CO_2 . The regeneration temperature (85 °C) was significantly decreased in comparison with standard amine processes (>120 °C). NPs show greater CO₂ desorption (92%-99%) than the free monomers (21%) or pure water. In terms of desorption, the amount of desorbed CO₂ reached 35 mL or 1.4 mmol per gram of polymer.

EXPERIMENTAL SECTION

General. All reactions were conducted under an argon atmosphere using standard Schlenk or glovebox techniques. All glassware used for water-sensitive reactions was heat-dried under vacuum prior to use. Unless otherwise stated, all chemicals were purchased from Sigma-Aldrich or ABCR and used as received. Chloroform, 4-amino-2,2,6,6tetramethylpiperidine, and triethylamine were dried over calcium hydride and distilled prior to use. The water used in the experiments was purified using a Merck Millipore Direct-Q system and degassed prior to use. 2,2'-Azobis(isobutyramidine) dihydrochloride (AAPH) was recrystallized twice from water, and *N*-isopropylacrylamide (NIPAM) was recrystallized twice from a 10:1 mixture of hexanes and toluene. ZelluTrans dialysis tubes with MWCOs of 12–14 000 from Carl Roth were used for the purification of nanogel particles.

NMR spectra were recorded on a Bruker AVIII-300. ¹H and ¹³C spectroscopic chemical shifts δ are reported in ppm relative to tetramethylsilane and calibrated to the residual proton and carbon

Table 1. Polymerization Data, Volume Phase Transition Temperature (VPTT), and Hydrodynamic Diameter of NPs with and without CO₂ along with Accessible Amine Content and Reversible CO₂ Capture

absorbent	TMPMA [mol %]	BIS [mol %]	yield ^b [%]	vol phase transition temp (VPTT) [°C]	hydrodynamic diam ^c [nm]	hydrodynamic diam CO ₂ saturated ^d [nm]	titrated amine content ^e [%]	reversible CO ₂ capture/ release per amine ^f [mol/mol]
TMPMA/NIPAM ^a	30 ^a	0					30	0.21
P(NIPAM)	0	2	91	34.0	134 ± 5	136 ± 7	0	
NP5s	5	2	88	47.0	212 ± 8	308 ± 29	4.6	~1.0
NP10s	10	2	85	66.0	354 ± 18	405 ± 23	8.9	~1.0
NP20s	20	2	76	72.0	415 ± 26	460 ± 32	16.3	0.95
NP30s	30	2	87	72.5	425 ± 38	464 ± 44	22.5	0.92

^{*a*}Identical monomer concentrations as in NP30s. ^{*b*}After dialysis and lyophilization. ^{*c*}Hydrodynamic diameter in degassed Millipore water. ^{*d*}Hydrodynamic diameter after CO₂ saturation for 1 h. ^{*e*}Titrated amine content in NPs compared with TMPMA content of the polymerization. ^{*f*}CO₂ capture and release in relation to titrated amine content. For all measurements, CO₂ uptake from water was subtracted.

signal of the deuterated solvent. Deuterated solvents were obtained from Sigma-Aldrich and used as received. Elemental analyses were conducted at the Laboratory for Microanalytics at the Institute of Inorganic Chemistry at the Technische Universität München. IR spectra were recorded on a Bruker Vertex 70 spectrometer with a Bruker Platinum ATR setup and an integrated MCT detector. Hydrodynamic diameters were measured on a Wyatt DynaPro NanoStar using regularization analysis for the time-dependent light intensity fluctuations. For the long-term hydrodynamic diameter measurements (VPTT), samples were subjected to an automatic temperature program in which the samples were heated in 2 K intervals from 30 to 85 °C and then cooled back to 30 °C. After reaching each temperature, the samples were equilibrated for 3 min before measuring 3×10 data points. The entire sequence was repeated four times. pH measurements were conducted with a Mettler-Toledo HA405-DPA-SC-S8/225 electrode, and data points were monitored with an HI2215 pH/ORP meter from HANNA instruments. High-resolution scanning electron microscopy (HR-SEM) was performed on a JEOL JSM-7500F instrument using an accelerating voltage between 0.5 and 1 kV for secondary electron observation. Samples were prepared on copper tape from a dilute aqueous solution. High-resolution transmission electron microscopy (TEM) was performed on a JEOL JEM100CX using an accelerating voltage of 100 kV. Samples were prepared from a dilute aqueous solution using a 2% uranyl acetate solution as the negative stain. The gaseous reaction products (CO₂) were determined by GC-TCD (Varian 490 GC). Gas samples (100 μ L) were drawn from the headspace above the solution and injected into the GC-TCD gas analyzer.

TMPMA Synthesis. 4-Amino-2,2,6,6-tetramethylpiperidine (20.0 g, 0.128 mol, 1.0 equiv) and triethylamine (14.2 g, 0.140 mol, 1.1 equiv) were dissolved in 300 mL of dry chloroform and cooled to 0 °C using an ice bath. Methacryloyl chloride (13.4 g, 0.128 mol, 1.0 equiv) in chloroform (15 mL) was added dropwise to the solution and stirred for 6 h at 0 °C and then allowed to warm to room temperature overnight. The reaction mixture was washed with bicarbonate solution $(3 \times 25 \text{ mL})$ followed by brine $(2 \times 25 \text{ mL})$ and dried over sodium sulfate. The combined organic phases were concentrated under reduced pressure, and the crude product was crystallized overnight. The crystals were filtrated, washed with pentane, and recrystallized from 2-propanol to obtain colorless crystals (22.4 g, 78%) of N-(2,2,6,6-tetramethylpiperidin-4-yl)methacrylamide (TMPMA). ¹H NMR (298 K, 300 MHz, CDCl₃): δ = 5.63 (m, 1H), 5.54 (br, 1H), 5.29 (m, 1H), 4.37-4.18 (m, 1H), 1.99-1.85 (m, 5H), 1.25 (d, J = 5.6 Hz, 6H), 1.12 (d, J = 6.2 Hz, 6H), 0.93 (t, J = 12.2 Hz, 2H). ¹³C NMR (298 K, 75 MHz, CDCl₃): δ = 167.7, 140.4, 119.3, 51.3, 45.3, 42.8, 35.0, 28.6, 18.8. EA: calculated: C 69.60, H 10.78, N 12.49; found: C 69.35, H 10.81, N 12.15. IR: 3282 (m), 2991 (s), 1674 (m), 1534 (s), 1221 (s), 928 (m).

Particle Synthesis. *N*-Isopropylacrylamide (2.31 g, 20.4 mmol, 0.68 equiv), TMPMA (2.02 g, 9.00 mmol, 0.30 equiv), and $N_{,}N'$ -methylenebis(acrylamide) (92 mg, 0.60 mmol, 0.02 equiv) were dissolved in 100 mL of water. Cetyltrimethylammonium bromide (74 mg, 0.20 mmol) was added as the surfactant, and the solution was degassed for 30 min at 70 °C. 2,2'-Azobis(isobutyramidine) dihydrochloride (AAPH; 70 mg) was dissolved in 2 mL of water, degassed, and added to the monomer mixture. The polymerization reaction was conducted for 3 h, and the reaction mixture was then cooled while being exposed to air. The reaction mixture was then dialyzed against water for 5 days, changing the water at least three times a day. The resulting solution was lyophilized, resulting in dried nanogel particles (3.76 g, 87%).

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macro-mol.5b01367.

NMR spectra of TMPMA and nanogel particles, SEM and TEM images, control experiments, and microGC chromatograms of released CO_2 (PDF)

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Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

AAPH, 2,2'-azobis(isobutyramidine) dihydrochloride; BIS, N,N'-methylenebis(acrylamide); CTABr, cetyltrimethylammonium bromide; DLS, dynamic light scattering; LCST, lower critical solution temperature; NPs, nanogel particles; TMPMA, N-(2,2,6,6-tetramethylpiperidin-4-yl)methacrylamide; VPTT, volume phase transition temperature.

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