A Systematic Synthetic Study of Polyelectrolyte Nanocapsules via Crystallized Miniemulsion Nanodroplets

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Synthesis of polyelectrolyte nanocapsules (NCs) by interfacial crosslinking of surfactant monolayers adsorbed on crystallized miniemulsion nanodroplets is systematically studied by using surfactants with varied lengths of hydrophobic *n*-alkyl tails. The results indicate that the *n*-alkyl tails of surfactants need to possess at least sixteen carbon atoms, in order to obtain stable surfactant monolayers for achieving well-defined NCs. The structural control of NCs via crystallized miniemulsion systems is discussed.

1. Introduction

With inner cavities that can be used for encapsulation and controlled release, polymeric nanocapsules (NCs) are an important class of nanomaterials with promising applications.[1-5] Among various approaches for the preparation of polymeric NCs, miniemulsion-based approaches via interfacial polymerization or crosslinking can be readily performed.[6-9] However, because surfactant molecules generally have low dynamic stability in emulsions (including miniemulsions and other types of emulsions) and their assemblies typically dissolve and rebuild themselves in timescales substantially shorter than template reactions, precise template synthesis of polymeric NCs via emulsions is highly challenging.[10-12] Previously we reported a novel synthetic method using crystallized miniemulsion nanodroplets as synthetic templates for the preparation of polyelectrolyte NCs.[13] As shown in the work, the dynamic stability of surfactant molecules was significantly enhanced by converting the liquid-liquid w/o interface to a liquid-solid one. As a result, on the surface of crystallized *n*-docosane (*n*-DS)-based nanodroplets dispersed in continuous water phase, the surfactant monolayers consisting of quaternary ammonium-based surfactants with a 22-carbon *n*-alkyl chain were stable enough to allow for crosslinking without noticeable destabilization of the w/o interface. The precise structural control of the resulting NCs with monolayer-thick shells was verified according to the characterization results of these NCs.

Because the limited dynamic stability of surfactant molecules in emulsions and other heterogeneous systems is a general issue,[10,11] the crystallization strategy potentially may have broad applicability in promoting dynamic stability of surfactants for achieving well-controlled surfactant-assisted template synthesis. However, while our previous study demonstrated the concept of crystallization-enhanced dynamic stability of surfactants, it did not provide specific insight to the effect of structures of surfactants on their dynamic stability in the crystallized miniemulsions. In particular, although the structural similarity between oil (i.e. *n*-DS, with melting point (MP) of 43-45 °C) and the *n*-alkyl tails of surfactants was thoughtfully designed for the crystallized miniemulsions, how the chain length of the *n*-alkyl tails of surfactants would affect the dynamic stability of the surfactants was not revealed. On the other hand, significant effects of surfactant chain length on other types of surfactant-stabilized systems have been reported.[14-20] Therefore, in the subsequent study, we further synthesized a series of monoacrylate and diacrylate-functionalized surfactants with different chain length of the *n*-alkyl tails (carbon atom numbers: 12, 14, 16, 18, 20 to 22), and investigated their dynamic stability in crystallized miniemulsions (Fig. 1). The assessment of dynamic stability of surfactants was made based on colloidal stability of crystallized miniemulsion nanodroplets upon dilution, because of difficulties in direct measurement. Structural control of NCs via these crystallized miniemulsion systems was also probed. Overall, the results indicate that, with the increase of the length of hydrophobic chains of surfactants, the dynamic stability of these surfactants increases and then permits precise template synthesis of NCs.

2. Experimental section

2.1 Measurements

All ^{1}H NMR spectra were obtained by using a Varian INOVA-500 spectrometer at 25 °C. Hydrodynamic diameter and zeta potential (ζ) values of nano-objects were measured by dynamic light scattering (DLS) using Nano ZS90 Zetasizer (Malvern Instruments) at room temperature. Each measurement was repeated at least three times at a measuring angle of 90°, with a 4mW 633nm He-Ne laser as the light source. The correla-

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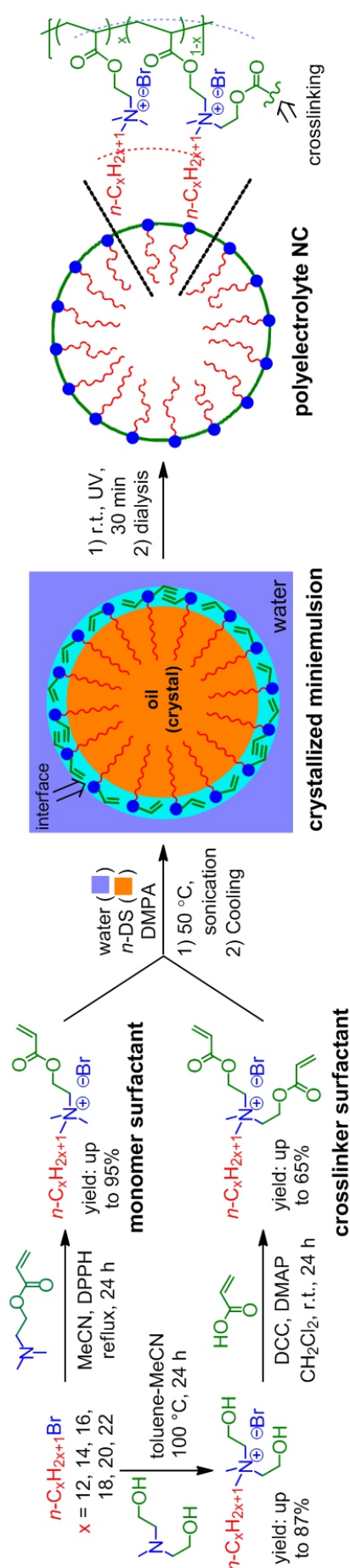***E-mail:** ccheng8@buffalo.edu*

Fig. 1 Schematic illustration of the synthesis of functional surfactants with different length of *n*-alkyl tails, and their conversion to polyelectrolyte NCs via crystallized miniemulsion.

tion decay function was analyzed with cumulants method to obtain size distribution. Colloidal stability of crystallized miniemulsion nanodroplets was assessed by using DLS to monitor the change of hydrodynamic diameters of the nanodroplets upon dilution using deionized water. Transmission electron microscopy (TEM) images were obtained by using JEOL 2010 microscope. TEM samples were prepared by evaporating the diluted sample solutions on 300 mesh carbon-coated copper grids. Then they were stained with a saturated uranyl acetate aqueous solution prior to imaging. Differential scanning calorimetry (DSC) measurements were performed by TA Instruments Q200 with a RCS-90 cooling device under nitrogen in the temperature range of 10-60 °C, with a heating or cooling rate of 5 °C/min.

2.2 Materials

1-Bromodocosane (98 %), 1-bromoeicosane (95 %), 1-bromooctadecane (97 %), 1-bromohexadecane (96 %), 1-bromotetradecane (97 %), and 1-bromododecane (98 %) were purchased from TCI Chemicals. 2,2-Diphenyl-1-picryl-hydrazyl (DPPH), and 2-(dimethylamino)ethyl acrylate (98 %) were purchased from Aldrich. 2,2-Dimethoxy-2-phenylacetophenone (DMPA, 99 %), *n*-DS (99 %), *N*-dimethanolmethylamine (99 %), 4-dimethylaminopyridine (DMAP, 99 %), and *N, N′*-dicyclohexyl-carbodiimide (DCC, 99 %) were purchased from Acros. HPLC grade of solvents, including dichloromethane (DCM), tetrahydrofuran (THF), diethyl ether, methanol, toluene, and acetonitrile were purchased from Fisher. Uranyl acetate dihydrate was purchased from Ted Pella.

2.3. Synthesis of monoacrylate-functionalized surfactants

A representative synthesis is described as follows: 1-bromooctadecane (2.40 g, 7.2 mmol), 2-(dimethylamino)ethyl acrylate (0.86 g, 6.0 mmol) and DPPH (8 mg) were dissolved in 15 mL of acetonitrile. The mixture solution was heated with an oil bath at 95 °C to reflux for 24 h. After solvent was evaporated from the reaction mixture, the residue was washed three times by diethyl ether. The resulting slightly yellow solid was dried under vacuum to give the monoacrylate-functionalized monomer surfactant with a 18-carbon *n*-alkyl chain as the product (2.98 g, 87 % yield). Monomer surfactants with other lengths of *n*-alkyl chains were synthesized with the same procedure and the same stoichiometric ratio of reactants, except using other types of 1-bromoalkanes (instead of 1-bromooctadecane).

2.4 Synthesis of diol-functionalized surfactants

A representative synthesis is described as follows: 1-bromooctadecane (2.35 g, 7.06 mmol) and *N*-methyldiethanolamine (8.41 g, 70.6 mmol) were dissolved in 70 mL of 50 vol% acetonitrile in toluene. The mixture solution was refluxed for 24 h using an oil bath at 100 °C. Then the solvent was removed by using rotatory evaporator to yield a white solid. The solid was washed by diethyl ether and dried under vacuum to give the diol-functionalized surfactant with a 18-carbon n-alkyl chain as the product (2.49 g, 78 % yield). Diol-functionalized surfactants with other lengths of n-alkyl chains were synthesized with the same procedure and the same stoichiometric ratio of reactants, but using other types of 1-bromoalkanes (instead of 1-bromooctadecane).

2.5 Synthesis of diacrylate-functionalized surfactants

A representative synthesis is described as follows: the diol-functionalized surfactant with a 18-carbon *n*-alkyl chain (0.887 g, 1.96 mmol), acrylic acid (0.420 g, 5.89 mmol), DCC (1.21 g, 5.89 mmol), and DMAP (48 mg, 0.39 mmol) were dissolved in 20 mL of dry DCM. The reaction mixture was stirred at 500 rpm for 24 h at room temperature under nitrogen protection. After 24 h, the reaction mixture was fil-

tered to remove precipitant. The solvent was removed from the filtrate by using rotatory evaporator. The resulting white solid was purified by flash chromatography over silica gel with gradient methanol-DCM eluent system (methanol: 0 to 5 %), to give the diacrylate-functionalized surfactant with a 18-carbon *n*-alkyl chain as the product (0.65 g, 59 % yield). Diacrylate-functionalized surfactants with other length of *n*-alkyl chains were synthesized with the same procedure and the same stoichiometric ratio of reactants, but using other types of diol-functionalized surfactants (instead of the one with a 18-carbon *n*-alkyl chain) in the reactions.

2.6 Preparation of crystallized miniemulsions

A representative preparation of crystallized miniemulsion is described as follows: the monoacrylate-functionalized surfactant with a 18-carbon n-alkyl chain (30 mg, 0.063 mmol), the diacrylate-functionalized surfactant with a 18-carbon n-alkyl chain (30 mg, 0.054 mmol),

Fig. 2 Representative ^{1}H NMR spectra of monoacrylate and diacrylate surfactants (with 20-carbon *n*-alkyl chains). Resonances from solvents are marked with stars (*).

docosane (71 mg) and photoinitiator DMPA (1 mg) were added into deionized water (3.50 g). The mixture was warmed to 50 °C by using oil bath. Then ultrasonication was performed for 30 min at 50 °C by using a 250 Sonifier (Branson Ulrasonics Corp.). The miniemulsion was cooled down to room temperature (21 °C) to obtain the corresponding crystallized miniemulsion. Crystallized miniemulsions derived from surfactants with other lengths of *n*-alkyl chains were prepared with the same procedure and the same stoichiometric ratio of monoacrylate to diacrylate surfactants, but using the surfactants with other length of *n*-alkyl chains. The crystallized miniemulsions prepared with the above formulation were used for the preparation of NCs. The crystallized miniemulsions for stability study also had the same formulation, except that DMPA was absent. For the crystallized miniemulsions for DSC analysis, DMPA was also absent and 90% less water (relative to oil and surfactants) was used as compared to the aforementioned formulation.

2.7 Preparation of NCs

The crystallized miniemulsions prepared following the representative procedure and formulation (see Sec. 2.6) were purged with nitrogen for 30 min. The resulting miniemulsions were applied to UV irradiation (λ_{max} = 365 nm) for 30 min. Then the dispersions were dialyzed against THF for 3 days to give NCs.

3. Results and discussion

3.1. Synthesis and characterization of functional surfactants

Functional surfactants used in this work were prepared by following Fig. 1, with their synthetic yields shown in Table 1. The monoacrylate surfactants were prepared by quaternization of 2-(dimethylamino)ethyl acrylate with different 1-bromoalkanes (1.2 equiv., with *n*-alkyl chains of 12, 14, 16, 18, 20 and 22 carbon atoms) in acetonitrile under refluxing for 24 h, in the presence of trace amounts of radical polymerization inhibitor DPPH. Acetonitrile-methanol mixed solvent used in our previous work was not employed in these reactions,[13] because pure acetonitrile as the reaction solvent could avoid unfavorable occurrence of esterification exchange side reaction and led to higher yield (up to 95%) and more simplified work-up procedure. Because all components of the reaction mixtures except the products are soluble in diethyl ether, the monoacrylate surfactants were readily separated from the dried reaction mixtures by washing out other components with diethyl ether. While other monoacrylate surfactants are white solids at room temperature, these surfactants with 12- or 14-carbon *n*-alkyl chains are liquids at room temperature, and accordingly the washing process was performed using cold diethyl ether (-20 °C) to improve yields.

The diol surfactants, as precursors of diacrylate surfactants, were also prepared by using quaternization chemistry with the same work-up process. Different with the synthesis of monoacrylate surfactants, N-methyldiethanolamine (10 equiv. relative to 1-bromoalkanes) was used as the amine reactant, with 1:1 (v/v) of acetonitrile-toluene as the reaction and refluxing solvent. The synthetic yields of these diol surfactants were 65-87 %.
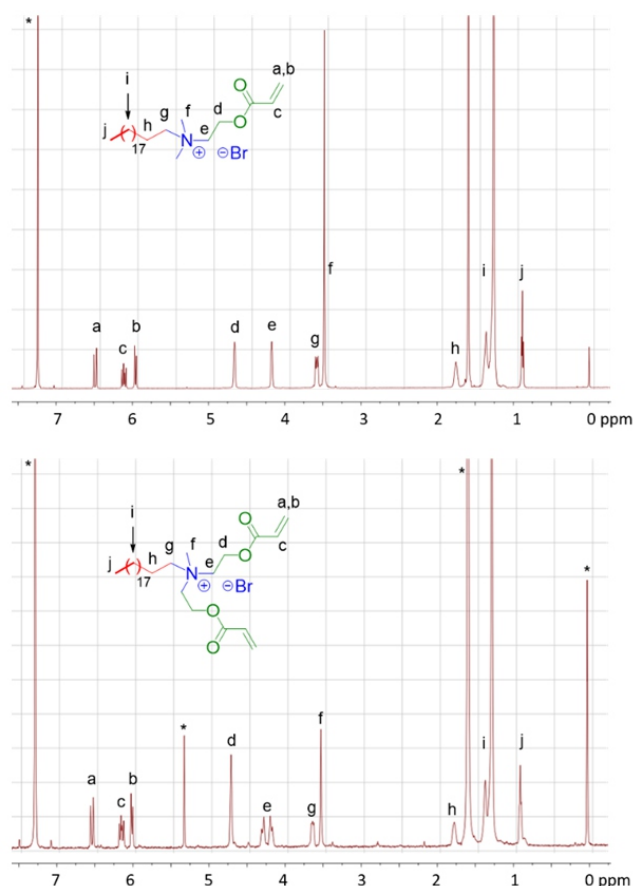
Table 1. Synthetic yields of functional surfactants.

# of C in *n*-alkyl tail	12	14	16	18	20	22
Monoacrylate surfactant	50%	78%	80%	87%	81%	95%
Diol surfactant	84%	87%	74%	78%	65%	72%
Diacrylate surfactant	55%	65%	30%	59%	60%	59%

The diacrylate surfactants were prepared by DCC/DMAP-catalyzed esterification reactions of diol surfactants with acrylic acid in DCM at room temperature for 24 h ([diol surfactant]$_0$:[acrylic acid]$_0$:[DCC]$_0$:[DMAP]$_0$ = 1:3:3:0.2). Column chromatography was used in the separation of these diacrylate surfactants (yields: 30-65 %) from reaction mixtures.

All of the surfactants were characterized by ^{1}H NMR analysis in CDCl$_3$. Their chemical structures were confirmed. The representative ^{1}H NMR spectra of monoacrylate and diacrylate surfactants for the use of subsequent studies were shown in **Fig. 2**. The same class of surfactants, with structural differences only at the length of n-alkyl chains, showed ^{1}H NMR resonances of the same types of protons at very similar

Fig. 3 Representative DSC curves of crystallized miniemulsions prepared from surfactants with n-alkyl tails having a) 12 carbon atoms, and b) 18 carbon atoms.

positions on spectra. The only remarkable spectral differences were resonance intensities of methylene (-CH$_2$-) protons at 1.10-1.45 ppm, which increased with the n-alkyl chain length as compared to the resonance intensities of other protons.

3.2. Stability study of crystallized miniemulsions

Crystallized miniemulsions were obtained by the preparation of emulsions (using monoacrylate and diacrylate surfactants, water and n-DS) at 50 °C, following by cooling to room temperature to allow for the crystallization of the oil phase. The crystallization and melting processes of the crystallized oil phases were observed by DSC analysis (**Fig. 3**), and correspondingly the crystallization temperatures (T$_c$s; showing in cooling cycle) and MPs (showing in heating cycle) were obtained (**Table 2**). T$_c$s (as peak values; 23.5-29.2 °C) are about 8-20 °C below the corresponding MPs (31.4-43.9 °C), due to supercooling effect. Still, all of the T$_c$s are slightly above room temperature. Therefore, by the general preparation process with slow cooling, these miniemulsions have crystallized oil phases at room temperature. Irregular crystallization peaks with shoulder or biomodal mode, as well as drafting baseline on low-temperature side of melting peak (together with smaller melting peak relative to crystallization peak), were observed in most samples, presumably because of different types of crystalline domains. The surfactants with 12-carbon n-alkyl chains led to slightly lower T$_c$ (23.5 °C) and more evidently lower MP (31.4 and 36.5 °C, due to a bimodal melting peak) of the crystallized miniemulsion nanodroplets than other surfactants (T$_c$s: 24.3-29.2 °C, and MPs: 43.0-43.9 °C), indicating that the crystallized miniemulsions using surfactants with 12-carbon n-alkyl chains have a little lower thermodynamic stability than others. However, DSC analysis could not reveal specifically thermodynamic stability of the surface layers of crystallized miniemulsion nanodroplets, because of the very low mass fractions of these surface layers in the nanodroplets.

DLS study of the crystallized miniemulsions in dilution experiments (from 0.6 wt% to 0.3 wt%, and then to 0.15 wt%) was further performed at room temperature to investigate the colloidal stability of the crystallized nanodroplets, which also reflects dynamic stability of surfactant molecules in the surfactant monolayer on the nanodroplet surface (**Fig. 4**). The increase of colloidal stability of the crystallized nanodroplets with the increase of n-alkyl chain length of the surfactants was observed. The may be ascribed to the enhanced intermolecular interactions of surfactant molecules in the surfactant monolayers with the increase of their n-alkyl chain length. The crystallized nanodroplets stabilized by using surfactants with 12 or 14-carbon n-alkyl chains showed evident increase of hydrodynamic sizes upon dilution with deionized water. The result indicates that the surfactant molecules have limited dynamic stability on the nanodroplet surface and a portion of them would be further dissolved in water during dilution process, leading to aggregation of the nanodroplets. On
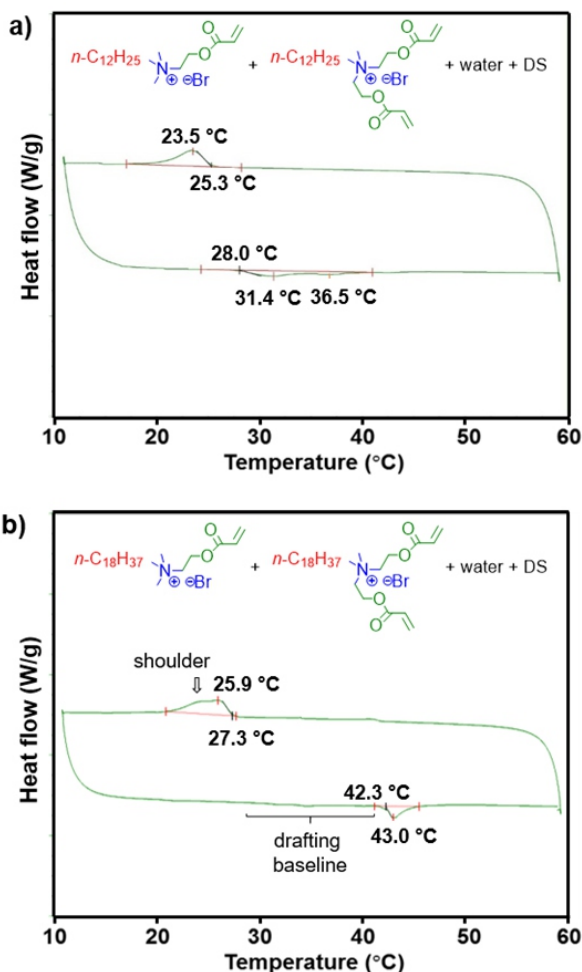
Table 2. Thermal transition temperatures of crystallized miniemulsions[a].

# of C in n-alkyl tail of surfactants	12	14	16	18	20	22
crystallization temperature (T$_c$)	23.5	24.3	25.4[b]	25.9[b]	24.1;27.4[c]	25.9;29.2[c]
melting point (MP)	31.4;36.5[c]	43.2[d]	43.9[d]	43.0[d]	43.0[d]	43.8[d]

Note: [a] By DSC measurements at 10-60 °C with heating/cooling rate of 5 °C/min, and the temperatures are represented by peak values; [b] With a shoulder on low-temperature side of thermal transition peak; [c] With a bimodal thermal transition peak; [d] With a drafting baseline on low-temperature side of thermal transition peak.
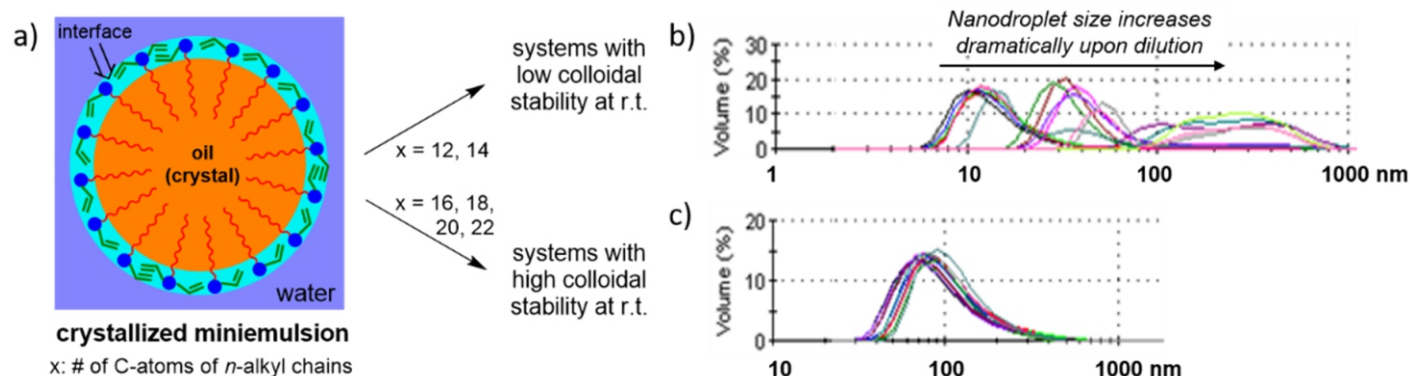
Fig. 4 a) Illustration of colloidal stability of crystallized miniemulsions; b-c) representative DLS results of crystal-forming systems upon dilution (b: x = 12; c: x = 16; dilution from 0.6 to 0.3 and 0.15 wt%, multiple measurements per concentration).

the other hand, the crystallized nanodroplets stabilized by using surfactants with 16-carbon or even longer *n*-alkyl chains exhibited remarkably stable hydrodynamic sizes upon dilution with deionized water, indicating that they may be able to serve as synthetic templates for precise synthesis of NCs via the crosslinking of the surface-adsorbed surfactant monolayers.

3.3. Synthetic study of NCs via crystallized miniemulsions
Synthesis of NCs using crystallized miniemulsion nanodroplets as templates was further performed to explore how colloidal stability of these nanodroplets would affect synthetic accuracy. Crystallized miniemulsions were prepared using the same formulations and procedure as these for stability studies, except that photoinitiator DMPA was added in each trail in the current case. Then they were irradiated with UV light (λ_{max} = 365 nm) for 30 min to highly cure the surfactant monolayers adsorbed on the surface of crystallized nanodroplets. Finally, the resulting reaction systems were dialyzed against THF to obtain NCs by removing the *n*-DS cores of the surface-crosslinked crystallized nanodroplets. DLS was used to monitor the systems throughout the process (i.e. before and after UV irradiation, and after dialysis; Table 3).

In a good agreement with colloidal stability results, crystallized miniemulsions using surfactants with 16-carbon or even longer *n*-alkyl chains led to well-controlled synthesis of NCs, but the systems using

surfactants with 12 or 14-carbon *n*-alkyl chains generated ill-defined products. For all of the trials before UV irradiation, crystallized miniemulsion nanodroplets showed z-averaged diameters (D_{z-ave}; 103.8-128.0 nm) a little over 100 nm with high ζ values (56-69 mV). After UV irradiation, while maintaining similar ζ values (56-70 mV), most trials exhibited slightly reduced D_{z-ave}, because UV-induced photo-crosslinking of the surfactant monolayers restricted their motions. Only the crystallized miniemulsion using surfactants with 12-carbon *n*-alkyl chains illustrated an increase of D_{z-ave}, from 103.8 ± 0.6 to 117.3 ± 1.5 nm, indicating that crosslinking was not limited to the surfactant monolayers of individual nanodroplets due to the low colloidal stability of the system. For all trials, the resulting NCs in THF showed significantly smaller D_{z-ave} values (46.6-73.2 nm) than the precursor nanodroplets, as a result of the removal of the *n*-DS cores. However, the crystallized miniemulsion using surfactants with 12 or 14-carbon *n*-alkyl chains resulted in visible insoluble substances after dialysis against THF, suggesting the occurrence of inter-nanodroplet surface surfactant layers crosslinking during UV irradiation; filtration of the THF solutions (using filters with pore size of 200 nm) was needed to remove the insoluble substances to get NCs for DLS analysis, and therefore, the yields of NCs were low (<50 %). On the other hand, dialysis of UV irradiated crystallized miniemulsions using surfactants with 16-carbon or even longer *n*-alkyl chains resulted in NCs in THF without undesired products, demonstrating well-controlled template synthesis.

Table 3. DLS results of crystallized miniemulsion nanodroplets and the derived NCs .

# of C in *n*-alkyl tail of surfactants	Before UV irradiation [a]		After UV irradiation [a]		After dialysis [b]
	D_{z-ave} (nm)	ζ (Mv)	D_{z-ave} (nm)	ζ (Mv)	D_{z-ave} (nm)
12	103.8 ± 0.6	62	117.3 ± 1.5	63	69.0 ± 3.5 [c]
14	121.4 ± 0.9	64	109.0 ± 0.7	68	58.2 ± 1.1 [c]
16	109.3 ± 1.4	64	105.4 ± 0.2	68	56.5 ± 5.6
18	128 .0 ± 0.6	66	115.7 ± 1.9	56	60.7 ± 0. 8
20	115.5 ± 2.0	69	104.4 ± 3.0	63	46.6 ± 1.7
22	122.7 ± 4.0	56	118.3 ± 2.5	70	73.2 ± 1.8

Note: [a] Crystallized miniemulsion nanodroplets in water; [b] NCs in THF (therefore ζ was not measured); [c] After filtration using filter with pore size of 200 nm.

Noteworthily, ζ values of NCs in THF were not measured, because THF is an aprotic solvent and can also dissolve the plastic base of the sample cell for measuring ζ.

A set of results for well-controlled template synthesis of NCs, using NCs derived from surfactants with 18-carbon n-alkyl chains as the representative sample, are shown in **Fig. 5**. Besides DLS monitoring the synthetic system before/after UV crosslinking and after dialysis, TEM imaging of the resulting NCs was also performed. In the TEM image, NCs demonstrated well-defined capsular morphologies with an average size of ~50 nm, narrow size distribution, and uniform shell having thickness of ~2 nm. The average size of these NCs on TEM grid is close to their $D_{z\text{-ave}}$ of 60.7 ± 0.8 nm in THF solution. Their uniform and small shell thickness supports the well-controlled crosslinking for precise template conversion of monolayer of surfactants to shells of NCs.
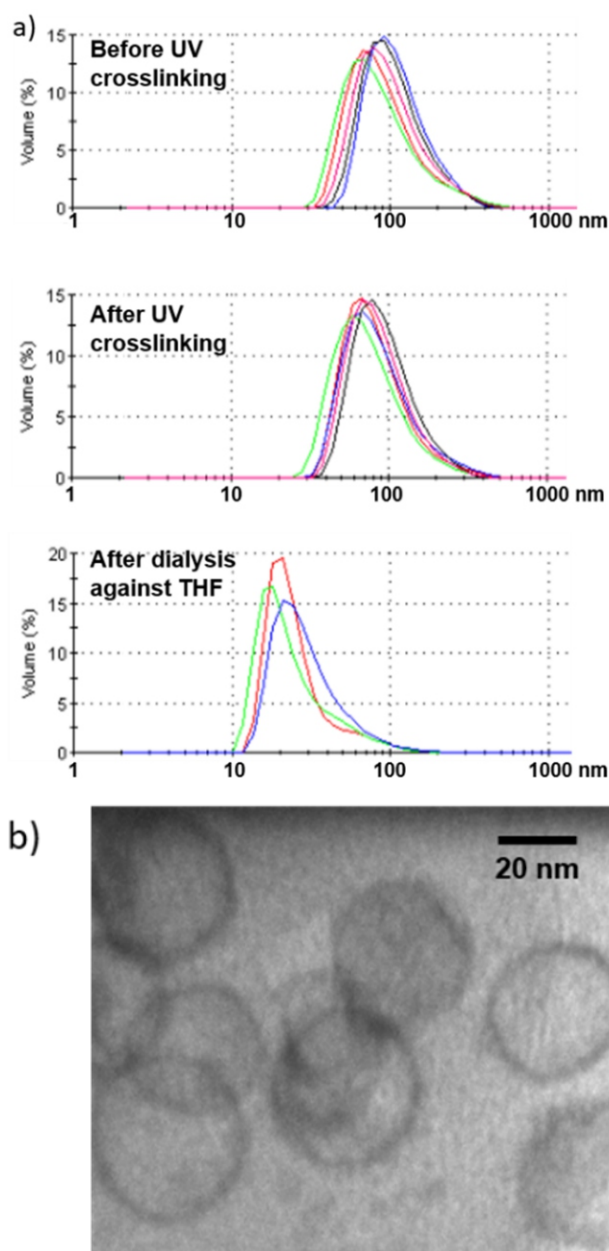

Fig. 5 a) DLS monitoring of the preparation steps for the preparation of NCs (multiple measurements per step); b) TEM image of the resulting NCs. The NCs were prepared using monoacrylate and diacrylate surfactants with 18-carbon n-alkyl chains.

4. Conclusions

A series of monoacrylate and diacrylate quaternary amine-based surfactants with varied length of n-alkyl chains were synthesized. Using these surfactants for interfacial stabilization, crystallized miniemulsions with n-DS cores dispersed in continuous water phase were studied to probe their thermodynamic and colloidal stability. Significant effects of the length of n-alkyl chains of surfactants on the colloidal stability of crystallized miniemulsion nanodroplets, corresponding to the dynamic stability of surfactants, were found. The nanodroplets stabilized by surfactants with n-alkyl chains having at least 16 carbon atoms possess high colloidal stability at room temperature, and therefore, can be used for the precise template synthesis of NCs by UV-induced photo-crosslinking of the surfactant monolayers adsorbed on the surface of nanodroplets. Overall, the results indicate the importance of structures of surfactants, especially their hydrophobic chain length, for the synthesis using surfactant-stabilized crystallized heterogeneous systems as templates.

Conflict of interest

There are no conflicts to declare.

Acknowledgements

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