Responsive Pickering Emulsions Stabilized by Frozen Complex Coacervate Core Micelles

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1. Materials

Anhydrous tetrahydrofuran (THF), methanol (MeOH), ethyl acetate (AcOEt), diethyl ether (Et₂O), n-hexane, aluminum oxide, anhydrous 1,4-dioxane, deuterium oxide, N,N-dimethylacrylamide (DMAA) monomer 99%, 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DDMAT), methacryloxyethyl thiocarbamoyl rhodamine B monomer, tert-butyl acrylate (tBA) monomer 98%, anhydrous N,N-Dimethylformamide (DMF), N-(3-(dimethylamino)propyl)acrylamide (DMAPAA) monomer, dopamine hydrochloride (DOPA.HCl), acryloyl chloride, ethyl acetate (AcOEt), p-toluenesulfonic acid (p-TsOH), anhydrous toluene, 2,2-dimethoxypropane, cyclohexane and dodecane were purchased from Sigma Aldrich and used without further purification. N-isopropylacrylamide (NiPAM) monomer and 2,2′-azobis(2-methylpropionitrile) (AIBN) were purchased from Sigma Aldrich and recrystallized once respectively from n-hexane and methanol. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was purchased from Biosolve and used as received. Ultrapure deionized water with a minimum resistivity of 18 MΩ.cm (milliQ, Millipore, France) was used for all experiments.

2. Instrumentation

Proton Nuclear Magnetic Resonance (¹H NMR)
¹H NMR experiments in D₂O, d6-DMSO and CDCl₃ were performed on a Bruker Avance III HD spectrometer operating at 400 MHz, using a standard 5 mm broadband Smart probe regulated at 25 °C. Chemical shift in ppm from tetramethylsilane referenced to the residual isotopomer solvent signal (HOD).

Size Exclusion Chromatography (SEC)
Size exclusion chromatography (SEC) was performed on a Viscotek GPCmax system equipped with a TDA 302 triple detector array (both Malvern). PolarGel L and PolarGel M columns (Agilent, 8 µm 30 cm) were fitted into the machine and kept at a temperature of 50 °C. N,N-dimethylformamide (DMF, 99.9 %, Sigma-Aldrich) with 0.01 M LiBr was used as eluent. Samples were dissolved in the eluent at a concentration of 2 mg.mL⁻¹ and passed through a 0.45 µm nylon filter prior injection. Near monodisperse PMMA standards (Polymer Standard Services) were used for the construction of a calibration curve. Data acquisition and calculations were performed using Viscotek OmniSec software version 5.0.

Cryo Transmission Electron Microscopy (Cryo-TEM)
An aliquot (3 µL) of sample was deposited on holey carbon-coated grids (3.5/1 Quantifoil Micro Tools, Jena, Germany) that were previously glow-discharged for 15 s. After the excess liquid was blotted for 4 s, the grids were vitrified in liquid ethane using a Vitrobot (FEI, Eindhoven, The Netherlands) and transferred to a FEI Tecnai T20 electron microscope equipped with a Gatan model 626 cryo-stage operating at 200 keV. Micrographs were recorded under low-dose conditions with a slow-scan CCD camera.
Dynamic Light Scattering (DLS)
Particles size and polydispersity were measured by photon correlation spectroscopy (PCS) at a
detection angle of 90°, using a Zetasizer Ultra Malvern Instrument equipped with a HeNe laser (λ =
632.8 nm). All analyses were performed with the software supplied by the manufacturer. The resulting
data were fitted with a cumulant function and the hydrodynamic diameter was calculated with the
Stokes–Einstein equation \(d_H = \frac{kT}{3\eta D}\) with \(k\) the Boltzmann constant, \(T\) the temperature (294 K), \(\eta\) the
solvent viscosity (0.97 mPa.s) and \(D = \frac{\Gamma}{q^2}\) the diffusion coefficient, \(\Gamma\) being the relaxation rate and \(q\)
the wave vector.

Tensiometry
Oil-water interfacial tensions were measured using the rising drop method (ITC Concept, Tracker). The
shape of the drops was fitted to the Laplace equation in order to determine the interfacial tension.
Dodecane oil with a purity of > 99% was used as received, and the C3MS aqueous solutions were
prepared using deionized water. The temperature of both the syringe used to form the drop and the
water cell was maintained at 21 °C by circulating water in a double-envelope system. Polymer solutions/
dispersions were prepared at \(C = 0.5 \text{ mg.mL}^{-1}\). 

3. Synthesis and protocols

3.1. Synthesis of pAA

**Figure S1.** Synthesis scheme of poly(acrylic acid) (pAA).

Tert-butyl acrylate (4.00 g, 31.2 mmol), DDMAT (0.076 g, 0.20 mmol) and AIBN (0.006 g, 0.04 mmol) were dissolved in DMF (8 mL) in a round bottom flask at room temperature and under N₂ flow for 20 min. The reaction medium was then heated to 70 °C while removing N₂ flow and allowed to proceed under continuous stirring. After 5 h, the reaction mixture was exposed to air and the flask was immersed into an ice-cold bath in order to stop the polymerization. The monomer conversion was measured to be 95 % by means of ¹H NMR. The synthesized polymers were purified from unreacted monomers by precipitation in an ice cold mixture of water and MeOH (1:1 v/v). After drying overnight under vacuum (31 mbar, 45 °C) the polymer chains were dissolved in HFIP (200 mL) in a large round bottom flask at room temperature. 2.2 mL of concentrated hydrochloric acid (37%) was added and the deprotection reaction was allowed to proceed under continuous stirring. After 18 h, volatiles were removed using a combination of N₂ bubbling, rotary evaporation and drying under vacuum (31 mbar, 45 °C). The polymer chains were dissolved in water and freeze-dried to obtain a white fluffy polymer with a yield of 87%.
**Figure S2.** $^1$H NMR of (a) reaction medium after five hours (CDCl$_3$), (b) purified poly(tert-butyl acrylate), ptBA, in CDCl$_3$, (c) purified poly(acrylic acid), pAA, in D$_2$O and (d) SEC chromatogram of ptBA in 0.01 M LiBr in DMF.

3.2. **Synthesis of p[(NiPAM)-co-(DMAA)]-b-pDMAPAA**

**Figure S3.** Synthesis scheme of p[(NiPAM)-co-(DMAA)]-b-pDMAPAA polycation diblock.
The first block, p[NiPAM-co-(DMAA)], was synthesized by thermally initiated RAFT polymerization. In a typical synthesis, NiPAM (3.00 g, 26.5 mmol), DMAA (0.66 g, 6.60 mmol), DDMAT (0.080 g, 0.22 mmol) and AIBN (0.007 g, 0.05 mmol) were dissolved in DMF (6 mL) in a round bottom flask at room temperature and under N₂ flow for 20 min. The reaction medium was then heated to 70 °C while removing N₂ flow and allowed to proceed under continuous stirring. After 4 h, the reaction mixture was exposed to air and the flask was immersed into an ice-cold bath in order to stop the polymerization. The monomer conversion was measured to 97% by mean of ¹H NMR. The synthesized polymers were purified from un-reacted monomers by precipitation in ice cold diethyl ether. The product was dried overnight under vacuum (31 mbar, 45 °C) to obtain a white polymer powder with a yield of 90%.

Figure S4. ¹H NMR of (a) reaction medium after 4 hours (DMSO-d₆) and (b) purified p[NiPAM-co-(DMAA)] (DMSO-d₆).

The second block, pDMAPAA, was attached to the p[NiPAM-co-(DMAA)] by thermally triggered macro RAFT polymerization. In a typical synthesis, macro-RAFT agent p[NiPAM-co-(DMAA)] (1.0 g, 0.06 mmol), DMAPAA (0.990 g, 6.40 mmol), AIBN (0.002 g, 0.01 mmol) and Rhodamine B monomer were dissolved in anhydrous 1,4-dioxane (5 mL) in a round bottom flask at room temperature and under N₂ flow for 20 min. The reaction medium was then heated to 70 °C while removing N₂ flow and allowed to proceed under continuous stirring. After 24 h, the reaction mixture was exposed to air and the flask was immersed into an ice-cold bath in order to stop the polymerization. The monomer conversion was measured to be 84 % by means of ¹H NMR. The synthesized polymers were purified from un-reacted monomers by precipitation in an ice cold mixture of n-hexane and THF (4:1 v/v). The
product was dried overnight under vacuum (31 mbar, 45 °C) to obtain a pink polymer powder with a yield of 64%.

Figure S5. $^1$H NMR of (a) reaction medium after 24 hours (DMSO-d$_6$), (b) purified p[(NiPAM)-co-(DMAA)]-b-pDMAPAA (DMSO-d$_6$) and (c) SEC chromatogram of p[(NiPAM)-co-(DMAA)] first block and p[(NiPAM)-co-(DMAA)]-b-pDMAPAA diblock in 0.01 M LiBr in DMF.
3.3.  Synthesized polymer chains composition

Monomer conversion and final product composition were determined by $^1$H NMR and enabled us to determine the size of the polymer chains:

| Monomer                        | DP$_n$ |
|--------------------------------|--------|
| pAA (-)                        | 147    |
| AAc                            |        |
| p[(NiPAM)-co-(DMAA)]-b-pDMAPAA (+) | 115    |
| NiPAM                          |        |
| DMAA                           | 29     |
| DMAPAA                         | 85     |

3.4.  C3Ms formation

pAA and p[(NiPAM)-co-(DMAA)]-b-pDMAPAA were separately dissolved in a 1 M NaCl solution of PBS buffer adjusted at pH 7 (10^{-2} M). The polyelectrolytes were combined in a 1:1 ratio of chargeable monomer units (total monomer concentration of 0.12 mol.L$^{-1}$). The homogeneous mixture was further dialysed (3.5 kDa cut-off regenerated cellulose membrane) for 4 hours against 0.5 M NaCl PBS buffer (pH 7). Then, the medium was dialysed against 10^{-2} M PBS buffer at pH 7 and finally against deionized water. The dialysis process was continued until the conductivity of the medium inside the bag matched the one of deionized water (10 μS/cm). The pH was continuously controlled to be 7 during the whole dialysis process. Finally, the resulting C3Ms were freeze-dried and stored as powder for further use.

3.5.  Emulsification Process

0.4 mL of dodecane (+ 1 v/v% of hexadecane or iso-octane) were emulsified with 1 mL of C3Ms dispersion in 0 M NaCl water ($C_{C3Ms} = 0.2 - 10$ mg/mL) by ultra-sonication (Sonic Vibra-Cell VCX-130, 130 W, 20 kHz) for 1 minute in interval of 5 seconds at 60 % amplitude to prevent overheating of the samples. During sonication, the samples were cooled in an ice bath to reduce coalescence.

4.  Cloud point of pNiPAM based polymer chains

![Figure S6](image.png)

**Figure S6.** Evolution of the scattering intensity of (a) p(NiPAM) and p(NiPAM)-b-pDMAPAA, (b) p[(NiPAM)-co-(DMAA)] and p[(NiPAM)-co-(DMAA)]-b-pDMAPAA solutions in water with temperature at 0 M and 1 M NaCl at a polymer concentration of 1 mg/mL and pH 7.
The cloud point of the pNiPAM homopolymer was determined at 34 and 22°C at 0 and 1 M NaCl, respectively. The copolymerization of NiPAM with 20 mol% of DMAA increased the cloud point temperature of the p[NiPAM-co-DMAA)] to 38 and 32°C for 0 and 1 M NaCl, respectively, ensuring full solubility of the corona at the working temperature of 21 °C for the whole range of NaCl concentrations investigated.
5. Titration of pAA and p[[NiPAM]-co-(DMAA)]-b-pDMAPAA

In order to determine the degree of ionization as a function of pH, pH titrations were performed on pAA and p[[NiPAM]-co-(DMAA)]-b-pDMAPAA solutions to determine the pK_ and the pK_. pH titrations were carried out on 5 mg/mL solutions at [NaCl] = 0.1 M, starting from a fully protonated form for pAA, and from a fully deprotonated form for p[[NiPAM]-co-(DMAA)]-b-pDMAPAA. Sodium hydroxide (NaOH) 0.1 M and hydrochloric acid (HCl) 0.1 M solutions were used to modify the pH. The effective pK and pK were taken as the pH halfway of the equivalence point and could be used to calculate the degree of ionization as a function of pH (Figure S7), according to the following equations:\(^1\)

\[ \alpha^- = \frac{10^{pH-pK_-}}{1 + 10^{pH-pK_-}} \]
\[ \alpha^+ = \frac{10^{pK_+-pH}}{1 + 10^{pK_+-pH}} \]

**Figure S7.** Titration curves of (a) pAA and (b) p[[NiPAM]-co-(DMAA)]-b-pDMAPAA. (c) Degree of ionisation of the two polyelectrolytes as a function of pH.
6. Optimum mixing ratio between polyelectrolytes

![Graph](image)

**Figure S8. (a)** Evolution of the scattering intensity of p[(NiPAM)-co-(DMAA)]-b-pDMAPAA and pAA mixture in water with the mixing ratio AAc/DMAPAA at pH 6, 7 and 8. **(b)** Overlaid $^1$H NMR spectra of C3Ms dispersed in 0 M (blue), 1 M NaCl (green) and of the subnatant of 0 M NaCl C3M dispersion centrifuged through a 30 kDa MWCO membrane (red). 1,4-Dioxane is used as internal reference. The absence of polymer related peak in the subnatant shows that all the chains are embedded in the C3Ms.
Figure S9. Measured intensity autocorrelation function $g_2^*(t)$, calculated electric field correlation function $g_1(t)$, cumulant fit and residuals of $g_1(t)$ for the C3Ms samples obtained by (a) direct mixing, (b) direct dialysis and (c) step dialysis.
8. Dynamics of the core of the C3Ms

Figure S10. Evolution of scattered light intensity and mean hydrodynamic diameter ($d_h$) versus polymer concentration in the C3Ms at a ratio (-) : (+) = 1 : 1 in water 0 M NaCl.

Figure S11. Average hydrodynamic diameter and light scattering intensity of a C3Ms dispersion in D$_2$O as a function of the NaCl concentration from 0 to 1 M (both at $C_{C3M} = 0.5$ mg.mL$^{-1}$).
The integral values between 0.5 and 2.5 ppm (containing protons $a_1, a_2, b, d, g$) were calculated to be 15.9 for the C3Ms at 1.0 M NaCl, and 13.6 for the p[NiPAM]-co-(DMAA)]-b-pDMAPAA copolymer. The difference between these integral values, a value of 2.3.

By calculating the ratio between the monomers in the diblock copolymer, and taking into account that we mixed the oppositely charge polymers with a ratio of 1 : 1 between DMAPAA and AAc, the expected integral value of AAc can be calculated to be 2.2 as shown in the Table below. The obtained integral values matchup between free polymer chains and C3Ms at 1 M NaCl.

According to the integral values determined for the diblock p[NiPAM]-co-(DMAA)]-b-pDMAPAA, the following ratios between monomers is determined as follows:

| Molar ratio | NiPAM | DMAA | DMAPAA | AAc |
|-------------|-------|------|--------|-----|
| NiPAM       | 1     | 0.25 | 0.74   | 0.74|

In the chemical shift range from 0.5 to 2.5 ppm we expect the following number of protons and the theoretical integral value compared to the methine peak of the NiPAM units chosen as internal reference:

| Monomer | No. protons | Theoretical integral value |
|---------|-------------|----------------------------|
| NiPAM   | 9           | $(9 \times 1) = 9$          |
| DMAA    | 3           | $(3 \times 0.25) = 0.75$    |
| DMAPAA  | 5           | $(5 \times 0.74) = 3.70$    |
| AAc     | 3           | $(3 \times 0.74) = 2.22$    |
9. Emulsions

9.1. C3Ms adsorption at dodecane / water interface

Figure S13. (a) Evolution of dodecane / water interfacial tension (black) in presence of pAA (red), p[(NiPAM-co-(DMAA)]]-b-pDMAPAA diblock (blue) or C3Ms (green) dissolved at 0.5 mg.mL⁻¹ in water at pH 7. (b) Flocculated aspect of dodecane-in-water emulsions in presence of C3Ms, p[(NiPAM-co-(DMAA)])-b-pDMAPAA diblock or pAA at a polymer concentration of 0.5 mg.mL⁻¹. The highly flocculated state of dodecane drops in the presence of C3Ms prevents the system to flow in the inverted container.

9.2. Imaging of oil-water interface

Figure S14. (a), (b) Cryo-TEM images of dodecane (+ 10 v/v% isoctane) drops in water stabilized by C3Ms adsorbed (scale bar is 200 nm).
10. Synthesis and characterization of chemically crosslinked core C3Ms (c-C3Ms)

10.1. Protected catechol monomer synthesis (pCat)

Figure S15. Synthesis scheme of CatAc and pCat monomers.

The following synthesis protocols were inspired from the work of Patil et al.²

DOPA.HCl (3.99 g, 21.0 mmol) and Et₃N (3.24 ml, 23.2 mmol) were dissolved in MeOH (70 ml) and cooled on an ice bath. THF solution (3 ml) of acryloyl chloride (2.05 ml, 25.2 mmol) and MeOH solution (5 ml) of triethylamine (4.23 ml, 30.3 mmol) were added dropwise to the DOPA.HCl solution. After adding the reagent, the reaction mixture was stirred at room temperature for 2 h. Solvent was removed under vacuo. The residue was dissolved in ethyl acetate (AcOEt) and washed with 1 M hydrochloric acid (HCl) and brine. The organic layer was dried over sodium sulfate, then filtrated, and concentrated by evaporation. The product was recrystallized from AcOEt, giving CatAc (2.40 g, 11.6 mmol) with 55% yield as a white solid.³

UV Vis (H₂O) λ max (ε) = 280 nm (2591 L mol⁻¹ cm⁻¹).

1.35 g (6.5 mmol) of CatAc and 0.62 g (0.36 mmol) of p-TsOH as a catalyst were dissolved in anhydrous toluene (75 ml) under nitrogen atmosphere. A Dean–Stark apparatus was attached and the solution was refluxed for 3 h. The flask was then cooled to 0 °C, and 7.5 ml (61.3 mmol) of 2,2-dimethoxypropane was added. A soxhlet extractor, whose thimble was filled with Stark apparatus was attached and the solution was refluxed for 2 h. The mixture was washed with water, brine and dried over MgSO₄. The solvent was removed in vacuum to yield a crude orange paste, which was further purified by flash silica gel column chromatography eluting with a cyclohexane–ethyl acetate (5 : 5) mixture giving pCat (1.24 g, 5.0 mmol) with 74% yield as a white solid.³

DOSAc (3.99 g, 21.0 mmol) and Et₃N (3.24 ml, 23.2 mmol) were dissolved in MeOH (70 ml) and cooled on an ice bath. THF solution (3 ml) of acryloyl chloride (2.05 ml, 25.2 mmol) and MeOH solution (5 ml) of triethylamine (4.23 ml, 30.3 mmol) were added dropwise to the DOPA.HCl solution. After adding the reagent, the reaction mixture was stirred at room temperature for 2 h. Solvent was removed under vacuo. The residue was dissolved in ethyl acetate (AcOEt) and washed with 1 M hydrochloric acid (HCl) and brine. The organic layer was dried over sodium sulfate, then filtrated, and concentrated by evaporation. The product was recrystallized from AcOEt, giving CatAc (2.40 g, 11.6 mmol) with 55% yield as a white solid.³

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UV Vis (H₂O) λ max (ε) = 280 nm (2591 L mol⁻¹ cm⁻¹).
Figure S16. $^1$H and $^{13}$C NMR spectra of (a), (b) CatAc and (c), (d) pCat in DMSO-d6.
10.2. p(AA-co-Cat) synthesis

The protocol for p[(AA)-co-(Cat)] synthesis is identical to the one of pAA. The only difference is that 5 mol% vs tert-butyl acrylate of pCat monomer (0.40 g, 1.6 mmol) was added in the medium.

Figure S17. (a) Synthesis scheme and (b) 1H NMR (in D$_2$O) of p[(AA)-co-(Cat)] polyanion and (c) SEC chromatogram of p[(tBA)-co-(pCat)] in 0.01 M LiBr in DMF.
10.3. \textit{p\{NiPAM-co-(DMAA)\}-b-p\{DMAPAA-co-(Cat)\} synthesis}

The protocol for \textit{p\{NiPAM-co-(DMAA)\}-b-p\{DMAPAA-co-(Cat)\}} synthesis is similar to the one of \textit{p\{NiPAM-co-(DMAA)\}-b-pDMAPAA}. The only differences are that 5 mol\% vs DMAPAA of pCat monomer (0.08 g, 0.32 mmol) was added in the medium to synthesize the second block. The deprotection of the catechol moieties in the \textit{p\{NiPAM-co-(DMAA)\}-b-p\{DMAPAA-co-(Cat)\}} was performed in a 2 M aqueous solution of HCl water for 12h at RT. The solution was then dialyzed until the pH reaches a value of 6 and then freeze-dried.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
\caption{(a) Synthesis scheme and (b) 1H NMR (in DMSO-\textit{d}_6) of \textit{p\{NiPAM-co-(DMAA)\}-b-p\{DMAPAA-co-(Cat)\}} polycation. (c) SEC chromatogram of \textit{p\{NiPAM-co-(DMAA)\}} first block and \textit{p\{NiPAM-co-(DMAA)\}-b-p\{DMAPAA-co-(pCat)\}} diblock in 0.01 M LiBr in DMF.}
\end{figure}

\textbf{10.4. Synthesized polymer chains composition}

Monomer conversion and final product composition were determined by $^1$H NMR and enabled us to determine the size of the polymer chains:

| Monomer                  | DP\textsubscript{n} |
|--------------------------|---------------------|
| P\{AA-co-(Cat)\} (-)     | AAc 145             |
| pCat                    | 8                  |
| \textit{p\{NiPAM-co-(DMAA)\}-b-p\{DMAPAA-co-(Cat)\}} (+) | NiPAM 115          |
|                          | DMAA 29            |
|                          | DMAPAA 89          |
|                          | pCat 4             |
### 10.5. c-C3Ms formation and behavior

p[(AA-co-(Cat))] and p[(NiPAM)-co-(DMAA)]-b-p[(DMAPAA)-co-(Cat)] were separately dissolved in a 1 M NaCl solution of PBS buffer adjusted at pH 7 (10^{-2} M). The polyelectrolytes were combined in a 1:1 ratio of chargeable monomer units (total chargeable monomer concentration of 0.12 mol.L^{-1}). The homogeneous mixture was further dialysed (3.5 kDa cut-off regenerated cellulose membrane) for 4 hours against 0.5 M NaCl PBS buffer (pH 7). Sodium metaperiodate (NaIO₄) was then added to the dispersion (inside the dialysis bag) at a ratio 1:2 compared to the catechol units to induce the oxidation-mediated catechol dimerization and form covalent crosslinks between associated chains. Then, the medium was dialysed against 10^{-2} M PBS buffer at pH 7 and finally against deionized water. The dialysis process was continued until the conductivity of the medium inside the bag matched the one of deionized water (10 μS/cm). The pH was continuously controlled to be 7 during the whole dialysis process. Finally, the resulting C3Ms were freeze-dried and stored as powder for further use.

Combination of DLS measurements and cryo-TEM imaging showed that the formed c-C3Ms did not disassemble even at 1 M NaCl thanks to the covalent crosslinking of the complex coacervate core (Figure S15).

**Figure S19.** (a) Average hydrodynamic diameter and light-scattering intensity of a c-C3Ms dispersion in H₂O in function of the NaCl concentration from 0 to 1 M. (b) Size distribution of the c-C3Ms at 0 M and 1 M NaCl in H₂O measured by DLS. Cryo-TEM images of c-C3Ms at (c) 0 M NaCl and (d) 1 M NaCl in H₂O. Scale bars are 100 nm.
11. pH and temperature responsiveness of the emulsions

**Figure S20.** Average hydrodynamic diameter and light-scattering intensity of a C3Ms dispersion in H₂O at 0 M NaCl in function of (a) the pH and (b) the temperature.
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