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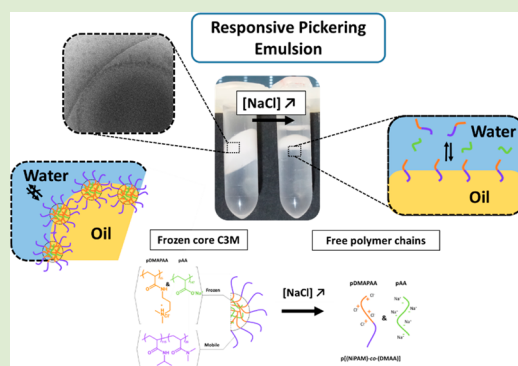


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Supporting Information

ABSTRACT: Frozen complex coacervate core micelles (C3Ms) were developed as a class of particle stabilizers for Pickering emulsions. The C3Ms are composed of a core of electrostatically interacting weak polyelectrolytes, poly(acrylic acid) (pAA) and poly-(dimethylaminopropylacrylamide) (pDMPAA), surrounded by a corona of water-soluble and surface active poly(*N*-isopropylacrylamide) (pNiPAM). Mixing parameters of the two polymer solutions, including pH, mixing method, charge ratio, and salinity of the medium, were carefully controlled, leading to monodisperse, colloiddally stable C3Ms. A combination of dynamic light scattering and proton nuclear magnetic resonance experiments showed that the C3Ms gradually disassembled from a dynamically frozen core state in pure water into free polyelectrolyte chains above 0.8 M NaCl. Upon formulation of dodecane-in-water emulsions, the frozen C3Ms adsorb as particles at the droplet interfaces in striking contrast with most of the conventional micelles made of amphiphilic block copolymers which fall apart at the interface. Eventually, increasing the salt concentration of the system triggered disassembly of the C3Ms, which led to emulsion destabilization.



Complex coacervate core micelles (C3Ms), also named polyion complex micelles (PICs), are a particular class of colloids which have been investigated for over three decades for applications ranging from protein encapsulation^{1,2} to sensing^{3–6} to surface modification.^{7,8} C3Ms consist of a core composed of electrostatically interacting oppositely charged polyelectrolytes thermodynamically favored by a combination of Coulombic attraction and entropy gain through counterion release surrounded by a corona usually composed of a neutral water-soluble polymer preventing macroscopic phase separation.^{9–11} The intrinsic supramolecular nature of the interactions (assuring the cohesion of the C3Ms'core) renders the structure both dynamic and responsive. Indeed, in the same way as macro-sized complex coacervates, C3Ms exhibit salt-responsive properties.^{12,13} Upon increasing the salt concentration of the medium, the driving force for micellization decreases, and the micelle's core transitions from a relatively rigid, nondynamic state to a swollen, dynamic, and deformable state at the same time as the aggregation number decreases. Eventually, above a critical salt concentration value (CSC), the micelles fall apart into a homogeneous solution of free polymer chains.^{14–17} As a consequence, C3Ms can be distinguished from conventional surfactant or amphiphilic block copolymer micelles as for low enough ionic strength, when the C3M core is rigid enough, their presence in solution is no longer dependent on the overall polymer concentration.^{12,18} In other words, the concept of

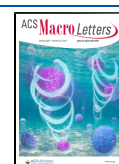
critical micellar concentration is not applicable anymore, and the C3Ms can actually be considered as inert colloidal particles. The particulate nature of C3Ms and the salt-activated drastic structural change render them good candidates as an emulsifier in responsive Pickering emulsions.

Pickering emulsions are a special class of emulsions for which the drops of the dispersed phase are stabilized with adsorbed nanoparticles.^{19–21} The particles are considered to be irreversibly adsorbed as the energy necessary to desorb them from the interface is usually several orders above the thermal energy.²² The excellent kinetic stability of Pickering emulsions originates from this irreversible adsorption, making them highly interesting for applications in catalysis, tissue engineering, and drug delivery.²³ Up to now, a wide variety of particles have been successfully used to stabilize emulsions whether it is inorganic, organic (latexes, microgels, and cross-linked amphiphilic block copolymer micelles), or even biopolymer (e.g., pollen) particles.^{24–30} Destabilization of these emulsions can be triggered by an external stimulus which usually relies on

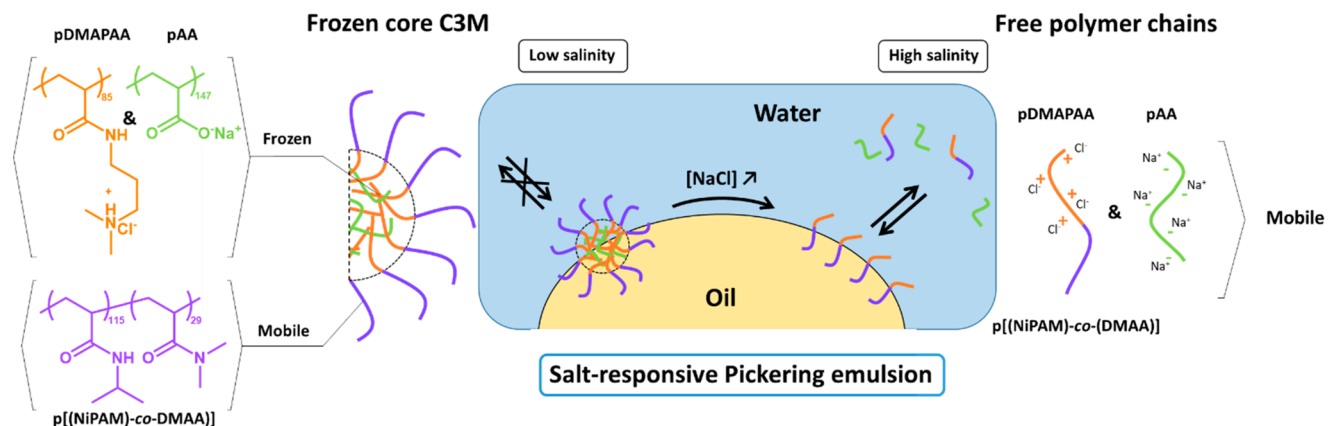
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Scheme 1. Scheme for Complex Coacervate Core Micelle Disassembly-Induced Destabilization of Pickering Oil-in-Water Emulsion



modification of the wetting properties of the particles and, in more scarce but not less elegant examples, on their deconstruction/solubilization.^{31–34} However, for the particular case of micelle-stabilized emulsions, the cross-linked nature of the particles' core prevents their triggered destabilization. To the best of our knowledge, the use of stimuli-responsive frozen micelle particles to develop salt-responsive Pickering-type emulsions has never been reported in the literature. In the present article, we report on the chemical design of complex coacervate core micelles (C3Ms) made of an electrostatically interacting poly(acrylic acid sodium salt) homopolymer and poly[(*N*-isopropylacrylamide)-*co*-(dimethyl acrylamide)]-*b*-poly(dimethylaminopropylacrylamide) (p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAA) block copolymer, allowing us to stabilize oil-in-water emulsions (Scheme 1). In pure water, we show that the core of the C3Ms can be considered dynamically frozen, preventing its disassembly at the interface of dodecane drops in water. We demonstrate that an increase in salinity represents an elegant and easy trigger to open up the C3Ms in water or at the oil–water interface, leading to a salt-responsive Pickering dodecane-in-water emulsion. This trigger represents a mild switch applicable to systems where on-demand emulsion destabilization is necessary without having to resort to harsh pH or temperature conditions.

The polyelectrolyte polymer chains were synthesized by RAFT polymerization. The p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAA diblock copolymer was obtained by extending the p[(NiPAM)-*co*-(DMAA)] macro-RAFT agent with DMAPAA, while pAA was obtained after acid deprotection of poly(*tert*-butyl acrylate) (Figures S1–S5).³⁵ Size exclusion chromatography and ¹H NMR were used to determine the polymer mass and dispersity ($M_{w,diblock} = 27.6 \text{ kg mol}^{-1}$, $D_{diblock} = 1.4$ and $M_{w,pAA} = 18.1 \text{ kg mol}^{-1}$, $D_{pAA} = 1.2$, Figures S1–S5). pNiPAM was selected as the corona because of its ability to stabilize emulsions due to its intrinsic surface-active properties.³⁶ Because of the salt-sensitive LCST behavior of pNiPAM in water, 20 mol % of DMAA was randomly copolymerized with NiPAM to ensure complete water solubility of the corona over the range of salt concentrations investigated (from 0 to 1 M NaCl) at the working temperature of 21 °C (Figure S6).^{37–39} pAA and pDMPAA are weak polyelectrolytes with an apparent pK_a of 5.3 and 8.8 (Figure S7), respectively, which have been successfully used to develop macroscopic complex coacervates.⁴⁰

p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAA was combined with pAA at pH 7 and a 1:1 stoichiometric ratio of chargeable monomer units in the medium, which are optimal conditions to fully complex the polyelectrolytes (Figure S8).⁴¹ Full complexation of both polyelectrolytes is of highest importance in our study as any imbalance of charge has been shown to lead to either extra free uncomplexed polymer chains in the medium or so-called “overcharging” of the core of the C3Ms.^{42,43} Both of these configurations are considered to be detrimental as, in the former case, additional free polymer chains could adsorb by themselves at oil–water interfaces even in the presence of C3Ms, and in the latter case, the overall charge of the core could favor its hydration and prevent it from being dynamically frozen. When mixed directly in pure water, particle formation was observed with an average hydrodynamic diameter measured by DLS of $36 \pm 5 \text{ nm}$ (Figure S9a) and a scattering intensity significantly higher as compared to the scattering intensity of free polyelectrolytes in solution (Figure 1a). However, when mixed at 1 M NaCl, no particle formation was discernible due to the screening of the electrostatic interactions, and the scattering intensity was comparable to a single polyelectrolyte solution (Figure 1a). It is worth noting that no sedimentation or macroscopic phase separation was observed for these samples, indicating an efficient stabilization of the complexes by the water-soluble corona at room temperature. After defining the salt concentration range where the coacervation is observed, the mixing protocol of both polyelectrolytes was investigated. The polyelectrolytes were either mixed directly in pure water or dialyzed against water from 1 to 0 M NaCl (direct dialysis) with or without the introduction of an intermediate step at 0.5 M NaCl (step dialysis). From a combination of DLS and cryo-TEM analysis, we found that fast formation of the micelles leads to a high polydispersity (Figure 1b and 1c and Figure S9). The step dialysis process resulted in thermodynamically stable micelles with low polydispersity ($D_h = 61 \pm 3 \text{ nm}$, $PDI < 0.1$) while the direct dialysis, identical to the direct mixing, was prone to form kinetically trapped configurations of the micelles with uneven size distribution ($PDI > 0.1$ or 0.2).⁴⁴ This last observation is actually a valuable hint which points out that at a low enough salt concentration the core of the micelle is dynamically frozen.

The frozen or dynamic nature of the core of the C3Ms can be probed by a combination of DLS and ¹H NMR measurements as a function of the salt concentration of the medium. Figure 2a shows the evolution of the average

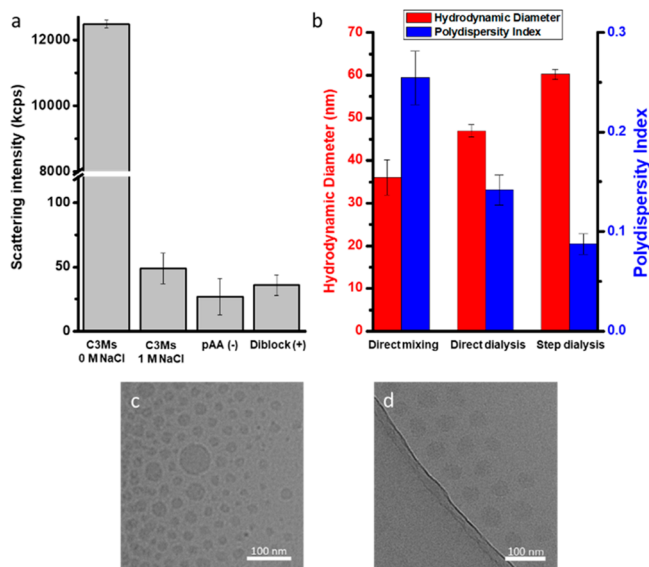


Figure 1. (a) Light-scattering intensity of combined pAA, polyanion, and p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAPAA, the polycation diblock, at 0 or 1 M NaCl and of single polyelectrolytes in water at pH 7 at a ratio (-):(+) = 1:1. (b) Average hydrodynamic diameter and polydispersity index of the C3Ms formed by direct mixing, direct dialysis, or step dialysis measured by DLS. Cryo-TEM images of C3Ms formed by (c) direct dialysis and (d) step dialysis. Scale bars are 100 nm.

hydrodynamic diameter of the C3Ms and of the light-scattering intensity from 0 to 1 M NaCl. From 0 to 0.8 M NaCl, a clear decrease in scattering intensity from around 15 000 kcps to almost 0 is observed. This decrease is a clear indication that highly scattering C3M nanoparticles gradually transition into low-scattering free polymer chains. In parallel, the value of the hydrodynamic diameter of the micelles below 0.5 M NaCl remains constant. A similar behavior has been observed by van der Kooij et al. for C3Ms made of poly(acrylic acid) (PAA) and poly(*N*-methyl-2-vinylpyridinium)-*b*-poly(ethylene oxide) (PM2VP-*b*-PEO) with polyelectrolytes of different molar masses.¹² This can be explained by the fact that while water penetrates into the micelles, inducing a decrease of the mismatch of refractive index between the dispersing medium and the particle and possibly a swelling, polyelectrolyte chains also get expelled, decreasing the aggregation number of the particles and consequently their size. Above 0.6 M, the scattering is so low that hydrodynamic diameter measurements become inaccurate and not reliable. In addition, at 0 M, the C3Ms are still present at extremely low concentration (0.01 mg mL⁻¹, 2×10^{-5} M chargeable monomer units), ruling out the notion of critical micellar concentration at such low salinity (Figure S10).¹⁸ Besides the DLS measurements, the evolution of ¹H NMR spectra with increasing salt concentration shows that the disassembly of the C3Ms is a gradual process (Figure 2b and Figure S11). At 0 M NaCl, the spectrum of the C3Ms superimposes with the one of the p[(NiPAM)-*co*-(DMAA)] corona, apart from the peak corresponding to the CH₃ groups of the pDMPAPAA which is broadened but still visible due to the fast internal rotation around the C–N–C axis (Figure 2c and Figure S12a).⁴⁵ In other words, at 0 M NaCl, the segmental mobility of the polyelectrolytes composing the core of the C3Ms is low enough to be considered as immobile or frozen in the time

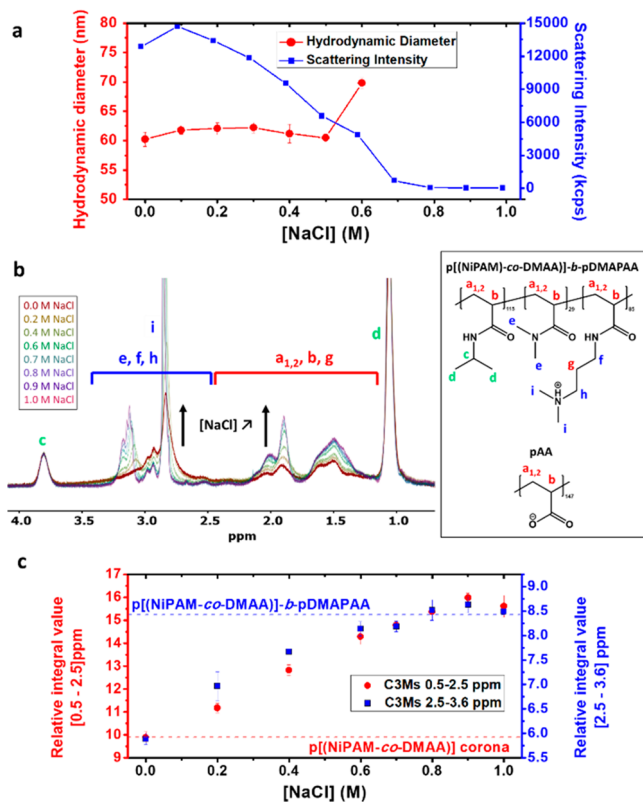


Figure 2. (a) Average hydrodynamic diameter and light-scattering intensity of a C3M dispersion in H₂O and (b) ¹H NMR spectra of a C3M dispersion in D₂O as a function of the NaCl concentration from 0 to 1 M (both at C_{C3M} = 0.5 mg mL⁻¹). (c) Evolution of the integral values of the chemical shift regions at 0.5–2.5 ppm (red) and 2.5–3.6 ppm (blue) and the methine peak of the NiPAM repetitive units (labeled c) being the reference. The red dotted line is indicative of the integral value in the range 0.5–2.5 ppm of the p[(NiPAM)-*co*-(DMAA)] corona. The blue dotted line is indicative of the integral value in the range 2.5–3.6 ppm of the p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAPAA diblock.

scale probed by ¹H NMR (tens of microseconds).⁴⁵ Upon increasing the salt concentration, the peaks related to the pAA and pDMPAPAA are recovered, and at 1 M NaCl, the spectrum of the dismantled C3Ms superimposes with the combined spectra of p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAPAA and pAA in a 1:1 ratio (Figure 2c and Figure S12b). These results unambiguously prove that the dynamics of the core of the C3Ms are drastically decreased at low salt concentrations, enabling the micelles to be used as a particle emulsifier.

Figure 3a shows dodecane-in-water emulsions stabilized by (i) C3Ms, (ii) p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAPAA, or (iii) pAA in pure water, all at pH 7 and 21 °C just after emulsification. The emulsions formulated with the C3Ms and the diblock copolymer show creaming due to the difference in density between dodecane and water. In addition, the diblock-stabilized emulsion shows some phase separation. This behavior is in agreement with the fact that both the diblock and the C3Ms spontaneously adsorb at the dodecane/water interface (Figure S13a). In addition, it is worth noting that the emulsion formulated with the C3Ms is highly flocculated, which is not the case for the emulsion formulated with the diblock copolymer (Figure S13b). A possible explanation for this could be that C3Ms cause bridging of neighboring drops as previously observed for emulsions stabilized by pNiPAM

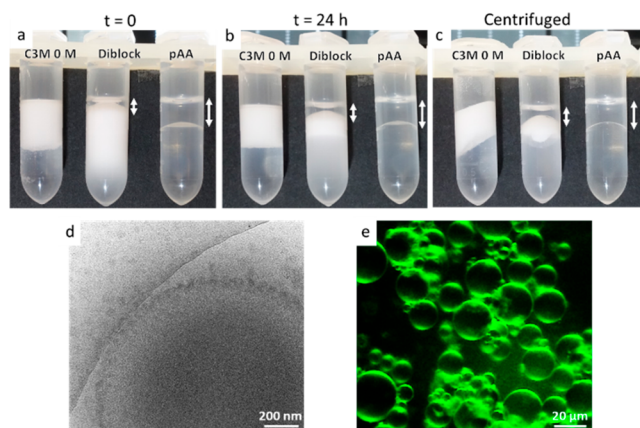


Figure 3. Dodecane-in-water emulsions in the presence of C3Ms, p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAA diblock, or pAA at a polymer concentration of 0.5 mg mL⁻¹ (a) directly or (b) 24 h after emulsification and (c) after centrifugation for 1 min at 1200g. The phase-separated dodecane is delimited by a white arrow. (d) Cryo-TEM image of dodecane (+10 v/v% isooctane) drops in water stabilized by adsorbed C3Ms (scale bar is 200 nm). (e) Fluorescence microscopy pictures of dodecane drops in water stabilized by fluorescent core C3Ms (scale bar is 20 μm).

microgels.⁴⁶ After 24 h, the emulsions formulated with pAA and with p[(NiPAM)-*co*-(DMAA)]-*b*-pDMPAA (albeit to a lesser extent), show phase separation between oil and water, indicating a lower kinetic stability (Figure 3b). Moreover, centrifugation of the emulsions at 1200g for 1 min confirms the higher stability of emulsions formulated with C3Ms (Figure 3c). These macroscopic observations show that the stabilizing mechanism is inherently different between C3Ms and individual polyelectrolytes in pure water. Indeed, it is well-known that particle-stabilized emulsions, i.e., Pickering emulsions, present high kinetic stability due to the irreversible adsorption of the particles at the oil–water interface in contrast to small molecules which present a dynamic adsorption mechanism which does not result in long-term stability of the emulsions.²¹ Besides this indirect proof that C3Ms adsorb at oil–water interfaces as micelles, we performed direct visual observations by cryo-TEM and confocal laser scanning microscopy (Figure 3d,e and Figure S14). On the cryo-TEM picture, a dodecane drop is visible that is dispersed in a vitreous water phase around which C3Ms are adsorbed. For the fluorescence microscopy imaging, we encapsulated a rhodamine B dye into the core of the C3Ms prior to micelle formation. In the images, we clearly see that the rhodamine B dye preferentially localizes at the oil–water interface of flocculated dodecane drops in water (Figure 3e). Consequently, the formulated C3Ms show the ability to adsorb at oil–water interfaces to stabilize emulsions without falling apart. In other words, the C3M core is frozen enough to prevent the disassembly into polymer chains as is usually observed for micelles made of amphiphilic polymers for which an extra covalent cross-linking step of the core is usually required to maintain the structural stability.

Finally, the salt-responsive behavior of the formulated Pickering emulsions was shown (Figure 4). By increasing the salt concentration of the medium up to 1 M NaCl, phase separation appeared after 24 h at rest and was accelerated by 1 min of centrifugation at 1200g (Figure 4a). To confirm that it is indeed the disassembly of the micelles at the oil–water

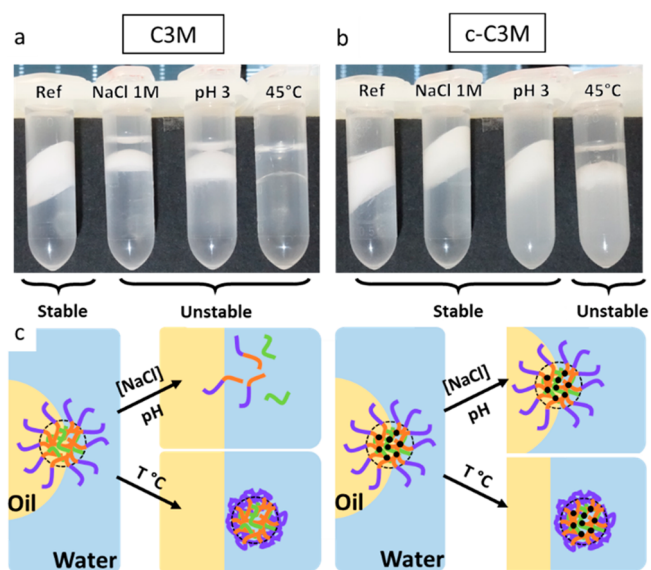


Figure 4. Dodecane-in-water emulsions in the presence of (a) C3Ms or (b) c-C3Ms at a polymer concentration of 0.5 mg mL⁻¹ after centrifugation for 2 min at 1200g (i) without any physicochemical modification of the medium, after adjusting (ii) the NaCl concentration to 1 M, (iii) the pH to 3, or (iv) the temperature to 45 °C. (c) Proposed mechanism for the salt-, pH-, or temperature-triggered emulsion destabilization of C3Ms and insensitivity for c-C3Ms.

interface which is the underlying mechanism of emulsion destabilization and not just an increase of osmotic pressure of the medium, we formulated emulsions with identical C3Ms but with a chemically cross-linked core (c-C3Ms), rendering the particles insensitive to an increase of salt concentration. The synthesis and characterization of these c-C3Ms are reported in Figures S15–S19. Figure 4b shows that the stability of the emulsions is conserved at 1 M NaCl and identical to the one formulated at 0 M NaCl. While salt addition represents an elegant way of destabilizing the formulated Pickering emulsions, the design of our system also allows the use of pH and temperature as triggers for emulsion destabilization (Figure 4a,b). Indeed, in the same way as salt, a decrease of pH to 3 leads to disassembly of the C3Ms as pAA is not charged anymore (Figure S20a). On the other hand, an increase of the temperature above the cloud point temperature of the pNiPAM-based corona induces a collapse of the corona and subsequent aggregation of the C3M particles (Figure S20b) followed by emulsion destabilization.⁴⁷

As a conclusion, we showed the possibility to design complex coacervate core micelles exhibiting core dynamics which can be controlled by the salt concentration of the medium. At low salt concentration, the dynamics of the core are slow enough (due to the strong polyelectrolyte–polyelectrolyte complexation) to ensure that the micelles do not disassemble even at very low polymer concentration. The frozen core C3Ms were observed to successfully adsorb at the oil–water interface without disassembling. In addition, no extra cross-linking step was needed, in striking contrast to usual micelles formed from amphiphilic polymers. Moreover, the formulated emulsions exhibited the classical characteristics of particle-stabilized Pickering emulsions, i.e., high kinetic stability and flocculation. In the end, we proved that an increase of the ionic strength as well as a pH change of the

medium are convincing triggers to transition from particle- to polymer-stabilized emulsions, inducing a decrease of emulsion stability, and eventually macroscopic phase separation between oil and water. We also showed that an increase of the temperature above the cloud point temperature of the polymer chains constituting the corona triggers emulsion destabilization by a different mechanism not discussed here. In our study, we chose to design micelles in the most favorable way using pNiPAM for the corona which is proven to be very effective for emulsion stabilization. From a fundamental viewpoint, it could be interesting to vary the amphiphilicity of the polymer composing the corona in order to evaluate its impact on the ability of the C3Ms to adsorb at oil–water interfaces. In a more applied vision, our system could be applicable to develop degradable functional emulsions or foams where one expects a triggered phase separation between oil and water for drug delivery purposes or for biological organism cultures. In the latter cases, our approach can be generalized to fully biosourced and biocompatible polymers already used in complex coacervate systems (e.g., chitosan, alginate, and hyaluronic acid).

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsmacrolett.1c00647>.

Materials, instrumentation, synthesis and protocols, cloud point temperature of pNiPAM-based polymer chains, titration of pAA and p[(NiPAM)-co-(DMAA)]-b-pDMAAPAA, optimum mixing ratio between polyelectrolytes, particle size depending on the mixing protocol, dynamics of the core of the C3Ms, emulsions, and synthesis and characterization of chemically cross-linked core C3Ms (c-C3Ms) (PDF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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