



Stimuli responsive Janus microgels with convertible hydrophilicity for controlled emulsion destabilization†

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Although the utilization of rigid particles can afford stable emulsions, some applications require eventual emulsion destabilization to release contents captured in the particle-covered droplet. This destabilizing effect is achieved when using stabilizers that respond to controlled changes in environment. Microgels can be synthesized as stimuli responsive polymeric gel networks that adsorb to oil/water interfaces and stabilize emulsions. These particles are commonly hydrogels that swell and collapse in water in response to environmental changes. However, amphiphilic functionality is desired to enhance the adsorption abilities of these hydrogels while maintaining their stimuli responsivity. Microfluidic techniques are used to synthesize Janus microgels with two opposing stimuli responsive hemispheres. The particles have a temperature responsive domain connected to a pH responsive network where each side changes its hydrophilicity in response to a change in temperature or pH, respectively. The Janus microgels are amphiphilic in acidic conditions at 19 °C and alkaline conditions at 40 °C, while the opposite conditions cause a reduction of the amphiphilicity. By stabilizing emulsions with these dual responsive microgels, “smart” droplets that respond to environmental cues are formed. Emulsion droplets remain stable with smaller diameters when aqueous solution conditions favor amphiphilic particles yet, coalesce to larger droplets upon changing pH or temperature. These responsive Janus microgels represent the advancing technology of responsive droplets and demonstrate the applicability of microgels as emulsion stabilizers.

Microgels, absorbent crosslinked polymer particles, can be used as emulsion stabilizers because of their energetically favorable adsorption at the interface of oil and water. The formation of

mechanically robust microgel monolayers at droplet interfaces is made possible by the particle's deformability in its swollen state where most of its hydrophilic bulk resides in the water phase and a small, slightly collapsed fraction protrudes into the oil phase.^{1,2} These swollen polymeric gels can be chemically designed to swell and de-swell upon changes in their environment such as temperature or pH that could enable stimuli-responsive particle covered emulsion droplets. Some temperature sensitive microgels swell at room temperature and shrink above their volume phase transition temperature (VPTT), leading to a large change in size. One of the most common temperature responsive microgels is poly(*N*-isopropylacrylamide) (PNIPAM). These hydrogels are usually prepared using *N,N*-methylenebisacrylamide as a cross-linker and can be modified by adding functional co-monomers. Swelling by water allows deformation and interpenetration at the surface of the hydrogel, which affects the particle–particle interaction while the microgel's porosity affects the hydrodynamic interactions. Alternately, with proper copolymerization and incorporation of acidic or basic co-monomers within the PNIPAM network, temperature/pH-responsive microgels are formed. These microgels can be modified to have charged groups concentrated at their core or surfaces in a core–shell microgel architecture or randomly distributed within the network.^{2–4} The temperature-responsive and or temperature/pH-responsive hydrogels can adsorb to oil water interfaces *via* changes in hydrophilicity throughout the overall particle volume.

It is well understood, however, that emulsion stabilizers that adsorb at the liquid–liquid interface with a contact angle closest to a 90°, maximize the desorption energy and subsequently enhance emulsion stability.^{5,6} A particle having distinct hydrophilic and hydrophobic sides resembling the molecular surfactant amphiphile may therefore enhance emulsion stabilization. For this reason, an amphiphilic microgel is desired. While microgel surface modification has been attempted *via* emulsion templating where one side of the hydrogel is hydrophobically functionalized while anchored to an oil water interface, their ability to form stimuli responsive microgel covered emulsion droplets was not demonstrated due to low yields and microgel rotation at the liquid–liquid interface.^{7,8}

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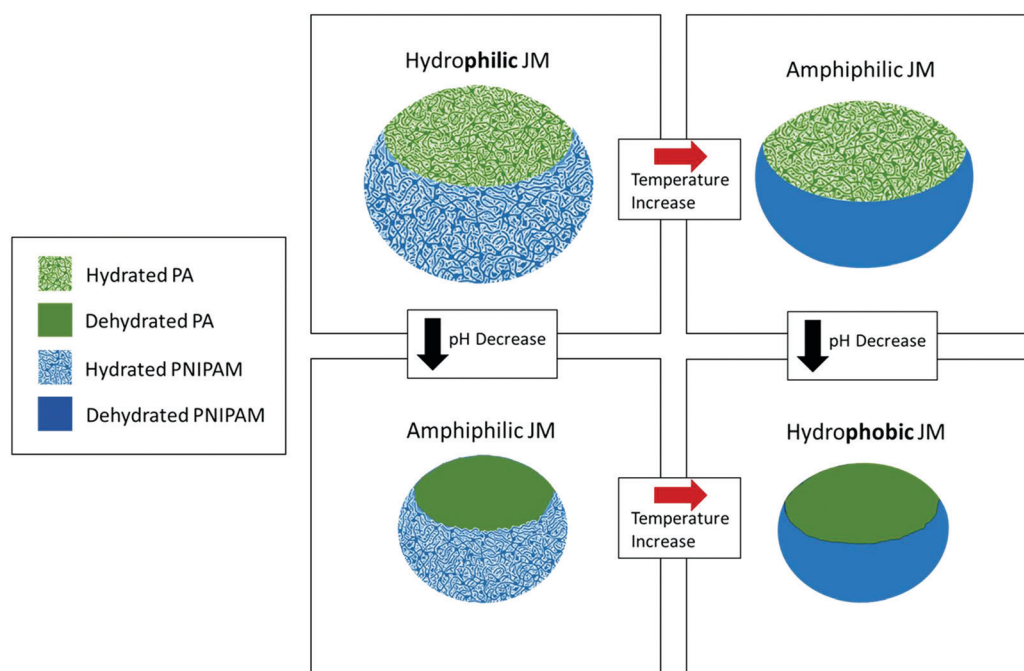
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Microfluidic techniques have been used to synthesize Janus droplets with two chemically distinct liquid sides.^{9,10} Janus particles can be formed by crosslinking the droplets *via* photopolymerization affording tunability of particle polydispersity, size, and ratio of hydrophilic to hydrophobic surface.¹¹ The work herein, presents the successful fabrication of a Janus microgel particles (JM) with contraphilic hemispheres: one composed of temperature responsive PNIPAM and the other of a pH responsive poly(acid) (PA) polymer network, where both can switch between hydrophilic and hydrophobic with orthogonal environmental triggers. Using separate temperature and pH polymer networks on different sides of a microgel yields a unique particle with the ability to be completely hydrophilic, hydrophobic, or amphiphilic depending on the environment. Hydrophilicity can be tuned by changing temperature and or pH to selectively swell or collapse a single JM hemisphere, as seen in Scheme 1. Both JM sides are hydrophilic at room/low temperature and basic pH conditions. Upon increasing the temperature, the PNIPAM side will dehydrate rendering the JM amphiphilic. Alternately, if the low temperature is held constant and the pH conditions become acidic, only the PA is dehydrated, also yielding an amphiphilic JM. At elevated temperatures and acidic conditions, the JM is hydrophobic as both polymeric hemispheres are collapsed. Because environmental changes can tune the hydrophilicity of both Janus sides, JM stabilized emulsions become stimuli responsive as the particle interfacial adsorption abilities are altered.

To form the stimuli-responsive amphiphilic Janus microgels (JM), two separate polymer solutions, one temperature responsive and one pH responsive, were gelled and fused together *via*

photopolymerization in a PDMS microfluidic drop-making device, as shown in Fig. 1a. The temperature responsive polymeric network side of the JM is synthesized from a precursor solution of 22 wt% *N*-isopropylacrylamide (NIPAM), 7 wt% polyethylene glycol diacrylate (PEGDA) as the crosslinker, 70 wt% water, and 1 wt% Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) as the photo initiator, corresponding to a crosslinking of 5 mol% (PEGDA-to-PNIPAM). To form the pH responsive polymeric network side, we employ multifunctional thiols and olefins as monomers in a thiol-ene step-growth polymerization for highly crosslinked gels as described in earlier work.¹² The tetrafunctional thiol, pentaerythritol tetra(mercaptopropionate) (PETMP) (56 wt%), is polymerized with the difunctional comonomers triethyleneglycol divinylether (TEGDVE) (24 wt%) and pentenoic anhydride (PenAn) (20 wt%) as a permanent cross-linker and transient cross-linker/acid source, respectively to form a hydrophobic poly(anhydride) side. Degree of crosslinking of the poly(acid) system after hydrolysis is 35 mol% (TEGDVE-to-pentanoic acid). These chemically different polymer solutions are pumped through microchannels and, upon contact, are sheared into small droplets by an immiscible fluorinated oil as seen in Fig. 1a. The thiol-ene monomers are water immiscible liquids and do not mix with the aqueous polymer solution during or after contact. The Janus droplets flow further downstream where they are exposed to ultra violet light to induce photopolymerization forming Janus particle gels with one PNIPAM network side and one crosslinked poly(anhydride) (PAN) side.

The particles are then washed with pure HFE 7500 engineered fluid and water to remove residual fluorinated surfactant and



Scheme 1 Janus microgel particles with contraphilic poly(NIPAM) and poly(acid) sides. Both Janus particle sides are hydrophilic at high pH low temperature. At high pH high temperature, the poly(acid) side remains hydrated while the poly(NIPAM) side is collapsed and dehydrated yielding an amphiphilic JM. At low pH low temperature, the poly(acid) side is protonated and dehydrated while the poly(NIPAM) remains fully hydrated rendering the JM amphiphilic. At low pH high temperature both JM sides are dehydrated.

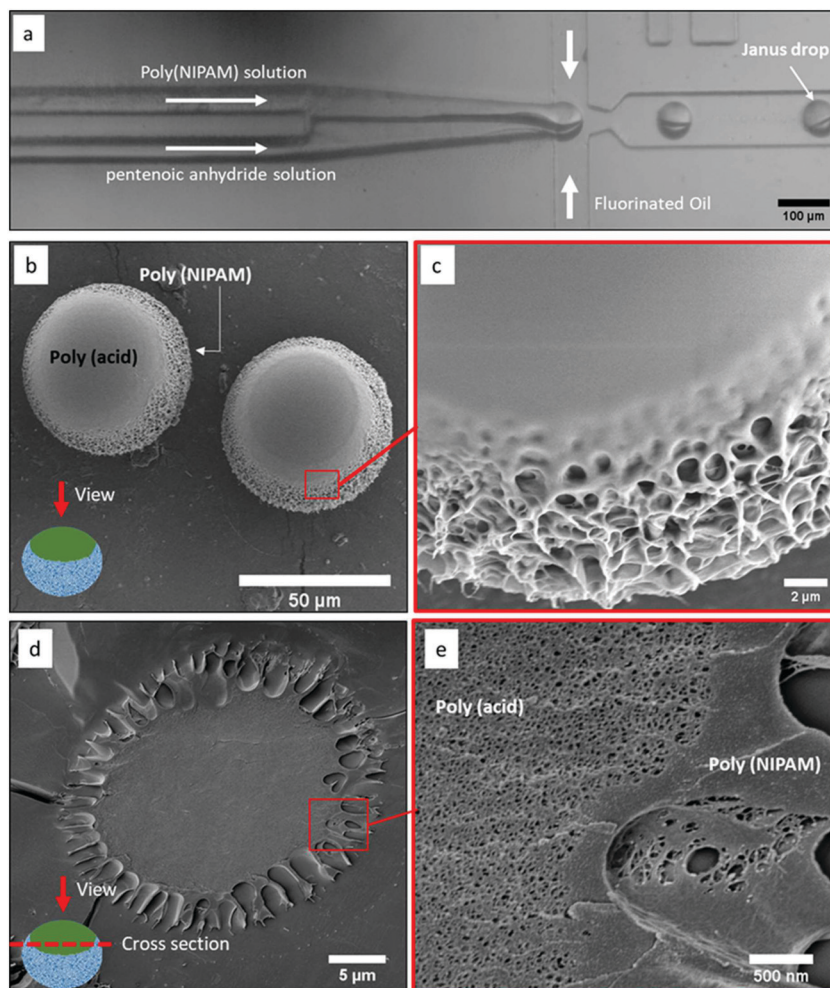


Fig. 1 Janus microgel particles with poly(NIPAM) side and poly(acid) side via Janus droplet templating. (a) Janus droplet formation of polymer precursor solutions via shear by fluorinated oil in microfluidic flow-focusing device. (b) SEM image of the JM showing smooth PA surface and porous PNIPAM periphery. (c) Magnified SEM image of the intersection of polymer networks showing the distinct transition from collapsed (smooth) PA to swollen (porous) PNIPAM network. (d) Cryo-SEM images of the internal fracture surface of the JM in water. (e) Magnified cryo-SEM image of the relative pore sizes in each polymer network at their intersection in water.

unreacted monomers, respectively. The as synthesized PNIPAM/poly(anhydride) particles are inherently amphiphilic with a temperature responsive hydrophilic side (PNIPAM) and a completely hydrophobic crosslinked PAN network side. To achieve amphiphilic temperature/pH responsive JMs, the hydrophobic poly(anhydride) side is hydrolyzed in alkaline solution. The transient anhydride monomer hydrolyzes in pH 11 aqueous solution to form polar and pH-responsive carboxylic acid functional groups tethered to the polymeric network increasing its hydrophilicity (Fig. S1, ESI[†]). Microgel poly(anhydride) sides are fabricated with molar comonomer ratios 1 : 1 between the permanent crosslinking agent TEGDVE and the hydrolyzable PenAn. After hydrolysis of the pentenoic anhydride units, the microgel poly acid side is composed of a pentanoic acid concentration of 0.25% [moles to PA-side network volume (no water)] based on complete hydrolysis of the anhydride in high alkaline conditions. Hence, at pH 11 and a temperature above 37 °C (volume phase transition temperature of NIPAM), a JM particle is amphiphilic with the poly(acid) (PA)

being the hydrophilic part and PNIPAM being the hydrophobic side, as illustrated in Scheme 1. The JM has an “embedded” shape where the PNIPAM poses as a surrounding polymeric network engulfing a PA sphere. Fig. 1b–e show the stimuli responsive JMs with the two chemically and structurally distinct sides of the particle. Fig. 1b shows a scanning electron microscopy (SEM) image highlighting the distinct two-sided shape and Janus surface heterogeneity of a JM removed from pure water (pH ~ 6). The dense PA phase is on the top side of the particle while the PNIPAM hemisphere is on the bottom. Fig. 1c shows a magnified view of the transition area from the dense hydrophobic poly(acid) to the porous poly(NIPAM). This shows the successful synthesis of microgel particles with completely different and orthogonally stimuli-responsive polymeric network chemistries on two separate sides, both of which switch their hydrophilicity with independent triggers. To gain insight towards the JM morphology and the differences in polymer networks in water, cryo-SEM of an internal fracture surface of an

amphiphilic Janus microgel in water has been performed. Fig. 1d shows the cryo-fractured cross-section of a JM where the more porous PNIPAM periphery is seen on the edges. At the magnified interface of the polymeric networks in Fig. 1e, a sharp transition is evident from a very dense cross-linked poly(acid) network to the much more porous poly(NIPAM) matrix at the edges.

PNIPAM is a well-known thermo-responsive polymer that, when co-polymerized with PEGDA, dehydrates above 37 °C to a collapsed state and re-swells when cooled below this temperature.¹³ Furthermore, the weak acidity of the carboxylic acid units renders the Janus microgel PA side reversibly responsive to changes in pH. At high pH, the poly(acid) network is charged due to the deprotonation of its acid groups, causing it to swell significantly with water. At low pH, protonation of the carboxylic acid causes hydrogen bonding within the uncharged polymer network, collapsing and deswelling the gel network. Hence, the degree of swelling of the JM poly(acid) side, and subsequent size of the JM, depends on the pH of the aqueous environment.

We use an inverted confocal microscope incased in a temperature-control box to image the microgels in different pH and temperature conditions as seen in Fig. 2. The inverted configuration views the particles as if the observer is under the sample. A difference in polymer network density in the absence of water may contribute to the microgels' consistent orientation. In the absence of water, the densities of the PNIPAM network and poly(acid) network are 1.1 and 1.15 g mL⁻¹ respectively. At room temperature pH 4 conditions (Fig. 2c), the PA is dehydrated and may have a larger density than the water filled PNIPAM network. At elevated temperature in pH 4 condition, we can assume the PNIPAM has dehydrated but its network density is still lower than the PA. At room temperature pH 11 conditions, both sides are hydrated yet the particles maintain this same orientation. We speculate that the heavier polymer network dominates. At elevated temperature in pH 11 conditions, this effect may still exist. The PNIPAM side of the microgel sits as a visibly larger lobe on the opposite side of the microscope objective, yet the full circumference of both polymer networks can be seen. We relate the swelling of the JM hemispheres to their apparent diameter changes in response to their environment when observed down the symmetry axis of the JM particle. Roughly 30 particles were measured and averaged where the PNIPAM diameter was taken as the length from edge to edge of the entire particle, and polyacid diameter was measured from beginning of the darker lobe to its end. Stimuli response is quantified in Fig. 2 where projected hemisphere diameters along the particle's symmetry axis for each side is measured in response to temperature and pH changes. Environmental pH was tuned using BDH pH reference standard buffers to demonstrate effective swelling and collapsing of the poly(acid) network. At pH 4, the PNIPAM and PA hemispheres have distinctly different diameters at any temperature. At 19 °C, the PNIPAM is swollen with water (51 µm diameter) while the PA is dehydrated and collapsed due to protonation (41 µm diameter). Upon increasing the system temperature to 40 °C, the PA side remains relatively unchanged while the PNIPAM shrinks to 48 microns. The JM increases in size when removed from pH 4 to pH 11,

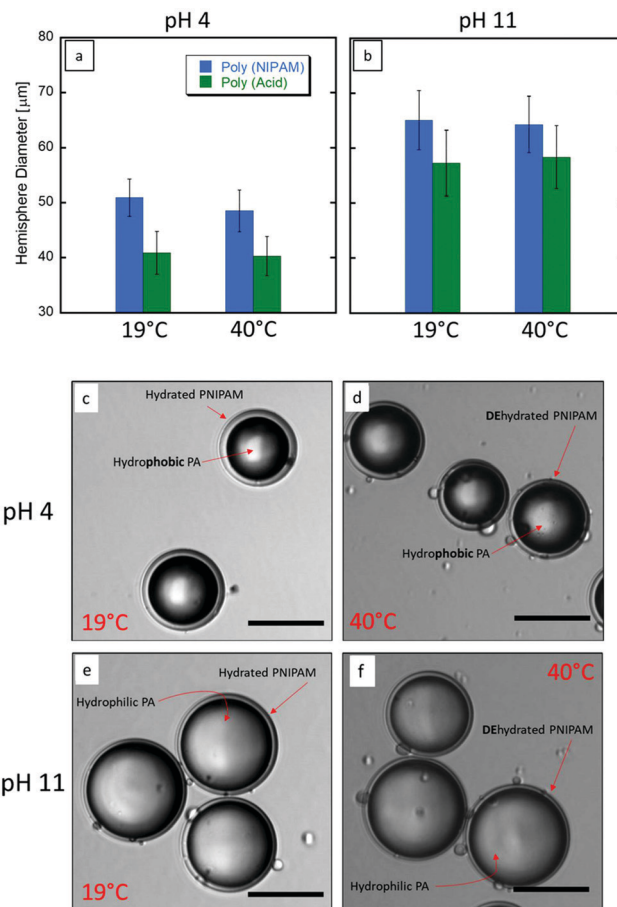


Fig. 2 Janus microgel hemisphere diameter as a function of temperature and pH. (a) average change in PNIPAM and PA hemisphere diameters in response to temperature in pH 4 aqueous solution. (b) Average change in PNIPAM and PA hemisphere diameters in response to temperature in pH 11 aqueous solution. (c) JMs in the amphiphilic state at pH 4/19 °C. (d) JMs in the hydrophobic state at pH 4/40 °C. (e) JMs in the hydrophilic state at pH 11/19 °C. (f) JMs in the amphiphilic state at pH 11/40 °C. Error bars represent standard deviation. Scale bars are 50 µm.

where temperature changes at pH 11 yield only a slight change in size. Particles can be completely hydrophilic or completely hydrophobic when both JM sides have the same functionality at specific environmental conditions. Both JM sides are hydrated in pH 11 solution at 19 °C as seen in Fig. 2e, while both sides are dehydrated in pH 4 water at 40 °C shown in Fig. 2d. When the JM sides have opposing functionalities (hydrophilic/hydrophobic), the particles are amphiphilic. In pH 11/40 °C water and pH 4/19 °C water as seen in Fig. 2f and c respectively: JMs have a collapsed and dehydrated poly(NIPAM) side with water swollen hydrophilic poly(acid) side in (Fig. 2f) and water swollen hydrated poly(NIPAM) side with collapsed hydrophobic PA side in (Fig. 2c). In all brightfield microscopy images, we see the full PA hemisphere circumference (the darker shaded circle inside the lighter circle) as well as the PNIPAM periphery (the lighter shaded circle on the outside of the darker circle).

At constant 19 °C, changing the JM environment from pH 4 to pH 11 results in a large increase in overall particle size, as seen quantitatively in Fig. 2a and b and qualitatively in Fig. 2c and e.

Because this transition is due to collapsing of only the PA network, such a dramatic decrease in JM size must be due to the “embedded” shape of the microgel particle where the PNIPAM sits around the bottom of the JM engulfing a PA sphere. Due to this particle shape, a size decrease in the engulfed PA sphere results in overall JM shrinkage while a size change in the surrounding/engulfing PNIPAM network has much less of an effect. This is consistent with the observation that at pH 11/19 °C, both JM sides are hydrated and swollen with water where upon increasing the temperature to 40 °C, there is a slight decrease only in the PNIPAM side while the overall JM size remains unaffected. The choice to use high alkaline conditions in this work are to assure complete hydrolysis of the anhydride and to achieve fast swelling and collapsing of the PA network. Future work will study the effects of alkalinity on pH response time at various microgel polyacid amounts (acidic nature) and polyacid volume size on the microgel (how much of the microgel is composed of the PA network).

When comparing hemisphere diameter changes in Fig. 2a, the swelling effects are not as significant between temperature changes at constant pH. The PNIPAM side of the Janus microgel particles show only a 5% decrease in hemisphere diameter from 19 °C to 40 °C in pH 4 water, while in pH 11 aqueous solution a 1.2% decrease in diameter is observed. This swelling effect may be due to the PNIPAM's restrictive contact with hydrated PA side preventing a dramatic size change near the tethered polymeric interfaces, as has been observed previously in multi-shell hollow PNIPAM nanogels.¹⁴ However, this small size change is measured by the visible PNIPAM periphery and may be misleading due to the JM orientation. It is possible that the temperature responsive hemisphere expands and shrinks both in the radial direction and in a direction normal to the JM polymeric interface. Upon hydration or dehydration, the PNIPAM hemisphere may respectively swell or collapse to a greater extent in areas furthest away from the polymeric intersection, which are not visible in the brightfield images due to the JM's orientation. However, the temperature responsive PNIPAM hemispheres do uptake and release water with temperature changes. This conclusion is corroborated by the swelling of PNIPAM-PEGDA microspheres of the same JM temperature-responsive-side composition in pH 4 and 11 aqueous solutions (Fig. S2, ESI†). Individual PNIPAM-PEGDA hydrogel beads synthesized using the same microfluidic technique as described above experienced a 37% decrease in diameter related to a 165% decrease in volume from 19 to 40 °C in pH 4 water. In pH 11 water, a 34% decrease in microsphere diameter is observed which is equal to a 137% decrease in volume. Because the hydrogel microsphere responds to temperature changes in high and low pH solutions, we can conclude that temperature also affects the analogous temperature responsive sides on the JM.

The amphiphilic Janus microgels in this work can be used to stabilize emulsions. The adsorption of microgels to oil/water interfaces can be attributed to their hydrophilicity. When a microgel is synthesized with both hydrophilic and hydrophobic monomers, the polymers are usually (1) randomly distributed through the network¹⁵ or (2) concentrated in the core or corona

of core-shell architecture¹⁶ where the particle can be considered amphiphilic. At the interface of oil and water, the polymer segments are able to orient toward their preferred fluid based on their hydrophilicity. However, this reorientation of chains is made possible due to the deformable nature of the microgel in the swollen state. Janus, or double sided, amphiphilic microgels would not require reorienting of polymer segments because the entire hydrophilic network is located on one side while the hydrophobic network is located on the other. Janus amphiphilic microgels adsorb to the oil/water interface when their predominantly hydrophilic polymer chains orient toward and penetrate the water surface while their predominantly hydrophobic chains move into the organic liquid phase. The stimuli responsive nature of the JMs however, give them the ability to destabilize these emulsions. Due to the large drop size of emulsions stabilized by the JMs, we are able to image the coalescence and growth of particle covered drops as the particles respond to environmental changes. Fluorinated oil (HFE 7500), commonly used in microfluidic applications as the continuous phase,^{17–19} is emulsified in aqueous medium by the amphiphilic Janus gels at 315 mg g⁻¹ particles to oil. The JMs are amphiphilic (1) in pH 4 aqueous solution at room temperature – PA (hydrophobic) and PNIPAM (hydrophilic) and (2) in pH 11 aqueous solution at 40 °C – PA (hydrophilic) and PNIPAM (hydrophobic). Oil in water droplets stabilized by the amphiphilic JMs at pH 4/room temperature spontaneously coalesce within minutes of increasing the temperature. As the temperature is increased, the PNIPAM side is dehydrated like the protonated and dehydrated PA side rendering the entire JM hydrophobic with less affinity for the oil water interface. As the adsorption abilities of the JMs decrease, the emulsion destabilizes and larger droplets form. The droplet coalescence continues for almost an hour as seen in Fig. 3a–c showing droplets of oil in pH 4 water stabilized by amphiphilic Janus microgels at 25 °C and the ensuing droplet coalescence when the temperature is ramped to 40 °C. Fig. 3a shows the oil in water droplets after 3 days with no coalescence before any temperature change. From Fig. 3a to b, the temperature is increased to 40 °C and we see the six separated drops in frame (a) become three separate drops in (b) after 16 minutes at the higher temperature. After 50 minutes at 40 °C, the four drops that existed in Fig. 3b coalesce to form two larger drops as seen in (c). The oil in water droplets, that were once kinetically stable for 3 days with amphiphilic particle covered surfaces, are destabilized within minutes upon temperature increase past the VPTT of PNIPAM due to a change to complete hydrophobicity of the entire JM.

Stable oil drops at pH 11/40 °C water also coalesce when cooled to room temperature. At the elevated temperature and pH 11, the JMs are in an amphiphilic state with a hydrophilic, deprotonated PA side, and a hydrophobic, dehydrated PNIPAM side. Upon cooling below the VPTT of PNIPAM, the entire JM turns hydrophilic with hydration of the PNIPAM, decreasing the particles' affinity to the oil–water interface, causing droplet coalescence. The stabilized emulsion at pH 11 and 40 °C and ensuing droplet coalescence due to cooling is shown in Fig. 3d–f. Fig. 3d shows oil in water droplets after 5 hours of no coalescence in the pH 11/40 °C water (JM amphiphilic state), while Fig. 3e

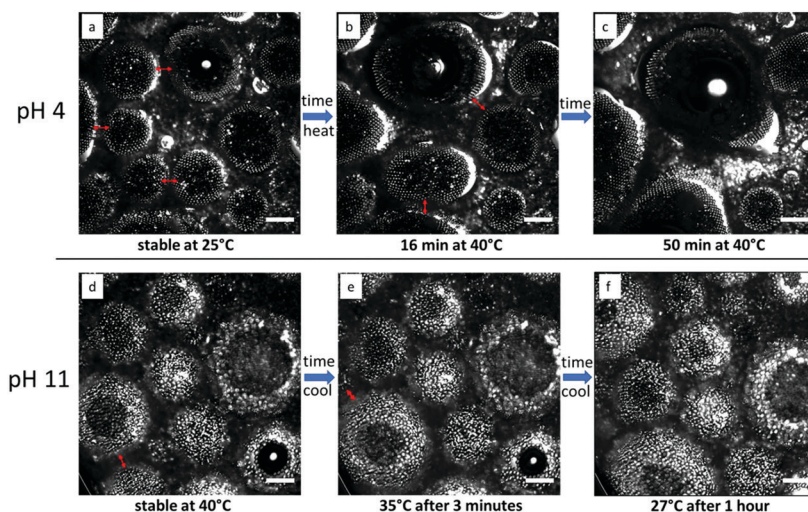


Fig. 3 Temperature response of JM stabilized oil in water emulsion droplets in aqueous solutions with different pH values. (a–c) The coalescence of oil-in-water (pH 4) droplets as temperature is increased to 40 °C. (d–f) The coalescence of oil-in-water (pH 11) droplets as temperature is decreased to 27 °C. The red double-sided arrows between droplets represent their eventual coalescence which will have fused in the following frame. All scale bars are 500 μm .

through Fig. 3f show the cooling effect on droplet coalescence. From Fig. 3d to e, the temperature decreases to 35 °C where after 3 minutes we see the coalescence of two drops into one. After 1 hour at 27 °C, the two drops that existed in Fig. 3e coalesce into one, seen in (Fig. 3f).

The oil in water emulsions stabilized by amphiphilic JMs (low pH low temperature) begin coalescence after 6 minutes at 40 °C (not pictured here), while droplets stabilized by amphiphilic JMs (high pH high temperature) begin coalescence after 3 minutes when the temperature has decreased to 35 °C. This shows a temperature triggered emulsion destabilization time on the scale of 10^2 seconds, making the JMs good candidates for controlled-release emulsion applications. When particles are in their amphiphilic state, they keep the oil in water droplets stabilized until a change in the environment triggers the decrease in particle amphiphilicity. Janus microgels are then less effective at adsorbing to the liquid–liquid interface and droplet coalescence occurs. This is further quantified in Fig. 4 where emulsion droplet diameter is measured as a function of its environment. When comparing droplet sizes for oil in pH 4 water at 19 °C to 40 °C, we see a large growth in diameter (101% increase), indicative of droplet coalescence and destabilization. The same is observed for oil drops in pH 11 water when temperature is changed from 40 °C to 19 °C (59% increase). When the JMs are amphiphilic in pH 4 or pH 11 water, stable drops of about the same size are formed.

As the temperature is increased to 40 °C, in the pH 4 system, or decreased to room temperature, in the pH 11 system, the particle sides gain similar lyophilicities. The direction of this solvent affinity (towards hydrophilic or hydrophobic) may be the reason oil droplets in pH 4 water seemingly grow larger upon temperature triggered destabilization than those in the high alkaline water as seen in Fig. 4. Fig. 4 shows the oil droplets sizes at the various pH and temperature conditions. The temperature induced droplet size change for pH 4 (101% size increase)

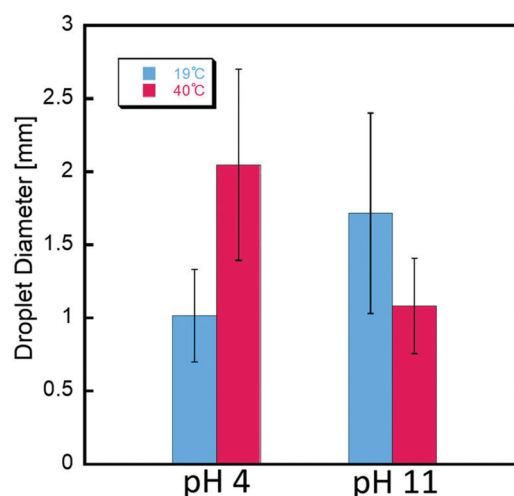


Fig. 4 Oil-in-water emulsion droplet diameter as a function of environmental pH and temperature.

and 11 (59% size increase) conditions are both significant at $p < 0.05$. If completely hydrophobic JMs move towards the interior of the drop (oil), the drops are less protected than when completely hydrophilic JMs move towards the continuous phase (water) while still being adsorbed at the interface. Amphiphilic Janus microgels in pH 4 water lose hydrophilicity in the PNIPAM side as the temperature is increased to 40 °C. Because the PA side is already hydrophobic due to the low pH, the JM refuses water as both sides are in the collapsed state. It may be easier for the now hydrophobic particle to be pushed into the oil away from the interface allowing uncovered oil surfaces to touch and join. In contrast, amphiphilic JMs in pH 11 water gain hydrophilicity in the PNIPAM side as the temperature is decreased from 40 °C. At the high pH, the poly(acid) is deprotonated, hydrophilic, and swollen with water. The decrease in temperature

triggers rehydration of the PNIPAM side, yielding a completely hydrophilic microgel swollen with water. Hydrophilic microgels (hydrogels) are well-known oil in water emulsion stabilizers owing to their soft features in the swollen state.^{1–3} While not as effective as in the amphiphilic state, the hydrophilic JMs at high pH low temperature move towards the continuous phase and act as the more familiar soft microgels that can anchor to an oil water interface. Therefore, for these oil in water emulsions, Janus balance switch from amphiphilic to hydrophobic affords greater destabilization in the form of triggered droplet coalescence than switching from amphiphilic to hydrophilic.

Conclusion

PDMS microfluidics was used to synthesis Janus amphiphilic microgels of poly(NIPAM) and poly(anhydride) separated polymeric networks. Upon hydrolysis of the poly(anhydride) hemisphere to a poly(acid) network, we gain temperature and pH responsive gel particles capable of stabilizing water and oil emulsions. Poly(NIPAM) serves as a thermo-responsive polymeric network while the poly(acid) responds to changes in solution alkalinity. A clear distinction from water solvated PNIPAM hydrogel to collapsed PA network can be seen in SEM images of the JMs removed from room temperature water at low pH. The Janus microgels are amphiphilic in two instances (1) at low pH low temperature, and (2) at high pH high temperature. At low pH in its amphiphilic state, increasing the temperature renders the JM hydrophobic where both particle hemispheres are collapsed and have decreased affinity for the oil water interface. At high pH in its amphiphilic state, decreasing the temperature renders the JM completely hydrophilic where both sides swell with water. This stimuli-responsive behavior translates to smart droplets that can coalesce on command when stabilized by the JMs. Droplet sizes are low when stabilized by particles in either amphiphilic states. Upon changing the temperatures, coalescence ensues in a matter of minutes and the droplet sizes are increased. This serves as demonstration of the synthesis and application of a truly amphiphilic swellable polymeric network that can respond to changes in its environment and stabilize water and oil emulsions. Adsorption mechanisms for microgel-stabilized emulsions require more research due to their major differences to solid particles. One of these differences is the location of the liquid–liquid interface to define a three-phase contact angle. While the interface sits on the surface of rigid particles, it is located inside the microgel particles. An amphiphilic microgel would limit this liquid interface to the intersection between the two gel sides. Future work will therefore use this microfluidic method to manipulate the hydrophilic–hydrophobic intersection-location on the amphiphilic microgel to study these adsorption mechanics. Furthermore, this work with stimuli responsive amphiphilic Janus microgel particles may prove useful for applications in biocatalysis, fuel production, and oil transportation.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 M. Destribats, *et al.*, Soft microgels as Pickering emulsion stabilisers: role of particle deformability, *Soft Matter*, 2011, **7**, 7689–7698, DOI: 10.1039/c1sm05240c.
- 2 Z. F. Li and T. Ngai, Microgel particles at the fluid–fluid interfaces, *Nanoscale*, 2013, **5**, 1399–1410, DOI: 10.1039/c2nr33503d.
- 3 S. Schmidt, *et al.*, Influence of Microgel Architecture and Oil Polarity on Stabilization of Emulsions by Stimuli-Sensitive Core–Shell Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) Microgels: Mickering versus Pickering Behavior?, *Langmuir*, 2011, **27**, 9801–9806, DOI: 10.1021/la201823b.
- 4 T. Ngai, S. H. Behrens and H. Auweter, Novel emulsions stabilized by pH and temperature sensitive microgels, *Chem. Commun.*, 2005, 331–333, DOI: 10.1039/b412330a.
- 5 S. E. Anachkov, *et al.*, Particle detachment from fluid interfaces: theory vs. experiments, *Soft Matter*, 2016, **12**, 7632–7643, DOI: 10.1039/c6sm01716a.
- 6 B. P. Binks, P. D. I. Fletcher, B. L. Holt, P. Beaussoubre and K. Wong, Phase inversion of particle-stabilised perfume oil-water emulsions: experiment and theory, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11954–11966, DOI: 10.1039/c0cp00558d.
- 7 D. Suzuki, S. Tsuji and H. Kawaguchi, Janus microgels prepared by surfactant-free pickering emulsion-based modification and their self-assembly, *J. Am. Chem. Soc.*, 2007, **129**, 8088–8089, DOI: 10.1021/ja072258w.
- 8 M. Destribats, *et al.*, Pickering Emulsions Stabilized by Soft Microgels: Influence of the Emulsification Process on Particle Interfacial Organization and Emulsion Properties, *Langmuir*, 2013, **29**, 12367–12374, DOI: 10.1021/la402921b.
- 9 Z. H. Nie, W. Li, M. Seo, S. Q. Xu and E. Kumacheva, Janus and ternary particles generated by microfluidic synthesis: Design, synthesis, and self-assembly, *J. Am. Chem. Soc.*, 2006, **128**, 9408–9412, DOI: 10.1021/ja060882n.
- 10 X. H. Ge, J. P. Huang, J. H. Xu, J. Chen and G. S. Luo, Water-oil Janus emulsions: microfluidic synthesis and morphology design, *Soft Matter*, 2016, **12**, 3425–3430, DOI: 10.1039/c6sm00130k.
- 11 B. Haney, D. Chen, L. H. Cai, D. Weitz and S. Ramakrishnan, Millimeter-Size Pickering Emulsions Stabilized with Janus Microparticles, *Langmuir*, 2019, **35**, 4693–4701, DOI: 10.1021/acs.langmuir.9b00058.

- 12 J. G. Werner, B. T. Deveney, S. Nawar and D. A. Weitz, Dynamic Microcapsules with Rapid and Reversible Permeability Switching, *Adv. Funct. Mater.*, 2018, **28**, 1803385, DOI: 10.1002/adfm.201803385.
- 13 K. H. Son and J. W. Lee, Synthesis and Characterization of Poly(Ethylene Glycol) Based Thermo-Responsive Hydrogels for Cell Sheet Engineering, *Materials*, 2016, **9**(10), 854, DOI: 10.3390/ma9100854.
- 14 A. J. Schmid, *et al.*, Multi-Shell Hollow Nanogels with Responsive Shell Permeability, *Sci. Rep.*, 2016, **6**, 22736, DOI: 10.1038/srep22736.
- 15 P. H. Li, *et al.*, Thermosensitive poly(*N*-isopropylacrylamide-co-glycidyl methacrylate) microgels for controlled drug release, *Colloids Surf., B*, 2013, **101**, 251–255, DOI: 10.1016/j.colsurfb.2012.07.009.
- 16 S. G. Kupal, B. Cerroni, S. V. Ghugare, E. Chiessi and G. Paradossi, Biointerface Properties of Core-Shell Poly(vinyl alcohol)-hyaluronic Acid Microgels Based on Chemoselective Chemistry, *Biomacromolecules*, 2012, **13**, 3592–3601, DOI: 10.1021/bm301034a.
- 17 A. Prastowo, A. Feuerborn, P. R. Cook and E. J. Walsh, Biocompatibility of fluids for multiphase drops-in-drops microfluidics, *Biomed. Microdevices*, 2016, **18**, 114, DOI: 10.1007/s10544-016-0137-0.
- 18 B. Haller, *et al.*, Charge-controlled microfluidic formation of lipid-based single- and multicompartiment systems, *Lab Chip*, 2018, **18**, 2665–2674, DOI: 10.1039/c8lc00582f.
- 19 M. S. Chowdhury, *et al.*, Dendronized fluorosurfactant for highly stable water-in-fluorinated oil emulsions with minimal inter-droplet transfer of small molecules, *Nat. Commun.*, 2019, **10**, 4546, DOI: 10.1038/s41467-019-12462-5.