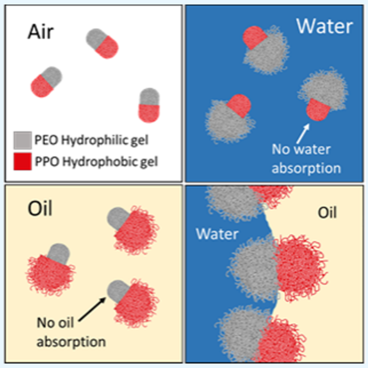
ACS APPLIED MATERIALS & INTERFACES

www.acsami.org Research Article

Absorbent−Adsorbates: Large Amphiphilic Janus Microgels as Droplet Stabilizers

Bobby Haney, Jörg G. Werner, David A. Weitz, and Subramanian Ramakrishnan*

Cite This: *ACS Appl. Mater. Interfaces* 2020, 12, 33439−33446 **Read Online**



ABSTRACT: Microgel particles are cross-linked polymer networks that absorb certain liquids causing network expansion. The type of swelling fluid and extent of volume change depends on the polymer−liquid interaction and the network's cross-link density. These colloidal gels can be used to stabilize emulsion drops by adsorbing to the interface of two immiscible fluids. However, to enhance the adsorption abilities of these predominantly hydrophilic gel particles, some degree of hydrophobicity is needed. An amphiphilic Janus microgel with spatially distinct lipophilic and hydrophilic sides is desired. Here, we report the fabrication of poly(ethylene glycol) diacrylate/poly(propylene glycol) diacrylate Janus microgels (JM) using microfluidic drop making. The flow streams of the two separate and immiscible monomer solutions are brought into contact and intersected by a third immiscible fluid in a flow-focusing junction to form Janus droplets. The individual droplets are cross-linked via UV irradiation to form monodispersed microgel particles with opposing hydrophilic and hydrophobic 3D-networked polymer matrices. By combining two chemically different polymer gel networks, an amphiphilic emulsion stabilizer is formed that adsorbs to the oil−water interface while its faces absorb their respective water or hydrocarbon solvents. The resulting water-in-oil emulsions are stabilized and destabilized via a thermal-responsive hydrogel. Stimuli-responsive droplets are demonstrated by adding a short-chain oligo ethylene glycol acrylate molecule to the hydrogel formulation on the Janus microgel particle. Droplets stabilized by these particles experience a sudden increase in droplet diameter around 60 °C. This work with absorbent particles may prove useful for applications in bio catalysis, fuel production, and oil transportation.

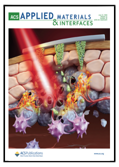
KEYWORDS: *amphiphilic, emulsion, microgel, absorb, Janus particle, temperature responsive*

INTRODUCTION

Emulsions are systems of two immiscible phases, usually water and oil, where one phase exists in the other as a dispersion of droplets. These droplets can be stabilized by small surface-active molecules or particles that prevent coalescence and subsequent full phase separation. Surfactants are commonly used for emulsion stabilization because of the presence of a hydrophilic and hydrophobic group within the same molecule that lowers the interfacial energy when adsorbed to an interface and provides a barrier to coalescence. Small molecule surfactants, however, in thermal equilibrium undergo constant desorption and adsorption from the water−oil interface onto an adjacent droplet or into the bulk continuous phase at room temperature.[1,2] For this reason, rigid particles with a lower thermal to interfacial energy ratio have been employed as emulsion droplet stabilizers. Due to the large surface area and smaller thermal motion, irreversible adsorption at oil−water interfaces is observed for some nano- and microparticles with intermediate wettability of both fluids. Optimizing these adsorption abilities requires tuning of the particle hydrophilicity and, thus, the contact angle between particle, oil, and water.[3,4] Recent work on polymer microgel particles suggests that the particle modulus also influences adsorption and emulsion stability.[5]

Microgels are particles made up of cross-linked networks of macromolecules that can swell in certain solvents and, at moderate hydrophilicity, partition to the interface of oil and water. Common types of these colloidal gel particles are soft hydrogels that are able to swell with water. Deformations of the hydrogel particles at the interface have been shown to enhance emulsion stability due to the enhanced viscoelastic properties of the microgel layer.[6−8] Because microgels are naturally hydrophilic, only a small, nonswollen portion of the particles protrudes into the oil while a larger portion resides in the water causing the deformation of the soft particle. It is well understood, however, that emulsion stabilizers that sit at the liquid−liquid interface closest to a 90° contact angle maximize the desorption energy and subsequently enhance emulsion

Received: June 23, 2020
Accepted: June 29, 2020
Published: June 29, 2020



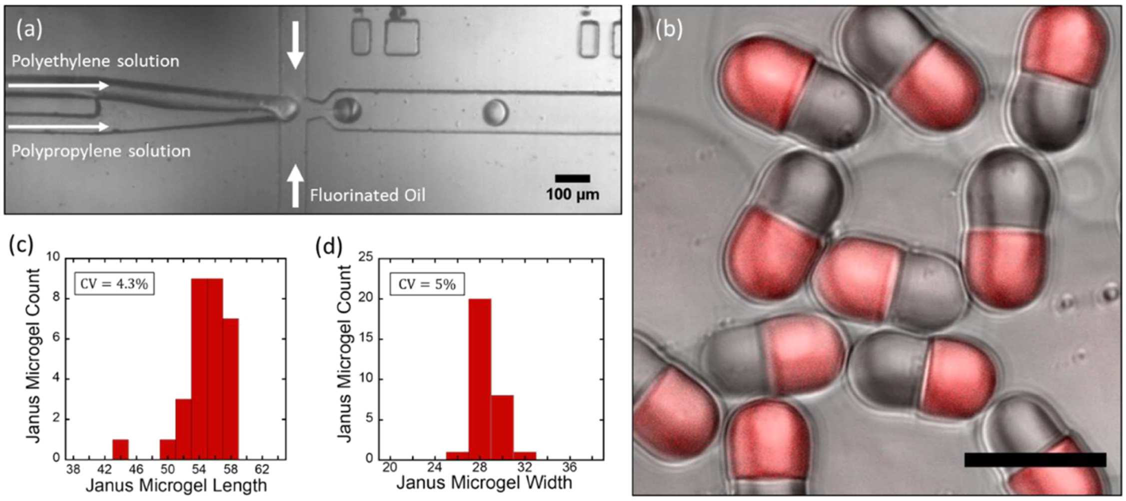


Figure 1. Fabrication of Janus Microgels (JMs). (a) Janus droplet formation of polymer precursor solutions via shear by fluorinated oil in a microfluidic flow-focusing device. (b) Synthesized amphiphilic Janus microgels showing the distinctive hydrophilic (gray) and hydrophobic (red) sides washed and submerged in acetone. Scale bar is 50 μm. (c) Histogram of final length (hydrophobic edge to hydrophilic) of Janus microgels (average 56 μm) with coefficient of variation (CV) as standard deviation/average length. (d) Histogram of final width (particle intersection) of Janus microgels (average 28.5 μm) with coefficient of variation (CV) as standard deviation/average length.

stability.[9,10] This can be realized with a stabilizer having distinct hydrophilic and hydrophobic sides resembling a molecular surfactant amphiphile. For this reason, an amphiphilic microgel is desired with two distinct hydrophilic and hydrophobic parts that will inherently prefer an oil−water interface as opposed to the water phase alone. Amphiphilic Janus microgel particles would incorporate the irreversible adsorption of a robust particle, the amphiphilicity of a surfactant molecule, and the deformability of a microgel into one stabilizer. Although there have been many reports on making amphiphilic rigid particles through meticulous surface functionalization[11−13] and microfluidics,[14−18] soft amphiphilic microgel particles remain a challenge.

Current work toward the formation of an amphiphilic microgel is limited to Pickering emulsion templating where microgels first migrate to the oil−water interface, where one side can be functionalized without the other.[19] This method, however, could not prevent rotation of the microgels at the interface for controlled surface functionalization. To address this limitation, there has been work where using lightly cross-linked PNIPAM-*co*-MAA microgels allowed short dangling chains on the particle surfaces to connect to neighboring microgels to prevent rotation.[20] Nevertheless, hydrogel surface functionalization via emulsion templating is used to selectively modify one section of the microgel, but the tunability over how much of the particle is modified is highly restricted by its initial wettability. A different technique may therefore be needed to obtain truly amphiphilic microgel particles.

Microfluidic techniques have been used to fabricate Janus droplets with controlled geometry. Two immiscible fluids that flow in parallel as the inner phases in microfluidic drop makers pinch off at the drop-making junction as homogeneous two-phase drops with controlled volumetric ratios and architectures.[15,21] To gain polymeric microgels, these Janus droplets are cross-linked via photopolymerization. This synthesis technique has major advantages over traditional emulsion templating: while the precursor composition is controlled before injecting into the microfluidic dropmaker, particle size, extent of cross-linking due to varied UV exposure, and ratio of hydrophilic to hydrophobic surface are managed with the microfluidic method. The work herein presents the successful fabrication of an amphiphilic Janus microgel particle (JM) with two opposing oil and water lyophilic sides that can stabilize oil−water emulsions. Poly(ethylene oxide) and poly(propylene oxide) are common polymers that have been studied for their use in many applications as hydrophilic and hydrophobic molecules, respectively.[22−24] Using their acrylate analogues, chemically cross-linked Janus particles with distinct hydrophilic and lipophilic parts are fabricated. We used droplet microfluidic templating to synthesize large-size (56 μm) amphiphilic Janus microgels capable of selective swelling at both sides of the oil and water interface. Because of the large water and oil absorption capacity of the two distinct sides, the Janus microgels exhibit very strong interfacial adsorption. These gel particles represent emulsion stabilizers with two distinct sides allowing them to adsorb at the water−oil interface due to the spatially selective absorption of oil and water within the same microgel particle.

■ RESULTS AND DISCUSSION

Amphiphilic Janus Microgel Synthesis. Microfluidic drop-making permits the control of droplet polydispersity, size, and shape and has been utilized for a variety of applications.[25−29] In a flow-focusing geometry, two counter-flowing streams of the outer fluid, called the continuous phase, orthogonally intersect the inner phase fluid at volume flow rate ratios of up to 100:1, respectively. At this intersection, the outer fluid shears the inner fluid to induce formation and break-off of a droplet from the inner phase stream. The inner fluid flow rates are 50 μL/h for the hydrophilic phase and 50 μL/h for the hydrophobic solution for the entire duration of Janus particle synthesis. This translates to a 1-to-1 ratio by volume between the two phases within the spherical Janus droplet with an approximate 50 μm diameter for both hemispheres. This droplet is collected at a frequency of 100 Hz and can be cross-linked to retain its shape via ultraviolet light (UV). By choosing separate hydrophilic and hydrophobic polymer solutions, we are able to form Janus droplets that are photopolymerized to retain their droplet shape. Poly(ethylene glycol) diacrylate and poly(propylene glycol) diacrylate polymer solutions were used as the hydrophilic and hydrophobic gel side precursors, respectively.

Figure 1a shows the Janus droplet formation where the two polymer precursor solutions come into contact and are then sheared by fluorinated oil in the microfluidic flow-focusing device. Flow rates are chosen to ensure laminar flow behavior for keeping the contact line between the polymer solutions steady and parallel to the direction of fluid flow. At equal flow rates, the two polymer solutions form a Janus droplet sheared by the continuous phase, fluorinated oil. As the droplets flow downstream, they are exposed to UV light and photopolymerization takes place. The particles are collected and washed with acetone to obtain the Janus microgel seen in the confocal microscopy image in Figure 1b, where the hydrophobic side is fluorescently labeled red. The final amphiphilic Janus microgels are anisotropic in shape with an average length from hydrophilic to hydrophobic end of 56 μm (± 2.4 μm) and average width, across the intersection, of 28.5 μm (± 1.4 μm). Figure 1c,d shows the size distributions.

Janus droplets formed in the microfluidic channels take on a spherical morphology, as seen in Figure 1a, yet upon washing with acetone to remove the fluorinated oil (continuous phase), form anisotropic Janus microgel particles with aspect ratios around 2. Since the hydrogel precursor solution contains almost 50% water, upon polymerization a hydrogel swollen with water is formed. After rinsing and submerging the particles in acetone, the hydrogel side shrinks much more than the hydrophobic side due to the removal of water. While shrinking occurs in the radial direction for spherical hydrogels, the hydrogel hemisphere on these Janus microgels seems to collapse in the radial direction of its circular base, which is in direct contact with the hydrophobic side. The hydrogel shrinking therefore morphs the initially round gel particles into rodlike shapes due to a larger decrease in microgel intersection width than in the length. We hypothesize that upon washing the JMs with acetone, shrinkage occurs faster at the polymer phase intersection due to a possible nonhomogeneous cross-linking. Although upon cross-linking the JM, one side is composed of a polyethylene network and the other is a polypropylene network, it is possible that some mixing of the monomers occurred at their intersection when flowing in the microfluidic device as liquids. The JM network intersection would therefore have a different cross-linking than the pure polymer JM sides due to spatial concentration variations at the JM intersection. This shape persists in all experiments including when particles are adsorbed to an interface.

The differences in polymer characteristics can also be qualitatively observed in Figure 2, where scanning electron microscopy (SEM) and Cryo-SEM images show the dried Janus microgels (Figure 2a) and its internal fracture surface (Figure 2c,d) in water, respectively. In Figure 2a,2b, the JMs with dehydrated hydrogel and slightly larger hydrophobic gel sides can be identified. The JMs keep their anisotropic shape even when dried from acetone and under vacuum during SEM. If submerged in water, the hydrogel is expected to swell and the hydrophobic polypropylene gel side (called organogel due to its ability to absorb organic solvent) to remain collapsed. Figure 2c shows the cross section of one JM fractured under cryogenic conditions. The hydrogel is the only polymer network that expands in the water showing a distinct transition from hydrophobic to hydrophilic in Figure 2d.

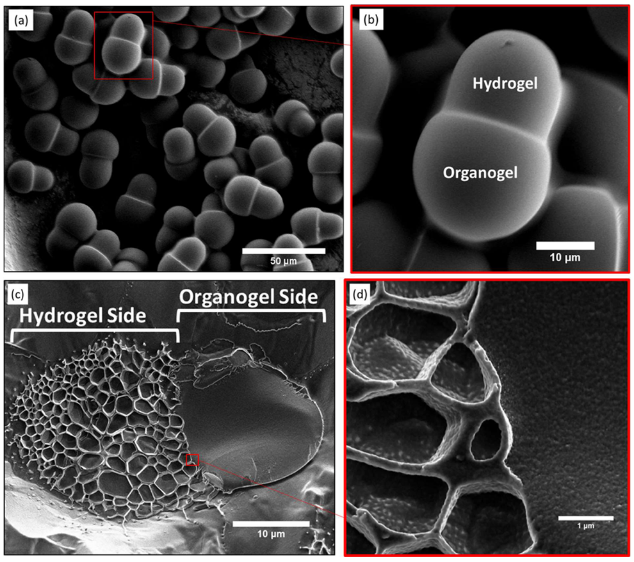


Figure 2. SEM images of the dried particles in air (a) and (b) magnified image where the dehydrated hydrogel side is collapsed smaller than the organogel side. Cryo-SEM images of the internal fracture surface of the amphiphilic Janus microgel in water. (c) One JM with hydrogel and organogel side notation. (d) Magnified image of the interface between the swollen hydrogel and the collapsed organogel on the same particle.

Microgel Swelling. While amphiphilic microgels can adsorb to the interface of oil and water droplets, each side of the particle also absorbs its respective solvent. This leads to swelling of the gel sides and a subsequent increase in overall microgel volume. Swelling by water allows deformation and interpenetration by the solvent in the bulk of the hydrogel, while swelling by toluene has the same effect on the organogel. Figure 3a shows the amount of solvent absorbed when the initially dry hydrophilic polyethylene gel and hydrophobic polypropylene gel sides of the composite particle swell while (1) immersed in only the pure solvents (water or toluene) and (2) at the water−toluene interface. Adsorbed solvent amounts were estimated based on the difference between the swollen and the collapsed paraboloid volume to yield the volume increase (fluid absorbed). In every sample, this estimate assumes that the collapsed volume amount is a pure polymer. The solvent amount absorbed for the hydrogel side in a pure solvent represents its size change on the JM when dispersed in water, while amount absorbed for the hydrophobic polypropylene gel side represents its solvent uptake when the JM is in only toluene. When at the interface of water and toluene, both gel sides are separately measured for their respective solvent absorption. Upon washing the synthesized microgels with acetone, they are allowed to dry in air as seen in Figure 3b. Figure 3c shows the resulting swell of the hydrophilic poly(ethylene oxide) side when the initially dry JM is submerged in water. The uncolored hydrogel swells while the hydrophobic side remains collapsed. Once submerged in toluene, the red dyed hydrophobic poly(propylene oxide) side swells as seen in Figure 3d, where the hydrogel remains collapsed. Finally, by adding roughly 10 μL of water, 1 mL of toluene, and slightly shaking the vial, we see the JMs at the interface of a water drop surrounded by toluene in Figure 3e.

An interesting aspect of this particle synthesis method is that two chemically different cross-linked polymer networks with opposing swelling characteristics are spatially distinct but

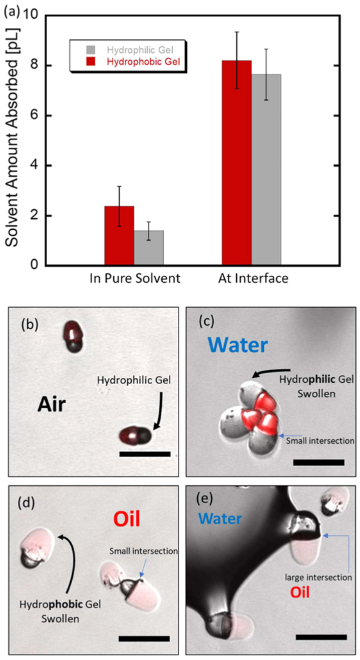


Figure 3. Swelling characteristics of the amphiphilic Janus microgels. (a) Amount of absorbed water or toluene for the hydrophilic and hydrophobic sides, respectively; swelling either individually in the pure solvents or simultaneously at the water−toluene interface. (b) Janus microgel sitting in air. (c) Janus microgel sitting in water with the hydrophilic side swollen. (d) Janus microgel sitting in toluene with the hydrophobic gel swollen. (e) Janus microgel sitting at the interface of a water drop in toluene with both sides swollen. The intersection widths indicated in (c−e) are 15.2, 18.3, and 28.7 μm, respectively. Scale bars are 50 μm.

attached together in one particle. In both cases of the JM submerged in a pure solvent or the particle at the oil−water interphase, the organogel side is able to absorb a larger amount of toluene than the hydrogel does water. This can be seen in Figure 3a where the red bar (amount of toluene absorbed) is higher than the gray bar (water absorbed). An adsorbed, swollen JM therefore has an average organogel to hydrogel volume ratio of 1.1, where the hydrophobic side is slightly larger than the hydrophilic side. Despite equal flow rates during synthesis, characteristics of the gel network seem to control the swollen particle Janus balance. The Flory−Rehner equation is commonly used to characterize equilibrium swelling of cross-linked polymers to obtain the cross-link density, n, assuming no ionized polymer groups[30,31]

$$\varphi + \ln(1 - \varphi) + \chi\varphi^2 = nV\left[\frac{\varphi}{2} - \varphi^{1/3}\right] \tag{1}$$

where φ is the volume fraction of polymer in the swollen network, χ is the polymer−solvent interaction parameter, and V is the molar volume of the solvent. The swelling ratio taken as the ratio of swollen lobe volume to collapsed gel volume is used to calculate φ, where

$$\frac{\text{volume of gel when swollen}}{\text{volume of gel when collapsed}} = \frac{\varphi_o}{\varphi} \tag{2}$$

and φ_o represents the polymer volume fraction in the collapsed state. The swell ratio of PEO in water is 21.42 and the organogel (PPO) in toluene is 9.64. The polymer−solvent interaction parameter for PPO in toluene is equal to 0.51, yet, network swelling occurs in all experiments conducted in this work. Using the average swell ratios and particle−solvent interaction parameters for PEO in water (0.426)[32] and PPO in toluene (0.51)[33] in the Flory−Rehner equation for equilibrium swelling of cross-linked polymers, the cross-link densities of the hydrogel and organogel are approximated to be 3.25×10^{-5} and 6.7×10^{-6} mol/cm^3, respectively. These data show that the hydrophobic side has an order of magnitude less cross-links per volume and may be capable of expansion for more of its solvent uptake than the hydrogel. The less stiff organogel may be capable of stretching its chains more than the hydrogel resulting in the slight difference in final swollen volumes on the JM at the water−toluene interface. To corroborate this conclusion, we measure the modulus of the bulk polymer gels at the JM compositions when swollen in their respective solvents under shear on an Anton Parr rheometer using parallel plates. Storage modulus for the cross-linked poly(propylene oxide) saturated with toluene is 8.63 kPa. Saturated and submerged in water, the storage modulus of the poly(ethylene oxide) gel is 18.1 kPa. The higher modulus in the hydrogel

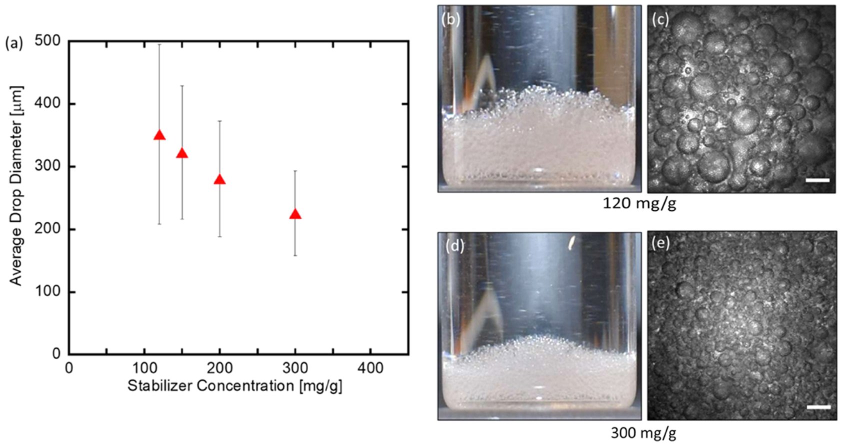


Figure 4. Changing emulsion droplet size with the amount of JM stabilizers. (a) Droplet diameter as a function of particle concentration for water-in-toluene emulsions. (b) Water-in-toluene emulsions sedimented on the bottom of the vial due to density differences using 120 mg JM to 1 g of water. (c) Optical micrographs of the emulsion droplets at 120 mg/g concentration. (d) Water-in-toluene emulsions on bottom of vial with 300 mg JM to 1 g of water. (e) Optical micrographs of the emulsion droplets at 300 mg/g concentration. Scale bars are 500 μm.

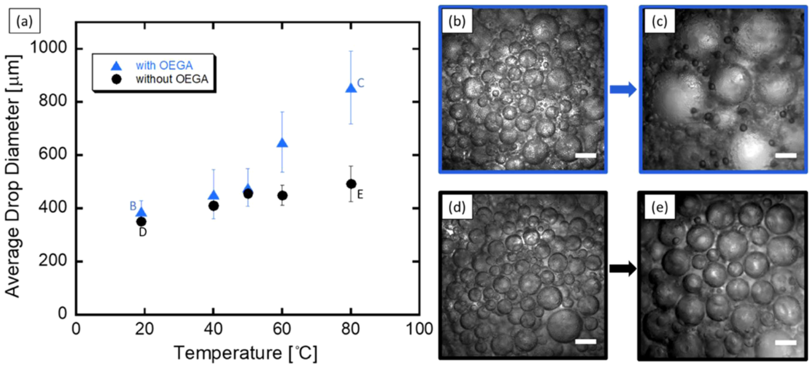


Figure 5. Temperature response of emulsions stabilized by amphiphilic Janus microgels. (a) Emulsion drop diameter as a function of temperature. (b, c) Droplets stabilized by JMs with additional oligomer functionality increasing in size from 19 to 80 °C, respectively. (d, e) Droplets stabilized by JMs with no additional oligomer functionality increasing in size from 19 to 80 °C, respectively. Scale bars are 500 μm.

than in organogel is consistent with the differences in cross-link densities.

We also observe that the JM distinctive gel sides swell less when submerged in pure toluene or pure water compared to when both sides are swollen at the same time at the interface. This may be due to a restriction of the polymer chains from expanding along the JM's hemispherical radial direction, where the two sides are connected. When the JM is in only water, the hydrogel swells while the hydrophobic side remains collapsed, which may prevent the full expansion of poly(ethylene oxide) chains that are connected to the poly(propylene oxide) network at the JM mid-section. This same effect is seen when the JM is in only toluene and the organogel swelling is limited. Nonetheless, the overall volume increase when the JM particles are adsorbed to a droplet surface, seen quantitatively in Figure 3a and qualitatively when comparing Figure 3b−3e, (from dry JM to JM at the oil−water interface), highlights the swelling nature of the gel sides that gives them their interesting adsorption properties.

Emulsion Stabilization. The amphiphilic Janus microgels in this work possess two distinctly different sides on one particle that swell with either water or an organic solvent, respectively. Having these opposing hydrogel and organogel domains on an emulsion stabilizer promotes strong adsorption to the water−oil interface when the hydrophilic side absorbs water and the hydrophobic side absorbs an organic solvent. While these JMs are much larger than colloidal microgels, their amphiphilic nature makes them ideal stabilizers of oil-in-water or water-in-oil emulsions. The JMs form stable (7 months to-date) water-in-toluene emulsions at room temperature, where the average droplet size is a function of their concentration in water. Figure 4 shows the relationship between particle concentration in the dispersed fluid phase (water) and emulsion droplet size. At constant JM amount, the sample contained 100, 80, 60, and 40 μL of water at 120, 150, 200, and 300 mg/g JM to water, respectively. When the weight ratio of JMs to water is low (120 mg/g), polydispersed spherical droplets of approximately 350 μm in diameter are obtained which are covered with Janus particles preventing coalescence. At higher JM content (300 mg/g), the droplets are smaller and yet stable, as shown in the inset of Figure 4a. Figure 4b,c shows water-in-toluene emulsions in the glass vials, where droplets are sedimented due to water's higher density. Like solid−particle-stabilized emulsions, there is a negative correlation between the amount of particles and emulsion droplet size when these Janus microgels are employed. As the JM particle to water weight ratio is increased, more surface area can be stabilized leading to smaller drops. Polydispersity presented in the form of standard deviation divided by the average drop sizes also decreased with particle concentration: 41% at 120 mg/g and 30% for 300 mg/g. To show oil-in-water stabilizing ability, toluene-in-water emulsions were also created as seen in Figure S1 of the Supporting Information. We can accredit the emulsion droplet formation to the amphiphilic nature of these JMs as opposed to gel particles formed from polymers of just one type. Using the microfluidic methods described for the JM formation, hydrogel microspheres of only the JM hydrophilic side composition were synthesized and added to water and toluene systems at the same concentrations studied for the JMs. Large (∼3 mm) and very densely covered irregularly shaped water drops were possible at hydrogel concentrations of 300 mg/g in the water. With the same vial and sample, in all experiments with lower particle concentration, no emulsion droplets could be formed and hydrogel microspheres can be seen in water films along the glass vial surfaces as shown in Figure S3a,b of the Supporting Information. Likewise, organogel microspheres of only the JM hydrophobic side composition were also synthesized and added to water−toluene systems. As shown in Figure S4b of the supporting information, at high particle concentration in water, no discernable particle-covered emulsion droplets are found. Barely covered water droplets stick to the bottom of the vial with most organogel microspheres unattached. At lower particle concentrations, the water droplet exists as a large drop at the bottom of toluene. While the "water loving" gel particles absorb water and adsorb to the interface, the hydrophobic polymer gels may prefer the toluene phase causing water to remain unemulsified. Only the use of these polymer networks as two separate faces on one particle affords the microgel anchoring needed to form these large emulsion droplets along this concentration range.

Temperature Response. Using microgels as stabilizers promotes stimuli-responsive emulsion droplets via the stabilizer's ability to swell and deswell upon changes in temperature. The current work uses poly(ethylene glycol) and poly(propylene glycol) as the hydrophilic and hydrophobic sides on the particle, respectively. The cross-linked amphiphilic Janus microgel is therefore similar to a commonly used nonionic macromolecular surfactant composed of the triblock copolymer—PEO-PPO-PEO.[34] These amphiphilic triblock copolymer chains are often used to form temperature-responsive physically cross-linked and water-swollen hydrogels due to their spontaneous assembly into micelles at room temperature and phase separation with PEO dehydration at elevated temperatures.[35] We therefore expect our Janus microgels to respond to thermal fluctuations in a similar manner. It has been demonstrated that careful control of the hydrophobicity of short oligo ethylene glycol acrylate (OEGA) polymers via the choice of backbone and ethylene glycol chain length allows tunable thermo-responsive behavior.[36] For example, the copolymerization of two short-chain oligo ethylene glycol monomers, where one is more hydrophobic than the other, has been shown to cause a decrease in the lower critical solution temperature.[37] We therefore incorporated an ethylene glycol monomer with four ethylene glycol repeat units connected to each acrylate, ethoxylated trimethylolpropane triacrylate (ETPTA), into the aqueous poly(ethylene glycol) diacrylate solution in an attempt to decrease the VPTT of the cross-linked gel. ETPTA is less hydrophilic than our PEGDA, most likely due to the lower number of PEG units per acrylate and its hydrophobic cross-linking group. Figure 5 shows the effects of temperature on average drop size for emulsions stabilized by amphiphilic Janus microgel particles with and without the addition of the short-chain OEGAs, where both JM concentrations are 120 mg/g JMs to water with 100 μL of water. While there is an increase in droplet size with increasing temperature for the emulsions formed with Janus microgels of poly(ethylene oxide) and poly(propylene oxide) alone, the response is much more pronounced with the addition of ETPTA on the hydrophilic side of the cross-linked particle as seen in Figure 5a. Figure 5b,c shows the JM-OEGA particle-covered droplets at 19 and 80 °C, respectively, where a distinct size increase can be seen. This transition at higher temperatures could be useful for the temperature-triggered release of oil or water in emulsion systems. Figure 5d,e shows the original JM particle-covered droplets at 19 and 80 °C, respectively, where there is less of an obvious droplet size change. In this regard, the JMs without OEGA may find use in emulsion systems that require elevated temperatures.

Because the stabilizer deformation at the interface can depend on environmental conditions, the mechanism governing emulsion stabilization with gel particles is not well understood. We can, however, assume that the temperature effects on our emulsion may be due to JM hydrogel side response as opposed to the organogel. The JM organogel side remains unaffected by the temperatures used in this work as observed by monitoring and measuring single cross-linked poly(propylene oxide) microspheres along our temperature range (Figure S2a, Supporting Information). Hence, there are a couple of reasons that the emulsion droplets covered with JMs with OEGAs may have experienced sudden destabilization at a specific temperature. Some researchers have suggested that this temperature-responsive destabilization may be due to retraction of the dangling polymer chains between adjacent microgels that were necessary for stability.[5,8] They report that increasing temperature reduces the deformability of microgels and decreases their stabilizer efficiency via reduced chain interpenetration between touching microgel surfaces. This would lead to less mechanically robust emulsion droplet interfaces that are more susceptible to coalescence. Although our polymeric JM particle hydrogel portions do collapse and become less deformable at increased temperature (Figure S2b, Supporting Information), this mechanism for destabilization is less likely due to the presence of an unaffected hydrophobic side. At the elevated temperature, while chain interpenetration may be reduced for adjacent hydrogel sides on the Janus microgel, the organogel side surfaces may continue to link with its nearest neighbors. Further study of the interfacial elasticity as a function of temperature for emulsions stabilized by the JM particles is therefore needed. Destabilization upon temperature change may occur for a simpler reason. One may be that shrinkage of the hydrogel side at the higher temperature reduced not just its size but also the overall size of the particles (as discussed above), leading to reduced interfacial coverage and subsequent droplet coalescence. It is true, however, that at the elevated temperature, hydrogen bonds are cleaved from the ethylene glycol chains causing the hydrogel side to become more hydrophobic. This results in a more completely hydrophobic stabilizer that slightly prefers the oil phase to the interface, leading to destabilization. Destabilization may therefore occur due to simultaneous hydrogel collapsing at the elevated temperature and decrease in overall particle size via deswelling of an individual side. Nevertheless, to gain a true understanding of stability and destabilization of these gel–particle covered droplets, thermodynamic relationships analogous to rigid particle stabilization of emulsions are needed. Yet, these relationships are nontrivial. For example, while rigid particle interfacial adsorption can be characterized by the three-phase water-oil-particle contact angle, the water–oil interface sits inside the Janus microgel particle suggesting an alternative adsorption mechanism. More research is therefore needed on our system of hydrophilic and hydrophobic polymers on two separate sides of an emulsion stabilizer.

■ CONCLUSIONS

Amphiphilic Janus microgel particles were synthesized using the co-flow of two immiscible polymer solutions in a microfluidic drop-making device. Cross-linking the solutions together in one drop via exposure to ultraviolet light leads to hydrophobic and hydrophilic 3D cross-link polymer networks on opposite sides of one particle. When the Janus microgels are placed in water, the hydrogel absorbs the solvent and swells leaving the organogel side collapsed. Likewise, when the Janus microgels are placed in only organic solvent toluene, the organogel absorbs and swells while the hydrogel side remains collapsed. Both sides swell when at the interface of water and toluene while the organogel volume is about 10% larger due to its more flexible network and lower cross-link density. Like rigid particle-stabilized emulsions, the JM-stabilized emulsions droplet size varies indirectly with particle concentration and prevents coalescence for months. Adding a short-chain oligo ethylene glycol acrylate molecule to the hydrogel formulation permits temperature-responsive action like that seen in the linear polymer analogues. Droplets stabilized by these particles experience a sudden increase in droplet diameter around 60 °C. While the JM organogel remains unaffected, the hydrogel polyethylene chains are dehydrated, rendering the JM more hydrophobic overall. The amphiphilic particulate stabilizers studied here are larger than the typical colloids used in the application (~1 μm). Future work requires decreasing the particle sizes via smaller microfluidic channels or high shear homogenizers to form small polymer droplets. Nonetheless, this work with absorbent particles may prove useful for applications requiring the uptake-release of active substances or the stabilization of hydrocarbon water systems.

METHODS

Microfluidic Device and Particle Synthesis. A flow-focusing PDMS microfluidic device, fabricated using soft lithography, is used to form Janus droplets in 100 × 100 μm channels. Poly(ethylene glycol) diacrylate (M_n 700) purchased from Sigma Aldrich, water, and 2-hydroxy-2-methylpropiophenone (HMP) photoinitiator from Sigma Aldrich were mixed at 50, 49, and 1 wt %, respectively, to form the hydrogel precursor solution. Poly(propylene glycol) diacrylate (M_n 800) purchased from Sigma Aldrich and HMP photoinitiator were mixed at 99 and 1 wt %, respectively, to form the organogel precursor solution. These two polymer solutions combine to form the inner phase stream in the microfluidic device. HFE-7500 Nevec engineered fluid and 2 vol % fluoro-surfactant were used as the continuous phase stream. All fluids were drawn into syringes and pumped into the microfluidic device using Harvard PHD 2000 series; Harvard Apparatus syringe pumps. At a combined flow rate of 0.1 mL/h, the inner phase stream is sheared at the intersection of the microfluidic device by the continuous phase stream (2 mL/h) to induce droplet break-off. The double-sided Janus liquid droplets flow downstream into a 200 μm inner diameter glass capillary, where they are exposed to ultraviolet light at 1.52 W/cm^2, for 3 s, at a 2.5 cm distance from an Excelitas OmniCure S1500 UV system with a >350 nm filter. The cross-linked Janus microgel particles are collected in the continuous phase and washed five times with acetone to remove any unreacted polymer, fluorinated surfactant, and the HFE-7500 fluid. The particles are allowed to dry to measure dry weight and redispersed into the desired solvent (water or toluene) for the experiments.

Confocal Imaging. Amphiphilic Janus microgels were imaged using a Leica SP5 confocal microscope. Nile red fluorescent dye (excitation 543 nm) was added to the hydrophobic polypropylene polymer solution before particle synthesis to allow identification of the organogel side of the Janus microgel in all experiments. Image J was used in conjunction to measure the dimensions of the collapsed and swollen Janus microgel sides for volume calculations. All volume measurements were calculated treating the particle sides as paraboloids.

SEM Imaging. For SEM imaging, washed Janus microgels were dispersed in acetone, pipetted onto a copper grid, and left to air dry of acetone. Five nanometers of platinum was then sputter-coated onto the surfaces of the particles to prevent electron charging during imaging. To obtain Cryo-SEM images, Janus microgels were first dispersed in water to allow the hydrogel to swell. Janus microgels dispersed in water were deposited on an aluminum specimen holder and frozen in liquid nitrogen. The sample was then transferred under vacuum to a preparation chamber equipped with a blade used to fracture the frozen sample. Once fractured, the sample was coated by a layer of platinum and transferred to the cooled SEM for imaging. Observations were then carried out with a Zeiss Ultra55 field emission scanning electron microscope equipped with liquid nitrogen cooled sample preparation and transfer units.

Emulsion Formation. Amphiphilic Janus microgel stabilized emulsions were formed by mixing particle, water, and toluene in a glass vial. Washed and dried Janus microgel particles were assembled in a glass vial. Three milliliters of toluene was added to the vial followed immediately by the desired amount of water (20−100 μL), and the contents were vortexed for 1 min to obtain emulsified water droplets at the bottom of continuous toluene.

Temperature Tests. Temperature tests on emulsion destabilization were conducted by heating the glass vial contents. Janus microgels with oligo ethylene glycol acrylate additions were synthesized using poly(ethylene glycol) diacrylate, ethoxylated trimethylolpropane triacrylate, water, and 2-hydroxy-2-methylpropiophenone at 30, 20, 49, and 1 wt %, respectively, as the hydrogel precursor solution. Emulsions were formed in a glass vial at room temperature, imaged, and immersed in an oil bath to increase temperature. After sitting at a specific temperature for 30 min, the emulsions were removed from the oil bath, immediately vortexed (to homogenize at that temperature), and imaged without further shaking. This was repeated three times for emulsions at 19, 40, 50, 60, and 80 °C.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.0c11408.

> Alternative oil-in-water emulsions (Figure S1); temperature response of Janus particle sides when synthesized as pure polymer microspheres unattached to the other polymer network (Figure S2); emulsion formation ability of pure hydrogel microspheres (Figure S3); emulsion formation ability of pure organogel microspheres (Figure S4) (PDF)

AUTHOR INFORMATION

Corresponding Author

Subramanian Ramakrishnan − *Department of Chemical and Biomedical Engineering, FAMU-FSU Engineering, Tallahassee, Florida 32310, United States;* orcid.org/0000-0001-5108-2198; Phone: 001 (850) 410-6159; Email: srama@eng.famu.fsu.edu

Authors

Bobby Haney − *Department of Chemical and Biomedical Engineering, FAMU-FSU Engineering, Tallahassee, Florida 32310, United States;* orcid.org/0000-0002-6462-8943

Jörg G. Werner − *Department of Mechanical Engineering and Division of Materials Science and Engineering, Boston University, Boston, Massachusetts 02215, United States; John A. Paulson School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, United States;* orcid.org/0000-0001-7845-086X

David A. Weitz − *John A. Paulson School of Engineering and Applied Sciences and Department of Physics, Harvard University, Cambridge, Massachusetts 02138, United States;* orcid.org/0000-0001-6678-5208

Complete contact information is available at: https://pubs.acs.org/10.1021/acsami.0c11408

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

B.H. and S.R. would like to acknowledge funding from NSF FAMU CREST center award # 1735968 and NSF TIP award # 1623206 for current work. This work was performed in part at the Harvard MRSEC (Grant DMR-1420570) and the Center for Nanoscale Systems (CNS), a member of the National Nanotechnology Coordinated Infrastructure Network (NNCI), which is supported by the National Science Foundation under NSF award no. 1541959. CNS is a part of Harvard University. D.A.W. and J.G.W. acknowledges partial support from the National Science Foundation (NSF) under the award no. DMR-1708729.

REFERENCES

(1) Binks, B. P. Particles as surfactants - similarities and differences. *Curr. Opin. Colloid Interface Sci.* **2002**, *7*, 21−41.

(2) Jin, F.; Stebe, K. J. The Effects of a Diffusion Controlled Surfactant on a Viscous Drop Injected into a Viscous Medium. *Phys. Fluids* **2007**, *19*, No. 112103.

(3) Cao, W.; Huang, R. L.; Qi, W.; Su, R. X.; He, Z. M. Self-Assembly of Amphiphilic Janus Particles into Monolayer Capsules for Enhanced Enzyme Catalysis in Organic Media. *ACS Appl. Mater. Interfaces* **2015**, *7*, 465−473.

(4) Wei, D.; Ge, L. L.; Lu, S. H.; Li, J. J.; Guo, R. Janus Particles Templated by Janus Emulsions and Application as a Pickering Emulsifier. *Langmuir* **2017**, *33*, 5819−5828.

(5) Li, Z. F.; Geisel, K.; Richtering, W.; Ngai, T. Poly(N-isopropylacrylamide) Microgels at the Oil-Water Interface: Adsorption Kinetics. *Soft Matter* **2013**, *9*, 9939−9946.

(6) Brugger, B.; Richtering, W. Emulsions Stabilized by Stimuli-Sensitive Poly(N-isopropylacrylamide)-co-Methacrylic Acid Polymers: Microgels Versus Low Molecular Weight Polymers. *Langmuir* **2008**, *24*, 7769−7777.

(7) Brugger, B.; Vermant, J.; Richtering, W. Interfacial Layers of Stimuli-Responsive Poly-(N-isopropylacrylamide-co-Methacrylicacid) (PNIPAM-co-MAA) Microgels Characterized by Interfacial Rheology and Compression Isotherms. *Phys. Chem. Chem. Phys.* **2010**, *12*, 14573−14578.

(8) Destribats, M.; Lapeyre, V.; Wolfs, M.; Sellier, E.; Leal-Calderon, F.; Ravaine, V.; Schmitt, V. Soft Microgels as Pickering Emulsion Stabilisers: Role of Particle Deformability. *Soft Matter* **2011**, *7*, 7689−7698.

(9) Anachkov, S. E.; Lesov, I.; Zanini, M.; Kralchevsky, P. A.; Denkovb, N. D.; Isa, L. Particle Detachment From Fluid Interfaces: Theory Vs. Experiments. *Soft Matter* **2016**, *12*, 7632−7643.

(10) Binks, B. P.; Fletcher, P. D. I.; Holt, B. L.; Beaussoubre, P.; Wong, K. Phase Inversion of Particle-Stabilised Perfume Oil-Water Emulsions: Experiment And Theory. *Phys. Chem. Chem. Phys.* **2010**, *12*, 11954−11966.

(11) Jiang, S.; Granick, S. Controlling The Geometry (Janus Balance) of Amphiphilic Colloidal Particles. *Langmuir* **2008**, *24*, 2438−2445.

(12) Kim, J. W.; Cho, J.; Park, B. J.; Kim, Y. J.; Choi, K. H.; et al. Synthesis of Monodisperse Bi-Compartmentalized Amphiphilic Janus Microparticles for Tailored Assembly at the Oil-Water Interface. *Angew. Chem., Int. Ed.* **2016**, *55*, 4509−4513.

(13) Kim, J. W.; Lee, D.; Shum, H. C.; Weitz, D. A. Colloid Surfactants for Emulsion Stabilization. *Adv. Mater.* **2008**, *20*, 3239−3243.

(14) Chen, C. H.; Shah, R. K.; Abate, A. R.; Weitz, D. A. Janus Particles Templated from Double Emulsion Droplets Generated Using Mcrofluidics. *Langmuir* **2009**, *25*, 4320−4323.

(15) Ge, X. H.; Huang, J. P.; Xu, J. H.; Chen, J.; Luo, G. S. Water-Oil Janus Emulsions: Microfluidic Synthesis and Morphology Design. *Soft Matter* **2016**, *12*, 3425−3430.

(16) Kim, S. H.; Abbaspourrad, A.; Weitz, D. A. Amphiphilic Crescent-Moon-Shaped Microparticles Formed by Selective Adsorption of Colloids. *J. Am. Chem. Soc.* **2011**, *133*, 5516−5524.

(17) Shepherd, R. F.; Conrad, J. C.; Rhodes, S. K.; Link, D. R.; Marquez, M.; Weitz, D. A.; Lewis, J. A. Microfluidic Assembly Of Homogeneous and Janus Colloid-Filled Hydrogel Granules. *Langmuir* **2006**, *22*, 8618−8622.

(18) Zhang, M. Y.; Zhao, H.; Xu, J. H.; Luo, G. S. Controlled Coalescence of Two Immiscible Droplets for Janus Emulsions in a Microfluidic Device. *RSC Adv.* **2015**, *5*, 32768−32774.

(19) Suzuki, D.; Tsuji, S.; Kawaguchi, H. Janus Microgels Prepared by Surfactant-Free Pickering Emulsion-Based Modification and Their Self-Assembly. *J. Am. Chem. Soc.* **2007**, *129*, 8088−8089.

(20) Destribats, M.; Wolfs, M.; Pinaud, F.; Lapeyre, V.; Sellier, E.; Schmitt, V.; Ravaine, V. Pickering Emulsions Stabilized by Soft Microgels: Influence of the Emulsification Process on Particle Interfacial Organization and Emulsion Properties. *Langmuir* **2013**, *29*, 12367−12374.

(21) Nie, Z. H.; Li, W.; Seo, M.; Xu, S. Q.; Kumacheva, E. Janus and Ternary Particles Generated by Microfluidic Synthesis: Design, Synthesis, and Self-Assembly. *J. Am. Chem. Soc.* **2006**, *128*, 9408−9412.

(22) Batrakova, E. V.; Kabanov, A. V. Pluronic Block Copolymers: Evolution of Drug Delivery Concept from Inert Nanocarriers to Biological Response Modifiers. *J. Controlled Release* **2008**, *130*, 98−106.

(23) Jalaal, M.; Cottrell, G.; Balmforth, N.; Stoeber, B. On The Rheology of Pluronic F127 Aqueous Solutions. *J. Rheol.* **2017**, *61*, 139−146.

(24) Martin, J. D.; Velankar, S. S. Unusual Behavior of PEG/PPG/Pluronic Interfaces Studied by a Spinning Drop Tensiometer. *J. Colloid Interface Sci.* **2008**, *322*, 669−674.

(25) Shah, R. K.; Shum, H. C.; Rowat, A. C.; Lee, D.; Agresti, J. J.; Utada, A. S.; Chu, L. Y.; Kim, J. W.; Fernandez-Nieves, A.; Martinez, C. J.; Weitz, D. A. Designer Emulsions Using Microfluidics. *Mater. Today* **2008**, *11*, 18−27.

(26) Nunes, J. K.; Tsai, S. S. H.; Wan, J.; Stone, H. A. Dripping and Jetting in Microfluidic Multiphase Flows Applied to Particle and Fibre Synthesis. *J. Phys. D: Appl. Phys.* **2013**, *46*, No. 114002.

(27) Utada, A. S.; Fernandez-Nieves, A.; Stone, H. A.; Weitz, D. A. Dripping to Jetting Transitions in Coflowing Liquid Streams. *Phys. Rev. Lett.* **2007**, *99*, No. 094502.

(28) Utada, A. S.; Chu, L. Y.; Fernandez-Nieves, A.; Link, D. R.; Holtze, C.; Weitz, D. A. Dripping, Jetting, Drops, and Wetting: The Magic of Microfluidics. *MRS Bull.* **2007**, *32*, 702−708.

(29) Castro-Hernández, E.; Gundabala, V.; Fernandez-Nieves, A.; Gordillo, J. M. Scaling the Drop Size in Coflow Experiments. *New J. Phys.* **2009**, *11*, No. 075021.

(30) Quesada-Pérez, M.; Maroto-Centeno, J. A.; Forcada, J.; Hidalgo-Alvarez, R. Gel Swelling Theories: The Classical Formalism and Recent Approaches. *Soft Matter* **2011**, *7*, 10536−10547.

(31) Sperling, L. H. *Introduction to Physical Polymer Science*, 4th ed.; John Wiley & Sons, 2006.

(32) Lin, S.; Sangaj, N.; Razafiarison, T.; Zhang, C.; Varghese, S. Influence of Physical Properties of Biomaterials on Cellular Behavior. *Pharm. Res.* **2011**, *28*, 1422−1430.

(33) Bentz, K. C.; Walley, S. E.; Savin, D. A. Solvent Effects on Modulus of Poly(Propylene Oxide)-Based Organogels as Measured by Cavitation Rheology. *Soft Matter* **2016**, *12*, 4991−5001.

(34) Dou, Q. Q.; Karim, A.; Loh, X. J. Modification of Thermal and Mechanical Properties of PEG-PPG-PEG Copolymer (F127) with MA-POSS. *Polymers* **2016**, *8*, No. 341.

(35) Malmsten, M.; Lindman, B. Self-Assembly In Aqueous Block Copolymer Solutions. *Macromolecules* **1992**, *25*, 5440−5445.

(36) Vancoillie, G.; Frank, D.; Hoogenboom, R. Thermoresponsive Poly(Oligo Ethylene Glycol Acrylates). *Prog. Polym. Sci.* **2014**, *39*, 1074−1095.

(37) Steinhauer, W.; Hoogenboom, R.; Keul, H.; Moeller, M. Copolymerization of 2-Hydroxyethyl Acrylate and 2-Methoxyethyl Acrylate via RAFT: Kinetics and Thermoresponsive Properties. *Macromolecules* **2010**, *43*, 7041−7047.