

Feature Article

Microfluidic fabrication of smart microgels from macromolecular precursors

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ABSTRACT

Stimuli-responsive polymer microgels can be produced with exquisite control using droplet microfluidics; however, in existing methods, the droplet templating is strongly coupled to the material synthesis, because droplet solidification usually occurs through rapid polymerization immediately after the microfluidic droplet formation. This circumstance limits independent control of the material properties and the morphology of the resultant microgel particles. To overcome this limitation, we produce sensitive polymer microgels from pre-fabricated precursor polymers. We use microfluidic devices to emulsify semidilute solutions of crosslinkable poly(*N*-isopropylacrylamide) and solidify the drops via polymer-analogous gelation. This approach separates the polymer synthesis from the particle gelation and allows each to be controlled independently, thus enabling us to form monodisperse, thermo-responsive microgel particles with well-controlled composition and functionality. In addition, the microfluidic templating allows us to form complex particle morphologies such as hollow gel shells, anisotropic microgels, or multi-layered microgel capsules.

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1. Microgels – small but smart materials

Stimuli-responsive or “smart” microgels are micrometer-sized polymer particles that are able to swell or shrink in response to changes in their surrounding [1–4]. It is this responsiveness which makes them attractive for applications in various fields such as drug delivery [5,6], catalysis [7–9], sensing [10–13], and photonics [14,15]. A very common material with pronounced responsiveness is poly(*N*-isopropylacrylamide) (pNIPAAm): it exhibits a lower critical solution behavior in aqueous media at temperatures around 32 °C [16] and has thus been used extensively to form thermo-responsive microgels [1–4,16–18]. Since the transition temperature of pNIPAAm shifts upon copolymerization with polar or non-polar comonomers, the sensitivity of pNIPAAm microgels can be controlled by their chemical composition. However, the microgel behavior also depends on geometric parameters such as the particle size and shape; it is therefore crucial to control both the particle morphology and polymer functionality to design advanced micro-materials with optimized performance.

One idea to control the size and shape of microparticles is to use emulsion droplets as templates for the particle synthesis; the key element of this strategy is to control the morphology of the pre-

microgel droplets and to retain their shape by subsequent droplet solidification. A powerful method to form pre-microgel droplets with exquisite control is droplet microfluidics [17–20]. The principle of this technique is to create a stream of a pre-microgel monomer solution in a microchannel and to induce its periodic break-up by flow focusing with a second, immiscible fluid (continuous phase). When these two fluids meet, droplets form in a “drop-by-drop” fashion due to a balance of interfacial tension and the shear of the continuous phase acting on the dispersed phase. This balance is influenced by a few basic parameters: the viscosities and polarities of the fluids, the flow rates of the fluids, and the dimensions of the microfluidic channels. Since all these parameters are controllable, microfluidic devices produce droplets with great control over their size and monodispersity.

To implement these microfluidic methods, two different techniques have been developed. One of them uses microfluidic devices assembled from glass microcapillaries [17,21], and the other one uses devices stamped into silicone elastomers through the use of soft lithography [22]. Both techniques offer versatile means to fabricate sophisticated channel geometries, and this operational feature opens a route to the formation of complex emulsion structures such as non-spherical droplets [20,23,24], anisotropic droplets [25–27], or multiple-emulsion “droplets-in-droplets” [21,28–34]. Again, these complex structures can be retained by subsequent droplet solidification, typically achieved through rapid on-chip polymerization [17–20,23–30]. However, despite extensive use, these existing techniques of microfluidic particle formation have an intrinsic

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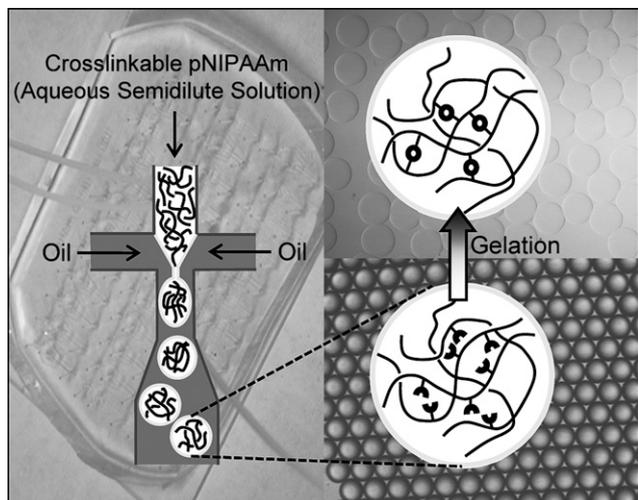


Fig. 1. Microfluidic emulsification of a semidilute solution of crosslinkable pNIPAAm precursors in water (schematic). Subsequent gelation of the monodisperse droplets, achieved through crosslinking the polymer chains by dimerization of pendant reactive side groups, forms monodisperse microgel particles. Reproduced in part from Ref. [37] by permission of The Royal Society of Chemistry.

limitation: since the microfluidic templating and the subsequent polymerization are coupled within one single step, independent control of both the material properties and the morphology of the resultant microparticles is limited.

An excellent strategy to circumvent this limitation is to form the pre-microgel drops from semidilute solutions of *pre-fabricated*

precursor polymers rather than from monomers, and to solidify these drops through polymer-analogous gelation rather than through monomer chain-growth gelation. This approach separates the particle formation from the synthesis of the polymer material and allows each to be controlled independently; it thus combines the control of microfluidic templating with the flexibility of preparative polymer chemistry.

In this paper, we review our work on the use of microfluidic devices to produce thermo-responsive pNIPAAm microgels from macromolecular precursors. We fabricate these microgels by microfluidic emulsification of semidilute solutions of crosslinkable pNIPAAm, followed by subsequent droplet gelation through a polymer-analogous reaction, as illustrated in Fig. 1. Using pre-functionalized precursors allows us to obtain particles with well-defined amounts of functional sites. Due to the control achieved through the microfluidic templating, these particles are highly monodisperse, and their size is determined. In addition, this approach allows us to form complex microgel structures such as hollow gel shells, anisotropic microgels, or multi-layered microgel capsules.

2. Macromolecular precursors – the smart way to smart microgels

To form microgels from macromolecular precursors, we use linear pNIPAAm chains with pendant dimethylmaleimide (DMMI) side groups; these polymers can be crosslinked through a photochemical reaction based on the triplet-sensitized dimerization of their DMMI moieties, as shown in Fig. 2 [35,36]. We prepare the precursors by copolymerizing *N*-isopropylacrylamide and a DMMI-functionalized acrylamide-derivative in a free-radical reaction in water, as also shown in Fig. 2. The molecular weight of the resultant

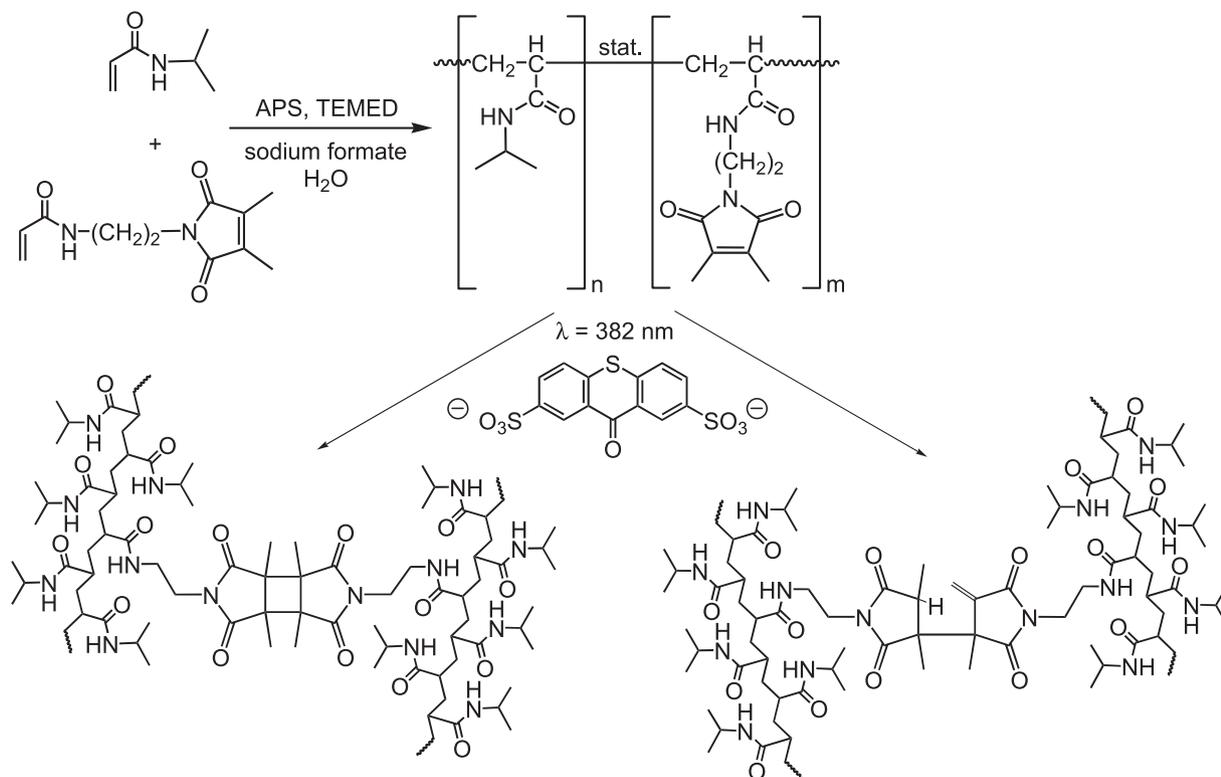


Fig. 2. Preparation of photocrosslinkable pNIPAAm by copolymerization of *N*-isopropylacrylamide and dimethylmaleimide (DMMI) functionalized acrylamide. Subsequent photocrosslinking of the chains is achieved through UV-induced dimerization of their DMMI moieties. In aqueous media, this reaction is mediated by a triplet sensitizer, thioxanthone-2,7-disulfonate (TXS), leading to two isomeric DMMI-dimers [35,36].

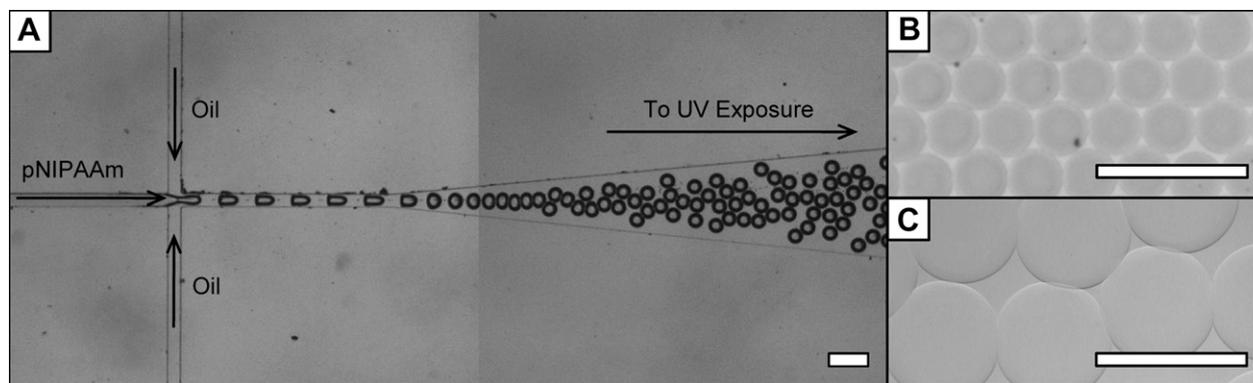


Fig. 3. Production of monodisperse pNIPAAm microgels from macromolecular precursors using a PDMS microfluidic device. (A) A cross-junction channel serves to form monodisperse pre-microgel droplets from a semidilute precursor solution, which are exposed to strong UV light as they flow through a basin channel to solidify them. (B) Monodisperse microgels obtained from the experiment in Panel A. (C) Larger microgels obtained from a similar experiment using a larger microchannel (cf. Ref. [37] for experimental details). All scalebars denote 200 μm . Reproduced from Ref. [37] by permission of The Royal Society of Chemistry.

copolymers can be controlled by performing this polymerization in the presence of sodium formate; typical weight average molecular weights obtained with this method are between $100,000 \text{ g mol}^{-1}$ (high content of sodium formate) and $2,000,000 \text{ g mol}^{-1}$ (no sodium formate) [37].

Once formed, the crosslinkable precursor polymers are used to create pre-microgel droplets in microfluidic devices, as sketched in Fig. 1. For this purpose, we emulsify aqueous precursor solutions with concentrations in the semidilute unentangled regime, an intermediate range right above the threshold for coil overlap, c^* , yet below the onset of chain entanglement, c_e^* . Working with a concentration above c^* ensures that a space-filling polymer network can be formed inside each droplet, whereas keeping the concentration below c_e^* ensures that the viscosity of the solution is not too high. If the precursor chains have molecular weights of not more than about $500,000 \text{ g mol}^{-1}$ (weight average), their microfluidic emulsification is highly controllable, whereas less control is achieved when chains with a higher molecular weight are emulsified [37].

After forming pre-gel droplets, microgel particles are obtained by droplet gelation, achieved through photocrosslinking of the precursor polymers inside the drops (Fig. 1). For this purpose, it is advantageous to employ a microfluidic device which allows exposure of the droplets to UV right after their formation. We use soft lithography to fabricate microfluidic devices from poly(dimethylsiloxane) (PDMS) [22] which consist of a cross-junction channel to form drops and a basin channel to cure these drops. In a typical experiment, we create droplets with diameters of about $60 \mu\text{m}$, as shown in Fig. 3A. These drops contain a 50 g L^{-1} precursor solution of crosslinkable pNIPAAm ($M_w = 200,000 \text{ g mol}^{-1}$, DMMI content 0.75 mol-%), along with 0.5 mmol L^{-1} of a photosensitizer, thioxanthone-2,7-disulfonate (TXS). Exposing them to strong UV light produces monodisperse microgel particles as shown in Fig. 3B. Similar microgel particles, but with diameters of about $150 \mu\text{m}$ obtained in a device with a larger channel, are shown in Fig. 3C.

The use of pre-polymerized precursors to form microgels provides a very useful benefit: since the particle gelation occurs independently of the polymer synthesis, microgels can be fabricated from highly pre-functionalized precursors. Such pre-functionalized polymers can be synthesized in a previous, independent step, and the subsequent microfluidic particle production imparts their functional sites into the resultant microgel particles with 100% efficiency. In addition, this strategy can be extended to the incorporation of many different functional sites by the use of several

different precursor polymers, each imparting its own functionality. These precursors need only to be terpolymers which consist of a main monomer, a crosslinkable comonomer, and another functional comonomer. Mixing several of such terpolymers allows particles to be produced with a precisely defined composition and type of functionalization.

To demonstrate this concept, we synthesize pNIPAAm particles which contain defined amounts of two different fluorescent dyes, representing two different types of arbitrary functionalities [37]. These dyes are easy to detect, and their concentration inside the

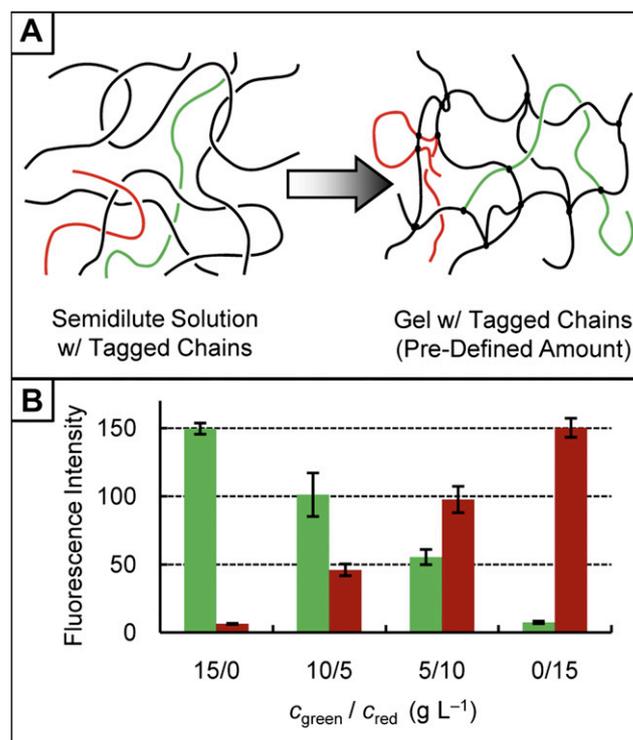


Fig. 4. Production of microgels with defined amounts of fluorescent tags. (A) Gelation of a semidilute polymer solution which contains red- and green tagged precursors yields a polymer gel with pre-defined concentrations of fluorescence labels. (B) Average fluorescence intensities of pNIPAAm microgels produced from semidilute precursor solutions which were doped with red- and green-labeled tracer chains with concentrations as denoted on the abscissa. Reproduced in part from Ref. [37] by permission of The Royal Society of Chemistry.

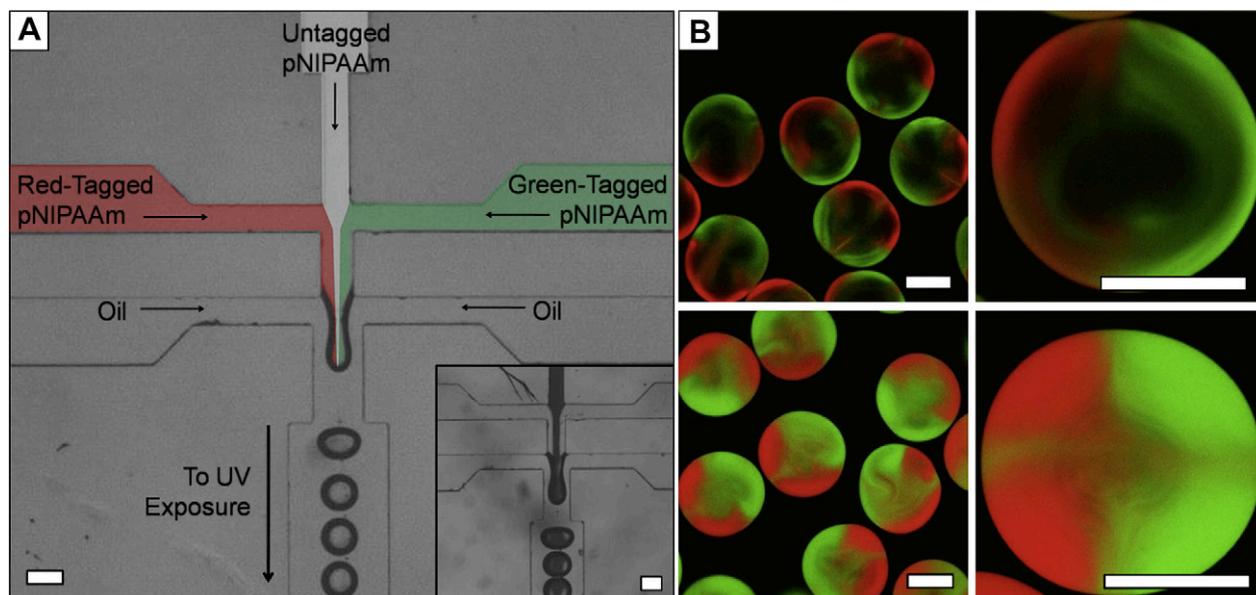


Fig. 5. Microfluidic templating of anisotropic microgels with two distinguishable sides (“Janus microgels”). (A) Optical micrograph of a microfluidic device forming aqueous droplets from three separate semidilute pNIPAAm solutions. In the first junction, these three solutions meet and form a laminar, co-flowing stream. In the second junction, this stream is broken to form monodisperse droplets by flow focusing with paraffin oil. For demonstration purposes, two of the three polymer phases are tagged with either red or green fluorescent dyes while the third phase is untagged; however, note that the color in Panel A was added digitally, because the true color of these polymer solutions is visible only through fluorescence. To visualize the flow pattern with greater clarity, the inset micrograph shows a similar experiment with a center phase that is doped with iron oxide nanoparticles (from Ref. [38]). Right after their formation, the droplets enter a wide basin channel, where they are gelled by UV exposure. (B) Fluorescence micrographs of the resultant microgel particles. Varying the flow rates of the two tagged outer polymer phases, the untagged center polymer phase, and the emulsifying oil phase from 105:105:30:500 $\mu\text{L h}^{-1}$ (upper row of micrographs) to 30:30:180:500 $\mu\text{L h}^{-1}$ (lower row of micrographs) yields particles with different inner morphology. All scalebars denote 100 μm . Reprinted in part with permission from Ref. [38]. Copyright 2010 American Chemical Society.

microgels can be precisely quantified. We use mixtures of an unlabeled crosslinkable matrix polymer (pNIPAAm) which is doped with defined amounts of red- and green-tagged crosslinkable tracer chains (also pNIPAAm) and cure these solutions as sketched in Fig. 4A. We prepare four different samples, each consisting of 35 g L^{-1} of unlabeled photocrosslinkable pNIPAAm as well as red- and green tagged pNIPAAm in quantities of 15 and 0, 10 and 5, 5 and 10, or 0 and 15 g L^{-1} . By emulsifying these solutions in a microfluidic device and photogelling the aqueous droplets, we obtain monodisperse particles which contain the same fractions of red and green dye as their corresponding precursor polymer mixtures. To prove this result, we image the resulting particle suspensions with a fluorescence microscope (Leica TCS SP5) and quantify their average

fluorescence intensities, which reflect the initial fractions of red and green dye in their respective pre-microgel solutions within experimental error, as detailed in Fig. 4B [37].

3. Microfluidic templating – from drops to complex structures

Apart from the production of isotropic, spherical microgels, microfluidic emulsion templating can also serve to form particles with complex morphology. By this means, the use of macromolecular precursors allows not only microgels to be formed with precisely determined *average* degree of functionalization, but can also serve to control the *spatial distribution* of the functional sites

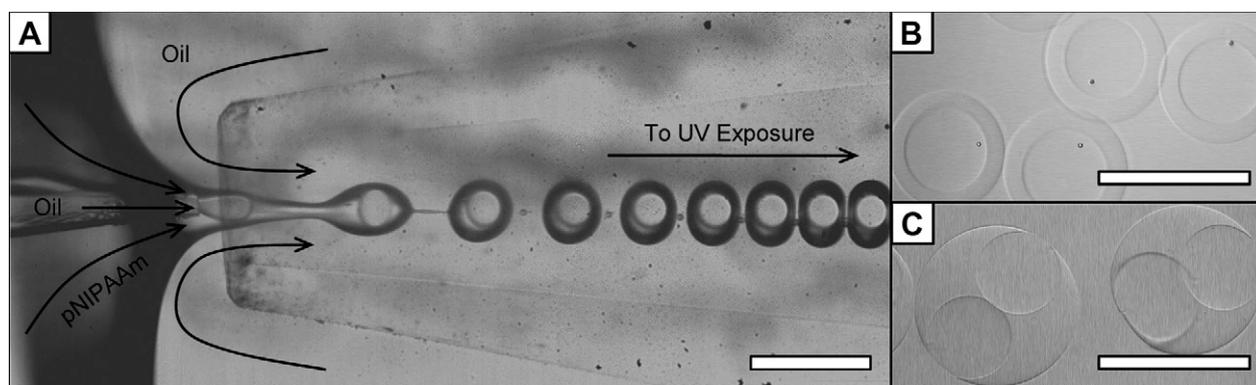


Fig. 6. Microfluidic production of hollow microgel shells. (A) A glass microcapillary device is used to create an oil-water-oil double emulsion with a semidilute solution of crosslinkable pNIPAAm as aqueous phase. Subsequently, these droplets are cured by UV exposure as they flow through a delay capillary a few centimeters downstream (not shown). (B) pNIPAAm microspheres obtained from the experiment in Panel A. (C) Double-core microspheres obtained upon slight variation of the flow rates in the experiment in Panel A (cf. Ref. [37] for details). All scalebars denote 200 μm . Reproduced from Ref. [37] by permission of The Royal Society of Chemistry.

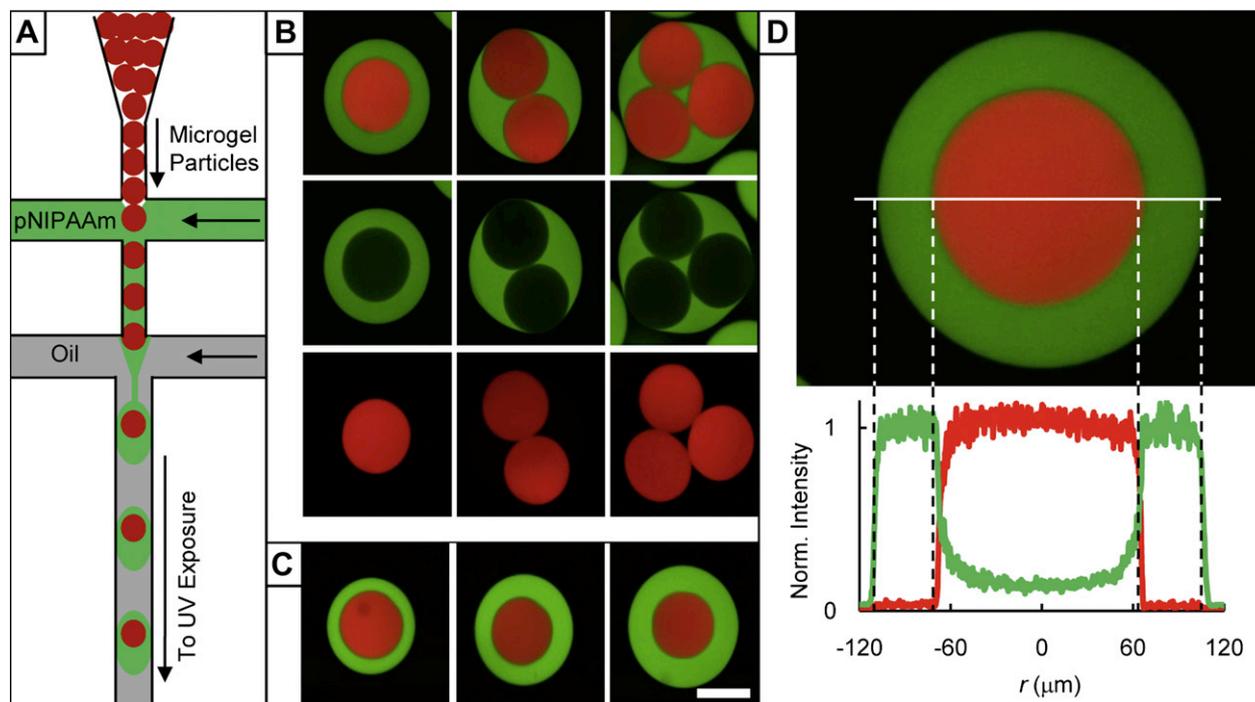


Fig. 7. Microfluidic fabrication of microgel capsules that consist of two miscible yet distinct layers. (A) Schematic of a microfluidic device forming aqueous pNIPAAm droplets that are loaded with a well-defined number of pre-fabricated microgel particles of a similar material, pNIPAAm or polyacrylamide. Subsequent droplet gelation leads to microgels with a distinct core–shell architecture. (B, C) The flow rates of the inner particle phase (red-tagged pNIPAAm), the middle polymer phase (green-tagged pNIPAAm), and the outer oil phase control the number of core particles in each shell (B) as well as the shell-thickness (C). Pictures in the upper row of Panel B show an overlay of the micrographs in the middle and lower row, which depict separate visualizations of the green-tagged pNIPAAm shell and the red-tagged pNIPAAm core. (D) Spatially resolved intensity profiles of the red and green fluorescence in the single-core particle shown in Panel B, evidencing only very little interpenetration of its two phases. The scalebar denotes 100 μm and applies to all micrographs in Panel B and C. Reprinted with permission from Ref. [39]. Copyright 2010 American Chemical Society.

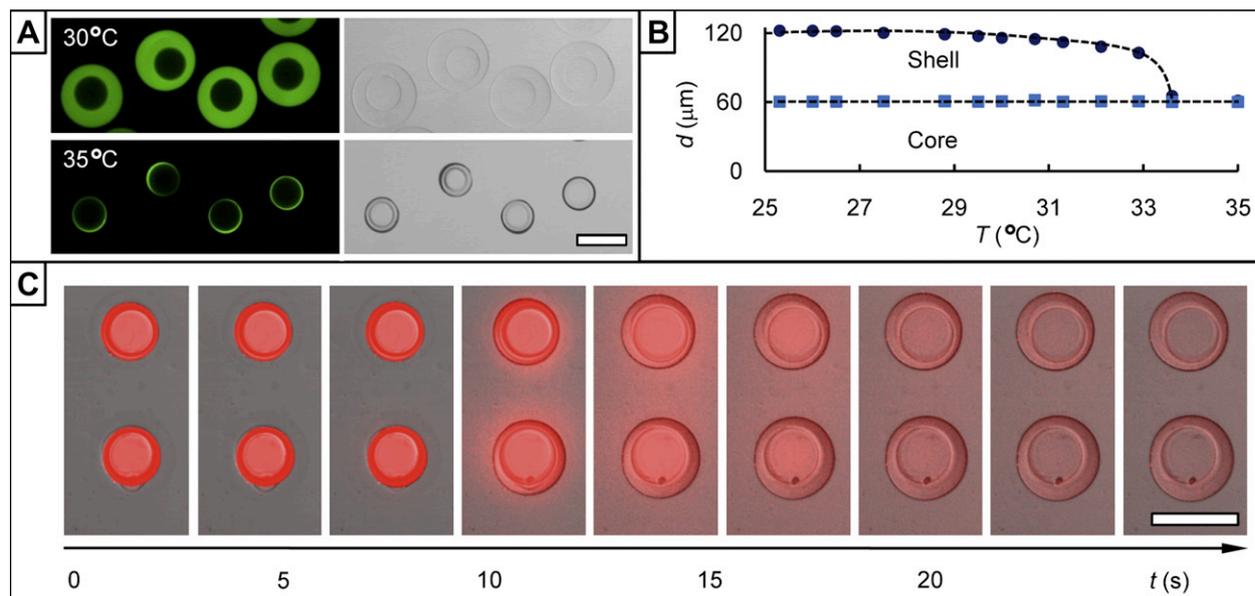


Fig. 8. Thermo-responsive behavior and controlled release application of pAAm–pNIPAAm core–shell microgels. (A) Fluorescence images (left column) and bright field micrographs (right column) of microgels consisting of a 60 μm untagged pAAm core encapsulated in a green-tagged pNIPAAm shell. At ambient temperatures (upper row), the shell is swollen, whereas it collapses at elevated temperatures (lower row). By contrast, the core dimension remains unaffected by the same changes of temperature. (B) Detailed plot of the particle-diameter, d , as a function of temperature, T . Dark blue circles represent the diameter of the entire particle, i.e., pAAm core plus pNIPAAm shell, whereas light blue squares represent only the pAAm core. The dotted lines are guides to the eye. (C) Controlled release of RITC-dextran ($M = 10,000 \text{ g mol}^{-1}$) from the particles in Panel A. In the course of the first 10 s of this experiment, the temperature remains above 33 $^{\circ}\text{C}$, and the particles remain sealed (left three pictures). As the temperature decreases, a spontaneous release of the active incorporated in the particles is triggered by the swelling of the pNIPAAm shells. All scalebars denote 100 μm . Reprinted with permission from Ref. [39]. Copyright 2010 American Chemical Society.

across the microgel particles. In an illustrative example, we form microgels which are anisotropic and exhibit two distinguishable sides (“Janus microgels”) [38]. We template these particles from three different polymer solutions, injected into a microfluidic device with two sequential cross-junctions as shown in Fig. 5A. The three polymer phases consist of aqueous solutions of crosslinkable pNIPAAm along with TXS. To visualize the formation of Janus structures, we dope two of these three polymer phases with trace amounts of red and a green fluorescently tagged crosslinkable pNIPAAm.

After their injection, the three precursor solutions meet at the first cross-junction and form a laminar co-flowing stream, as shown in Fig. 5A. The tagged materials flow in the outer threads, whereas the untagged material flows in the middle. About 500 μm downstream, this co-flowing stream enters a second cross-junction, where it is broken to form monodisperse droplets by flow focusing with paraffin oil that contains a surfactant. During the drop formation, the continuous oil phase flows past the growing drop and creates a convective flow [25] inside each droplet, which distorts the three-striped pattern into a core–shell-like structure with two colored hemispheres and an uncolored center. Exposing these structured droplets to strong UV light crosslinks the precursor chains, thereby forming microgel particles with distinguishable red and green halves and a core–shell-like structure. The spatial distribution of the tagged precursors inside these microgel particles is controlled by the fluid flow rates, as demonstrated in Fig. 5B [38].

The principle of the microfluidic fluid-in-fluid emulsification can be extended to form double, triple, and higher order emulsions [21,28–34]. These “drops-in-drops” are useful to template core–shell microparticles; in a typical experiment, we use them to form hollow gel shells [37]. For this purpose, we use a glass microcapillary device [21] to form monodisperse drops of a semidilute pNIPAAm precursor solution in a continuous phase of paraffin oil. At the moment of their formation, these droplets are loaded with inner droplets of kerosene, thereby creating a shell structure as shown in Fig. 6A. After droplet formation, the shell is gelled by exposure to UV light, yielding uniform pNIPAAm microshells as shown in Fig. 6B. Operating the device with different flow rates produces shells with two cores, as shown in Fig. 6C.

In the preceding example, the microgel templating occurs from multi-layered droplets with alternating polarity. Apart from their utility to form hollow gel shells, these droplets can also serve to produce bipolar microparticles [29]. However, it is impossible to use them for the creation of distinct core–shell structures with similar polarity in both the core and the shell. To circumvent this limitation, we employ a step-by-step approach [39]: first, we create monodisperse, micrometer-sized hydrogel particles which serve as the core material. Then, we wrap these particles into monodisperse, aqueous polymer shells using a microfluidic device that consists of two cross-junctions in series, as sketched in Fig. 7A. In the first junction we add a semidilute, aqueous solution of crosslinkable pNIPAAm chains as the shell phase. In the second junction we add oil to form bi-layered pre-microgel drops. We then lock these structures by crosslinking the pNIPAAm chains in the shell. The resultant particles consist of a hydrophilic polymer core nested in a hydrophilic polymer shell, both crosslinked and swollen in water, but both formed from different macromolecular precursors.

To demonstrate the utility of this technique, we use a shell phase that is tagged with a green fluorescent tracer polymer, along with red-tagged core microgel particles; this strategy allows us to visualize the formation of core–shell structures which exhibit a well-controlled number of core particles in each

shell and a well-controlled shell-thickness, as shown in Fig. 7B and C. Since we use *macromolecular* precursors to create the shell, there is no marked interpenetration of the shell material into the core. This circumstance is evidenced by the middle and lower row of micrographs in Fig. 7B, which show separate visualizations of the green-labeled shells and the red-labeled cores of the microgels in the upper row. To substantiate this finding, spatially resolved profiles of the fluorescence intensity across the micrographs in the left column of Fig. 7B are plotted in Fig. 7D, proving that the red-tagged core material and the green-tagged shell material are well separated.

In an implementation of this experiment, we incorporate non-thermo-responsive polyacrylamide (pAAm) core particle (not labeled) into thermo-responsive pNIPAAm shells (green fluorescently labeled). The behavior of the resultant core–shell microgels upon increase of the temperature to 35 $^{\circ}\text{C}$ is visualized in Fig. 8A and detailed in Fig. 8B: while the shell collapses due to the volume phase transition of pNIPAAm, the core remains unaffected. Due to this selective sensitivity, these particles are applicable for encapsulation and controlled release purposes: when the pNIPAAm shell is swollen it is permeable, whereas it becomes impermeable when it collapses. By contrast, the pAAm core is always permeable and its degree of swelling remains unaffected by temperature, thereby providing stability of shape. Thus, when the shells are swollen, the particles can be loaded with hydrophilic low molecular weight or mesoscopic additives. Upon increase of the temperature, the thermo-responsive shell collapses and encapsulates these actives in the pAAm core. Then, all surrounding feed material can be removed and the loaded particles can be stored at elevated temperatures. However, as soon as the temperature is decreased, the actives are rapidly released. This application is substantiated in Fig. 8C, which shows a sequence of images from an experiment where RITC-tagged dextran ($M = 10,000 \text{ g mol}^{-1}$) is released from pAAm–pNIPAAm microgels.

4. Conclusions and outlook

The combination of microfluidic droplet templating with subsequent polymer-analogous droplet gelation offers promising means to form functional microgel particles with independent control of their morphology and chemical composition. These materials are useful for various applications, such as the encapsulation and controlled release of actives. If the implementation of the techniques presented in this paper is achieved through the use of microfluidic devices made by soft lithography, the microgel fabrication can be scaled up by device parallelization, offering the potential to produce larger quantities of sensitive microparticles.

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David A. Weitz is Mallinckrodt Professor of Physics and Applied Physics at Harvard University. He received his bachelor's degree in physics from the University of Waterloo and his Ph.D. in physics from Harvard University. He joined the technical staff at Exxon Research and Engineering, where he worked for nearly 18 years. Weitz then began his academic career as a Professor of Physics at the University of Pennsylvania, and then moved to Harvard University, where he has a joint appointment in the Physics Department and the School of Engineering and Applied Sciences. He is director of Harvard's Materials Research Science and Engineering Center, funded by the National Science Foundation. He is also a co-director of Harvard's Kavli Institute for Bionano Science and Technology, and the BASF Advanced Research Initiative. Weitz' primary research interests are in experimental soft condensed matter science