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Focus Article, *Mendeleev Commun.*, 2020, **30**, 555–562

Mendeleev Communications

Stimuli-responsive aqueous microgels: properties and applications

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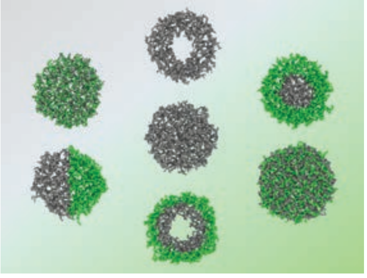
DOI: 10.1016/j.mencom.2020.09.002

Water-soluble microgels have been known for over than three decades. Initially introduced as thermoresponsive polymer colloids with tunable softness, these macromolecular objects become a versatile platform for a broad range of potential applications due to the bursting growth of the diversity of their chemical architecture through the years. The recent progress in the design of stimuli-responsive microgels together with the notable examples of their applications is discussed in this paper.



Keywords: microgels, stimuli-responsiveness, drug delivery, emulsion stabilization, catalysis.

Introduction

Microgels are macromolecular objects of ultra-high molecular mass with a network-like structure in the size range from tens of nanometers to several microns.[1,2] The chemical architecture of such objects gives rise to a unique combination of physical properties of both macromolecules and conventional hard colloids. On the one hand, in a good solvent the network is highly swollen, which provides softness and porosity. On the other hand, microgels collapse in a poor solvent expelling most of the solvent from the interior, and in this state resembling the hard colloids. In addition, the colloid-like behavior arises upon the increase of the microgel concentration in solution, which eventually leads to crystallization.[3] Meanwhile, microgels are also known for their high interfacial activity at the fluid interface, which draws a parallel between them and the surfactants.[4] Stimuli-responsive and water-soluble microgels are of special interest since their sensibility to variation of external conditions (such as the temperature or the pH level) can find its place in a number of contemporary applications, for instance, in functional nanomedicine[5–7] and food industry.[8] In this mini-review, we highlight the most interesting physicochemical properties of synthetic aqueous microgels and microgel-based systems and give a brief overview of the recent advances in this field. Finally, we discuss the possible applications and provide some notable examples.

Main features

The sensitivity to various stimuli primarily relies on the chemical composition of the microgels[9] (Figure 1). The earliest reported and simultaneously the most common to date example are

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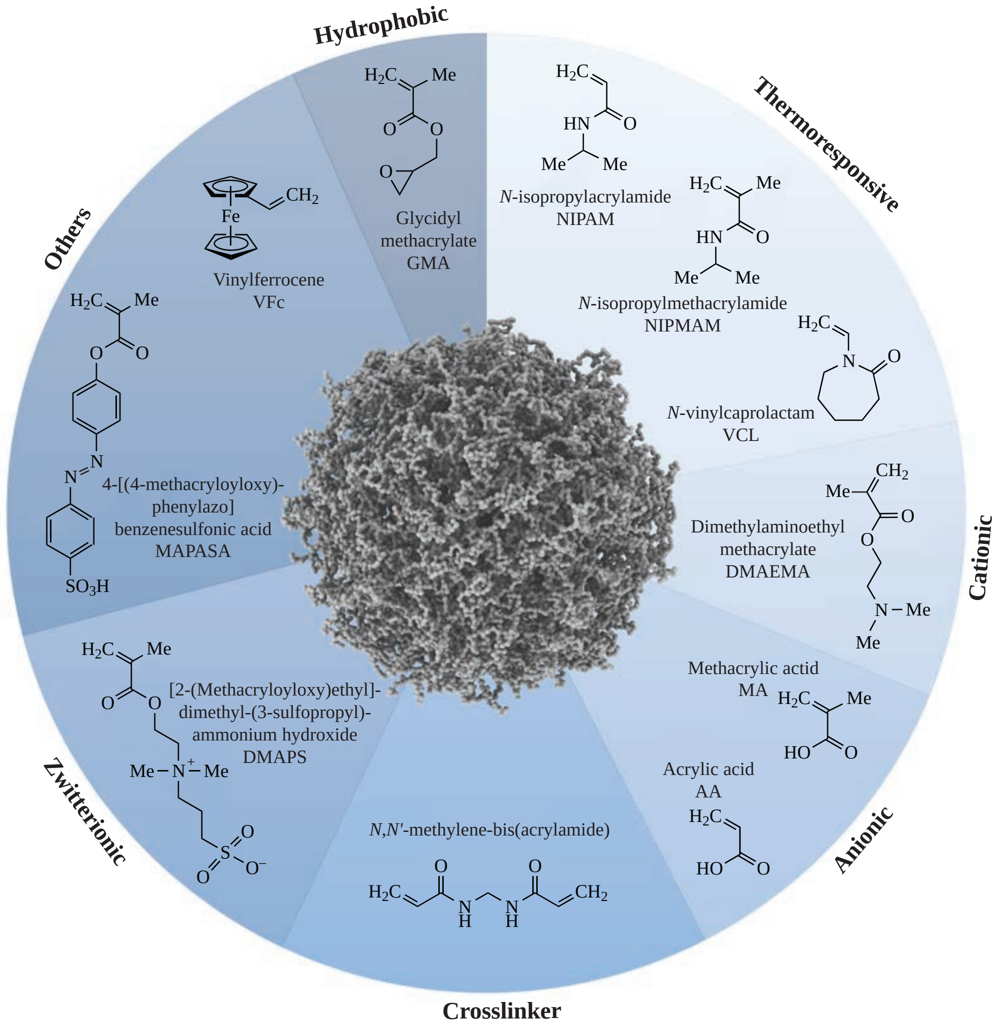

Figure 1 The functional monomers wheel representing the examples of various groups constituting a microgel particle. Inspired by ref. 1.

thermoresponsive microgels based on *N*-isopropylacrylamide (NIPAM),[10–12] which swell when the temperature is below the volume phase transition temperature (VPTT, about 33 °C) and collapse when the temperature is above VPTT. This feature is a result of the presence of both hydrophilic and hydrophobic parts in monomer unit. The hydrophilic part forms hydrogen bonds with water while hydrophobic interactions of hydrophobic groups increase with the temperature. Another notable monomers providing thermoresponsivity are: *N*-vinylcaprolactam (VCL),[13–15] which forms polymers that have similar VPTT and are known by good biocompatibility,[15] *N*-isopropylmethacrylamide (NIPMAM) with higher VPTT (about 45 °C),[16–18] and NIPAM isomer *N*-*n*-propylacrylamide (NNPAM) with lower VPTT (about 23 °C).[19–21]

Thermosensitive microgels are usually synthesized *via* relatively simple method of free radical precipitation polymerization in aqueous solution at the temperatures around 60–80 °C when water is a poor solvent for the base polymer.[9] Network formation is achieved by introduction of cross-linker, usually *N*,*N'*-methylene-bis(acrylamide). The addition of thermoresponsive comonomer with VPTT different from that of the base monomer may adjust the VPTT of the whole particle. For instance, the VPTT of poly-*N*-isopropylacrylamide (PNIPAM)[22] or poly-*N*-vinylcaprolactam (PVCL)[23] microgels can be raised or decreased by incorporation of NIPMAM or NNPAM, respectively. Note that for microgels based on secondary amides the solvent composition may also regulate their swelling degree, and thus the particular mixture of two good solvents (usually, water and alcohols) can act as a poor solvent (cononsolvency effect).[24] This is a result of the enthalpic preferential adsorption of one of the co-solvents to the subchain monomers.[25]

Another way to lower the VPTT and to provide the amphiphilicity is to introduce the hydrophobic comonomers, such as *N*-*tert*-butylacrylamide (TBA),[26,27] styrene,[28,29] glycidyl methacrylate (GMA),[30,31] methyl methacrylate (MMA),[32] and recently reported 4-*tert*-butylcyclohexylacrylate (TBCHA).[33] As a result, the more hydrophobic content is incorporated in the microgel, the less responsive it becomes. On the contrary, the increase of VPTT can also be achieved by incorporation of charged comonomers (anionic[34–37] or cationic[38–40]). Here, the electrostatic repulsion between like charges causes an enhanced stretching of network subchains. In turn, the interplay between these long-range and hydrophobic interactions can lead to an unexpected outcome upon the collapse, such as the intraparticle segregation inside the structurally homogeneous network with denser shell and inner ‘cavity’.[41]

The presence of charged groups not only gives a higher swelling degree but also endows microgels with sensitivity to pH-level, as well as to the ionic strength.[42,43]A more diverse behavior can be found for polyampholyte[44–46] and polyzwitterionic[47,48] microgels. In the first case, an increased swelling is observed when the level of pH is either low (pH 2–3) or high (pH 9–10), *i.e.* when only cationic or anionic groups are activated.[44] Simultaneously, at the intermediate level of pH the complexation of oppositely charged groups with each other leads to the shrinkage of microgels regardless of the temperature.[46] Meanwhile, in the second case, the presence of zwitterionic moieties results in the emergence of second VPTT at lower temperatures where the physical cross-links are formed due to the dipolar interactions.[48]

The spectrum of microgels responsivity can be further extended *via* the incorporation of other functional groups during copolymerization[49–52] and thus allowing, for instance, the response to the light[49,50] or to the change of electrochemical potential[51,52] to occur. For the first example it has been shown that the incorporation of 4-[(4-methacryloyloxy)phenylazo] benzenesulfonic acid (MAPASA) into the VCL-based particles allows the deswelling of the network to proceed *via* the UV irradiation (λ = 365 nm) though the transition from *trans* to *cis* state usually makes the photosensitive pendant groups more polar.[50] A possible explanation of such effect was proposed, namely that the approach of the sulfonic acid groups of *cis*-ABSA toward the polymer backbone causes the disruption of hydrogen bonding between water molecules and the carbonyl groups of VCL.[50] Finally, microgels can be post-modified in order to achieve a desirable functionality.[31,53,54]

Structural diversity

Along with the chemical composition, the properties of responsive microgels also depend on the overall structure of the network. Modern synthesis methods allow one to achieve the particles with diverse architectures and tailored properties (Figure 2). Regarding the aforementioned precipitation polymerization, a characteristic feature of microgels produced by this method is that their segment density decreases from the center to the periphery. This distribution is caused by higher cross-linker reactivity in comparison to the base monomer,[55] which leads to the formation of highly cross-linked center at early stages of polymerization process and fuzzy-periphery at the late stages (a core-corona structure).[56–58] Moreover, for amphiphilic particles the formed network will possess a core–shell structure where core will be mostly hydrophobic and the shell will be mostly hydrophilic.[28,30] An optimization of the preparation method including the continuous monomer feeding (so-called semi-batch approach)[59–61] or the use of pre-polymers[62] provides the uniform density of the fabricated microgels [Figure 2(*a*)]. In terms of thermoresponsive behavior, a homogeneous network will bear a more continuous volume phase transition upon the heating.[61] Alternatively, one can use the different polymerization technique, namely, the miniemulsion polymerization,[33,62,64] which also facilitates a uniform distribution of functional monomers regardless of their hydrophilicity [Figure 2(*c*)].[33,64]

Microgels might be organized in a core/shell structure with chemically different inner and outer parts [Figure 2(*d*)], and the possibility of combining networks with different properties could give rise to new features.[16,45,65–68] For instance, it was shown that if the VPPT of the core is lower than that of the shell, a two-step shrinking behavior is observed.[65] In the opposite case (the VPTT of the shell is lower),[16,66,67] the microgels could reveal a linear thermoresponsivity[66] and the inversion of the core at the intermediate temperatures.[67] In addition, for polyampholyte core–shell microgels with oppositely charged core and shell,[45,68] one could tune pH level in a such way that the occurred complexation of compartments will lead to a quasi-hollow morphology.[68] The applicability of this feature will be discussed in the next section.

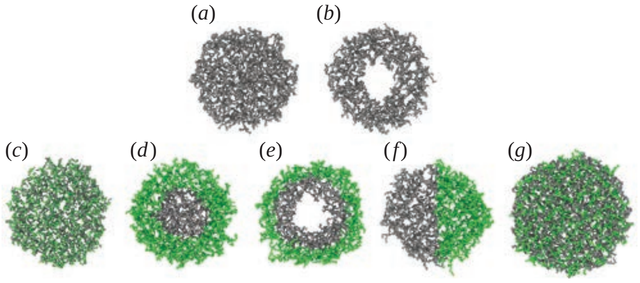

Figure 2 The most common architectures of stimuli-responsive microgels: (*a*) regular, (*b*) hollow, (*c*) random copolymer, (*d*) core–shell, (*e*) multi-shell, (*f*) Janus, and (*g*) from interpenetrating networks.

An important type of microgels in terms of drug delivery are hollow ones with a solvent filled cavity, which can be achieved by the dissolution of sacrificial core [Figure 2(*b*)].[69–73] The shape of the core can be arbitrary in principal, and thus the network of anisotropic shape with non-spherical cavity can be achieved.[72] In turn, the size of the resulting cavity mainly depends on the cross-linking density: the higher it is, the less the shell swells into the interior.[70,71] In the case of polyelectrolyte networks, the size of the cavity can be also tuned *via* the level of pH and the ionic strength.[73] The combination of core–shell and hollow-shell approach results in the obtaining of microgels with multi-shell architecture [Figure 2(*e*)],[74,75] where the permeability of the inner shell can be tuned *via* temperature while the colloidal stability is preserved by the swollen outer shell.[74,75]

A promising pathway to produce large amount of microgels is the use of microfluidics-based polymerization methods,[76–78] providing the fabrication of responsive particles of desirable shape (cylindrical[77] or complex[78]) on the micrometer scale (>10 μm). Besides, one can produce the Janus microgels comprising spatially separated comonomers or functional groups [Figure 2(*f*)].[76] However, the obtaining of such particles of complex architecture on the nanometer scale is still quite challenging. Some notable advances have been reported recently, such as the cubic-shaped microgels *via* electrochemical-initiated radical polymerization with a photovoltaic cell as power supply[79] or the polyampholyte Janus-like microgels by coacervation of reactive precursors in precipitation polymerization.[80]

Finally, one should mention the microgels composed of interpenetrating networks [Figure 2(*g*)].[81–85] Here, the second network [usually based on the poly(acrylic acid)][81,83,85] is grown inside of the thermoresponsive (usually a PNIPAM-based one) network. As a result, the stimuli-responsive particle will not reveal a shift in VPTT like in copolymer microgels,[34,36] and the swelling degree of each network can be tuned independently. Moreover, one could expect an emergence of non-trivial morphologies, namely a core–shell–corona morphology.[84]

Interactions with guest molecules

Adjustable and permeable structure allows one to use microgels for uptake, storage and release of guest molecules.[64,86–103] Usually, the driving force of the uptake is of electrostatic nature since microgels might have charged moieties in their structure due to the initiator or specially introduced functional groups. The ability to absorb different substances including ionic surfactants,[88,97] metal ions and salts,[86,100] dyes,[91,93,94] nanoparticles,[96] polyelectrolytes,[98] and, notably, proteins[90,99,101] through the electrostatic attraction has been demonstrated. As a rule, the absorption decreases the swelling ratio of microgels in comparison with the unloaded state due to the complexation between the charged groups and oppositely charged guest species. Meanwhile, the absorption may also provide the additional functionality, for instance, the responsivity to the magnetic field[96] or UV irradiation.[97] Besides, the uptake of metal salts can lead to the formation of metallic nanoparticles within the network, which will serve as seeds (adsorption centers) in the further uptake cycle.[100] Such ‘recognition’ can also be used for the obtaining of composite raspberry-like microgels, where the hydrophobic seeds are stabilized by initially absorbed surfactants.[103] However, here the driving force is of hydrophobic nature, which distinguish the second uptake mechanism.

The hydrophobic–hydrophobic interactions play an important role in the case of drug loading.[7] Being insoluble in water, the drug molecules can be concentrated in the hydrophobic domains inside amphiphilic microgels[64] or during deswelling of responsive particles.[6,92] Similar mechanism works when microgels absorb the minor fraction from the asymmetric mixture of immiscible liquids.[89,102] On the other hand, if the liquids themselves act as good solvents for the microgel, the uptake occurs mainly due to the incompatibility between the liquids: the mutual contacts are minimized when the minor liquid gets absorbed by microgel.[102] The other notable examples of uptake mechanisms include the formation of hydrogen bonds which are responsible for polar polymers loading[87] and the sponge-like behavior of swelling microgels, where the guest molecules are absorbed with a surrounding water.[95]

A crucial point lies not only in the uptake but also on the retention of the molecules in the loaded carriers. A good solution can be found in using core–shell or multi-shell microgels.[7] It was shown that the anionic shell shields the cationic core and thus entraps the absorbed polyelectrolytes inside the core of polyampholyte network.[98] The same effect of the entrapment of cytochrome *c* together with the stability of the complex towards the mechanical deformations has been demonstrated recently for microgels with reverse architecture (anionic core and cationic shell).[101] Regarding the hollow particles of complex architecture, one can absorb the guest molecules during the collapse of the inner shell while the outer swollen shell provides the stability toward the interparticle aggregation.[7,74] In turn, the presence of the cavity should also increase the loading capacity of the microgels. As an alternative, for hollow interpenetrating network microgels the stability of such molecular cargo is carried out through the electrostatics of the second network while the first network forms a dense shell encapsulating the drugs.[92]

Interfacial behavior

The behavior of responsive microgels at the various types of interfaces: fluid/fluid (air/water[104–111] and oil/water[112–128]), fluid/solid,[18,31,36,61,105,129–132] and even biomembranes[133–135] has been extensively studied. We start with the first type since the physicochemical effects occurring here explain the behavior of the network particles at the other types of interfaces. Similar to the hard colloids, microgels adsorb at fluid interfaces in order to reduce the interfacial tension. However, the adaptivity of microgel structure leads to the strong deformation (flattening) and attaining ‘fried-egg’ conformation at the interface [Figure 3(*a*)].[110,111,115,118,124,127] The overall shape of the adsorbed particles is strongly dependent on several parameters. In many cases, the shape is determined by the balance between the elastic free energy of the network (which is a measure of the softness) and the interfacial energy. Namely, the deformation ratio increases with: (i) the decrease of cross-linking density,[105,107,114,118,119,121,124,128] (ii) the increase of the adsorption strength (surface tension between the water and air/oil),[114,121,124] (iii) the decrease of microgel molecular weight (size),[118,121,122,128] (iv) the presence of the cavity.[119] Moreover, in the limiting case of ultra-low crosslinked microgels,[123,131,136] the overall conformation of the particle will be almost two-dimensional.[123] In case of oil/water interfaces, the compatibility of the network segments with the different liquids plays an important role: the more microgel swells in the particular liquid, the more it protrudes into this phase.[106,119,120,124,126–128] In the case of the ‘symmetric’ interactions (both liquids are good solvents for the microgel), the particles interior could serve as a mixer of the liquids if the incompatibility between them is not strong enough [Figure 3(*b*)].[120,121] Alternatively, one can use the amphiphilic microgels,[33] for which the effect of mixing could be observed for a wider range of liquid pairs.[125] Besides, the adsorbed particles remain sensitive to the external stimuli (at least, to the temperature[110,112,118,127,128]), although the character of the collapse changes significantly. Initially, the microgels deswell mainly perpendicularly to the interface (even after VPTT)[111,127,128] due to the high interfacial energy.[110,127,128] Simultaneously, such deswelling causes the decrease of the surface tension due to the increase of the polymer concentration, *i.e.* due to the decrease of the number of contacts between the fluids molecules.[108,112,116,128] The further increase of the temperature leads to the shrinkage of the particles in lateral dimensions while the overall shape remains aspherical.[128] However, the observation of standalone microgels is seldom possible.

During the adsorption to the interface, the microgels tend to form a monolayer with hexagonal packing [Figure 3(*c*)], and therefore the shape of the network particles also depends on the packing density. In the case of liquid droplets[105,110] and oil/water emulsions,[112–114] such parameter cannot be tuned easily since the spontaneous character of the adsorption.[105,113] On the contrary, the packing density can be controlled on a flat interface, *i.e.* by using the Langmuir–Blodgett trough. In the majority of the studies, the monolayers of PNIPAM-based microgels prepared by precipitation polymerization core–shell (or core–corona for the one-step synthesis) architecture are considered.[107,109,111,115,116,119,122,123,127] The compression of the monolayers leads to the compaction of the particles and to their deformation. Several distinct regimes have been observed here [Figure 3(*d*)]:[127] (i) a 2D ‘gas’ of weakly interacting particles, (ii) the ordered monolayer with shell–shell interparticle contact, (iii) the monolayer with mixed inteparticle interactions (shell–shell and core–core), (iv) the monolayer with core–core contacts, (v) the fail of the monolayer. In turn, the presence of regimes (ii)–(iv) depends on the parameters mentioned in the previous paragraph. Namely, when the microgels are small[122] and loosely-crosslinked,[107,116] the regime (iii) disappears and the continuous compression is observed. Meanwhile, the increase of the temperature excludes the regime (iv) due to increased polymer density in the core: the further compression in the lateral direction of the monolayer becomes impossible.[111,127] Shape of the microgels also influences an ultimate structure of monolayers. For example, less ordered structures are observed in dense monolayers of cubic microgels.[137] In the case of polyelectrolyte networks, the long-range electrostatic interactions could induce the ordering even without the physical contact[115,126] though they have almost no effect at the higher degrees of compression.[109]

The topography of the monolayers is in general analyzed by atomic force microscopy (AFM), which means the transfer of the monolayer onto the solid surface [see Figure 3(*d*)]. While it was proven[111,127] that the observable regimes emerge at the fluid interface, one cannot exclude the interactions of microgels with the surface. Overall, the adsorption at this type of interface (solid/fluid) also may cause the flattening of the particles [Figure 3(*e*)], and the degree of deformation depends on the structural properties of microgels similarly to the fluid interfaces.[18,31,36,61,105,129–132] In addition, for solid/liquid interface the particles also remain responsive, which could lead to some interesting effects. For instance, it was shown that if the solid surface is porous, the microgels could enter the pore upon the collapse and exit the pore upon the swelling.[129] However, the driving force of the adsorption here is not always the reduction of the surface tension[18,31,105] but also is a result of attractive interactions.[129–132] Moreover, the deformation is often amplified during the drying because of the increase in the surface tension and the quasi-one-dimensional deswelling of the particles.[105,131]

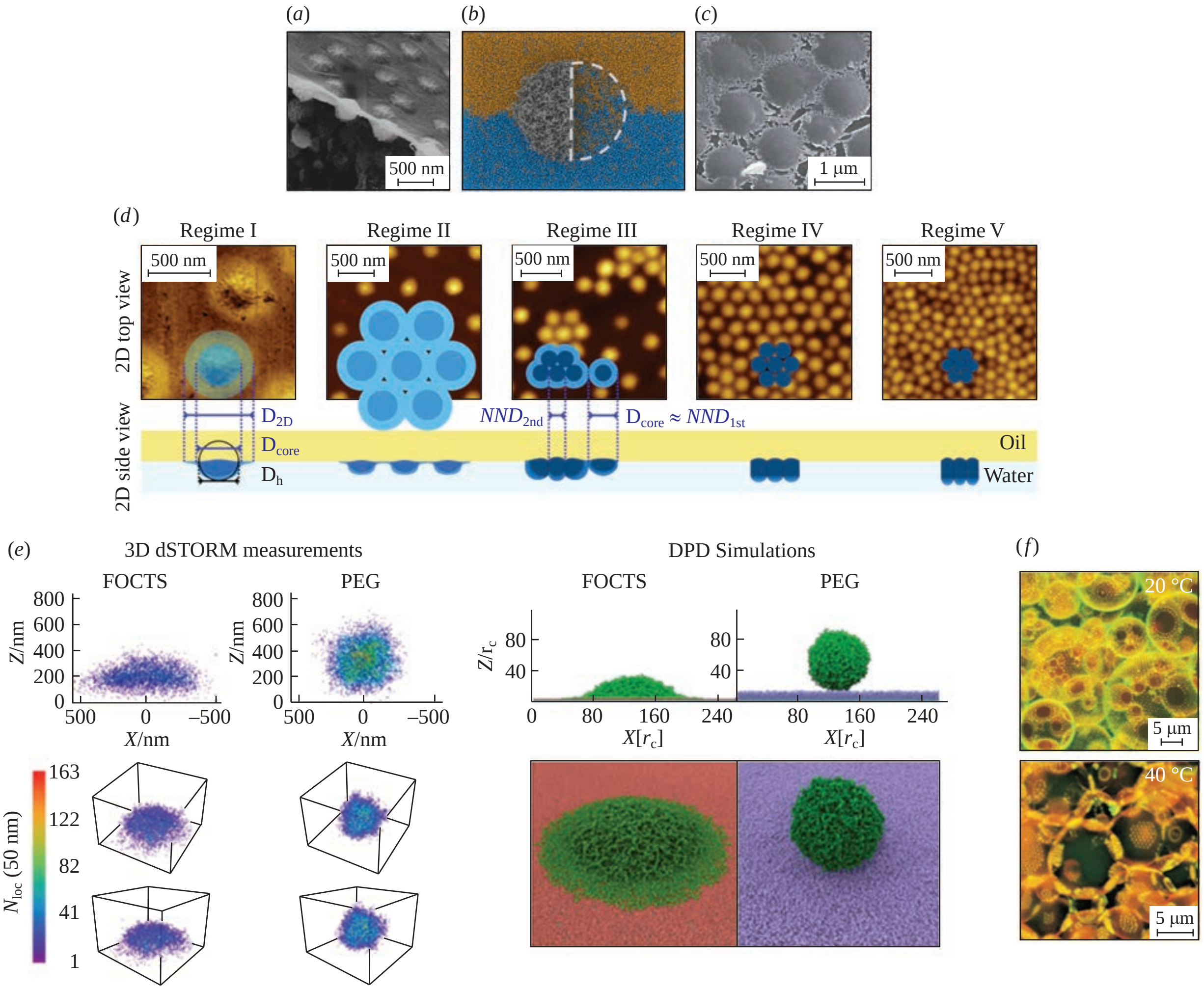

Figure 3 (*a*) Side view of PNIPAM microgels adsorbed to the oil/water interface obtained by freeze-fracture shadow casting cryo scanning electronic microscopy (FreSCa). Reproduced with permission from ref. 118. © 2015 The Royal Society of Chemistry; (*b*) Side view of single microgel and its interior in the case of equal solubility of the microgel segments (grey) in both liquids (blue and yellow) obtained by dissipative particle dynamics (DPD) simulations; (*c*) Cryo SEM image of oil/water emulsion stabilized by PNIPAM microgels. Adapted with permission from ref. 114. © 2011 The Royal Society of Chemistry; (*d*) The AFM images of PNIPAM microgel monolayers deposited from water–decane interface at different degrees of compression. Adapted with permission from ref. 127. © 2019 American Chemical Society; (*e*) Three-dimensional images of dSTORM measurements and DPD simulation snapshots of adsorbed poly(*N*-isopropylmethacrylamide) (PNIPMAM) microgels at hydrophobic (FOCTS) and hydrophilic (PEG) surfaces. Adapted with permission from ref. 18. © 2019 American Chemical Society; (*f*) Fluorescence confocal micrographs of lipid giant vesicles decorated with PNIPAM microgels at 20 and 40 °C. Reproduced with permission from ref. 133. © 2013 American Chemical Society.

On the other hand, one can use the AFM in liquid medium[131]or direct stochastic optical reconstruction microscopy (dSTORM)[18] to study the microgels in the rehydrated state. Besides, the use of the latter technique could allow one to visualize the network particles in their native state at the hydrophilic surface [see Figure 3(*e*)].[18]

Finally, let us describe the case of biomembranes.[133–135] Similarly to the fluid interfaces, microgels form a monolayer with a hexagonal packing on the lipid bilayer [Figure 3(*f*)]. The physical reason for the adsorption is the attraction between the charged lipid heads with the opposite residual charge on the microgels surfaces inherited from the substances used in the synthesis (the initiator and the surfactant).[133,135] In turn, the deswelling of the particles leads to their partial desorption from the membrane [see Figure 3(*f*)]. However, if the microgel segments have the affinity to the lipid tails, one could expect the wrapping of the particles or the incorporation into the bilayer upon the collapse.[134]

Applications

Having observed the properties of responsive microgels, we thus can formulate the ongoing application trends. The first and one of the ‘oldest’ trend is the already mentioned drug delivery.[5–7,64,92,138–142] As an example, the effective drug encapsulation and *in vitro* release has been shown for of isoniazid,[92] ibuprofen,[64] doxorubicin[139,140] and aescin.[142] The uptake of multiple drugs is also possible[138,141] including the further successful *in vivo* delivery.[141] The expansion of potentially deliverable drugs together and the increase of microgels degradability are the subjects of the current studies.[2]

The second trend, which also utilizes the microgels tunable permeability, is the scavenging of the various substances from the liquid phase. The particles could be used in the purification of water from different pollutants,[143] such as heavy metal ions[18,143] or the organic compounds.[93,102] Oppositely, microgels could be employed as the purifiers of the oils and fuels from the residual water and water-soluble molecules.[89] The advantage of using the responsive networks is that the absorption of the molecules will lead to the collapse and flocculation, which in turn will make it possible to gather the particles and reuse. In addition, the flocculation could be controlled *via* the temperature.[143]

The next major trend is the development of the effective catalytic systems. The catalysts themselves can be embedded into the network, and thus the resulting microgel can be easily removed from the product *via* the change of the external conditions.[144,145] Moreover, the high interfacial activity allows one to use the microgels in the biphasic catalysis.[146–148] It is known that the emulsions stabilized by responsive microgels can be broken on demand *via* temperature or pH level.[149,150] Therefore, the networks will localize the catalyst at the interface, and the resulting products dissolved in different liquids can be eventually separated. Meanwhile, the enhanced mixing of the liquids inside the network[120,121] could provide an enhanced catalytic rate in comparison with the linear polymers modified with catalytic groups.[147]

The ability to control the interparticle distance in the microgel monolayer as well as their spatial ordering (the pattern) by an external mechanical force can find its application in nanolithography, namely in the fabrication of the nanowire arrays which are grown on the microgels deposited from the fluid interface.[122,151,152] In addition, the peculiarities of microgel–surface interactions can be applied to the obtaining of functional (for instance, biosensing[153,154] and antimicrobal[155]) coatings or the microgel-coated membranes with controlled permeability.[156,157]

Finally, knowing the principles of responsive behavior of the network, one can create the microgel-based micromachines[158–160] which can implement the directed motion or be manipulated through the collapse of the particular part of the network caused by the external stimuli.

Conclusions

Aqueous responsive microgels are unique macromolecular objects combining the properties of solid colloids, polymers and surfactants as well. The possibility to incorporate the various functional groups into the network, which in turn will be both deformable and sensitive to the various stimuli, makes microgels a versatile platform for a wide spectrum of applications. Simultaneously, the continuing application trends induce the fundamental studies which discover the new properties of such particles. Despite the bursting amount of possible microgel systems, there is a serious ‘bottleneck’ which lies in the fabrication of the microgels on the industrial scale. So far, the ongoing improvements of the synthetic approaches could overcome this problem. Overall, the scientific interest to the microgels will be kept at the high level within the foreseeable future.

The financial support from the Russian Foundation for Basic Research (project nos. 19-03-00472 and 20-33-70242), the Government of the Russian Federation (within Act 211, contract no. 02.A03.21.0011), and the Deutsche Forschungsgemeinschaft (DFG) within Collaborative Research Center SFB 985 ‘Functional Microgels and Microgel Systems’, is gratefully acknowledged.

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Received: 12th June 2020; Com. 20/6236