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# Microgels Self-assembly at Liquid/Liquid Interface as Stabilizers of Emulsion : Past, Present & Future

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## Abstract

The most recent developments on Pickering emulsions deal with the design of responsive emulsions able to undergo fast destabilization under the effect of an external stimulus. In this scenario, soft colloidal particles like microgels are considered novel class suitable emulsifiers. Microgels particles self-assemblies are highly deformable at interfaces covering higher surfaces than hard particles and their interfacial behavior strongly depends on external-stimuli. Microgels are very diverse owing to the large variety of them from the point of view of possible combinations of stimuli-responsiveness and different microstructures (crosslinking density and distribution). Herein, we illustrate the use of different types of responsive microgels not only from a structural point of view but also even from physical one. For that, the effect of different microgels parameters such as internal structure and charge density on mechanical properties of the interface will be discussed.

**Keywords:** Pickering emulsions, microgels, stimuli-responsive, microstructure, interface, mechanical properties

## Introduction

Emulsions are out-of-thermodynamic equilibrium colloidal systems, in which one phase —whose size is about 10 nm–100 µm in at least one of its dimensions— is dispersed in another medium [1]. These metastable systems require a third building block, known as stabilizer, to be kinetically

stabilized. In this regard surfactants have been the most used stabilizers to lower the surface tension and to prevent the droplets from coagulating, flocculating and Oswald ripening. Surfactants, usually amphiphilic organic compounds, are able to diffuse in water and adsorb at interfaces conferring colloidal stability to emulsions [2,3]. When the stabilizers are particles the emulsions are known as Pickering or Ramsden emulsions [3].

Although the first description of Pickering emulsions dates back to more than a century ago, only during the last two decades the potential of them has been fully recognized for various applications such as cosmetic, printing, and home care among others [1,4]. Nowadays, Pickering emulsions are having a renewed interest due to the abandonment in the use of non eco-friendly and non-recyclable surfactants and the great variety of particles that can be used for emulsion stability with great success [4].

Usually the particles considered are hard and non-deformable as lattices or silica particles. Those particles organize at the interface forming a dense shell (Figure 1) and conferring an excellent stability to Pickering emulsions. The origin of the stability comes from the plastic behavior of the interface due to the lateral interfacial interactions between adsorbing particles [5-9].

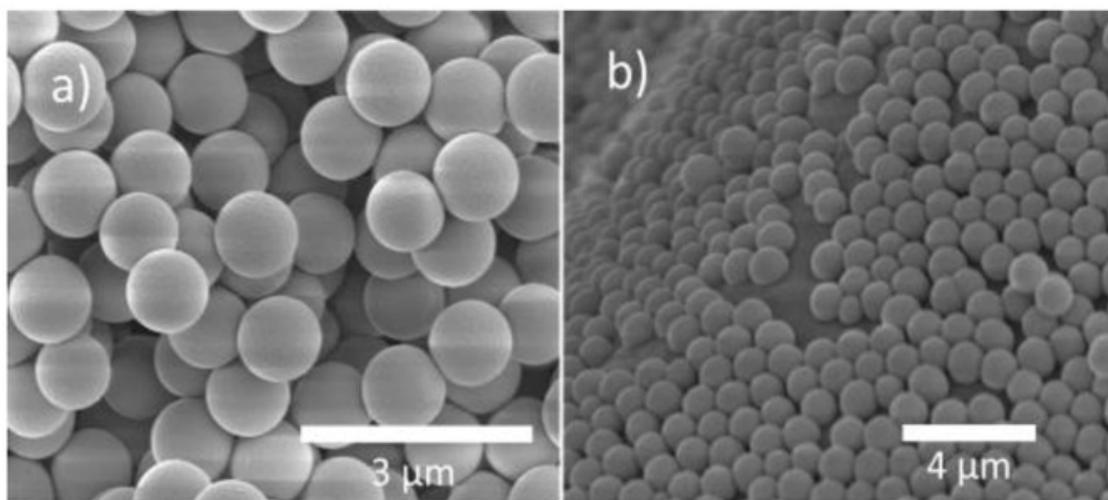


Figure 1: (a) Hard silica particles able to stabilize emulsions and (b) organisation at the solidified Pickering emulsion interface. [Reproduced with permission from Ref. [5]].

The high stability of Pickering emulsions is really appreciated for long time storage but from the point of view of some applications the possibility to control *in situ* the interactions between the drops or the particles themselves located at the interface is necessary [4]. In this sense, research in the field of Pickering emulsions has considerably evolved towards smart emulsions and different systems have been reported being their stability sensitive to different stimuli such as pH [8,11],

temperature [10,12-15] and magnetic field [16]. Of particular interest are emulsions stabilized with stimulus-sensitive microgels as soft particles. Microgels are environmentally responsive cross-linked colloidal particles able to form stable aqueous colloidal dispersions and to swell rapidly in a thermodynamically good solvent as a respond to external stimuli (temperature, pH, magnetic field...). The advantage of this type of stabilizer is that they act as a versatile surfactant that respond to stimuli without the need to create hybrid systems like surface-modified latexes or other inorganic/polymer hybrid particles who are longer to synthesize [15,17]. In addition, the stimuli-responsiveness of microgels opens the possibility of an easy phase inversion or breaking of the emulsion together with a facile removal of particles from the interface obtaining high-quality products [15]. Therefore, the use of stimuli-responsive microgels in stabilizing Pickering emulsions lead to even more potential applications such as biocatalysis, oil refinery and drug delivery, among others [15,17]. Microgel particles are physical materials with a defined volume, but they do not have a clear defined interface with the surrounding medium in the swollen state contrarily to hard particles, *i.e.* a microgel is the sum of the polymeric network and its solvent [4]. In addition, the study of the use of microgels as stabilizers in Pickering emulsion is more complex than the study of solid particles. Microgels can easily deform in the interface and parameters such as contact angle are not applicable for controlling emulsion stability [17].

For these reasons, the aim of this review it to highlight the main aspects of the use of sensitive microgels for the stabilization of Pickering emulsions in order to contribute to widespread the understanding of the influence of different microgels parameters on controllable stabilization. For that, the influence of different parameters such as the size, charges and distribution of monomers and cross-linkers will be discussed for different types of microgels. Then, the behavior of microgels at the interface will be discussed in terms of deformation, packing and monolayer behavior. Finally, the mechanical properties of the interface will be discussed for different stimuli-responsivities.

### **Emulsion stabilization with stimulus-sensitive microgels**

As mentioned above, microgel particles are highly deformable at the oil/water interface and therefore, their interfacial behavior strongly depends on external-stimuli [18]. In this regard, microgel particles can have a much larger diameter at the interface than in the bulk and therefore, they can cover up much more oil-water interface than hard particles (Figure 2a) [19]. Special interest has been focused on thermo-responsive microgels made of poly(*N*-isopropylacrylamide) (PNIPAM) after the easy synthetic route discovered by Pelton *et al.* [20-21]. This method, known as precipitation polymerization, produces highly uniform particles size and spherical shape with a volume phase transition temperature (VPTT) around 32 °C [21].

More than a decade ago, Tsuji *et al.* reported the controllable stabilization of different oil-in-water (O/W)-type emulsions using PNIPAM microgels and PNIPAM-carrying hairy particles [22]. Last ones were based on polystyrene core and PNIPAM hairy shell (Figure 2b-e). They observed that all Pickering emulsions prepared were very stable at room temperature, but phase separation occurred when temperature increase to 40 °C. Few years after, Monteux and coworkers studied the interfacial properties of PNIPAM microgels at the *n*-dodecane/water interface [23]. Using tensiometry technique, they concluded that the destabilization of Pickering emulsions with temperature came from the rearrangements of microgel particles forming aggregates at the interface and not from particle desorption. Style *et al.* reported the theoretical study of the adsorption of soft particles at fluid-fluid interfaces [19]. They were able to identify a critical point where deformable particles were really sensitive to small changes in the surface tension driving between complete spreading and desorption.

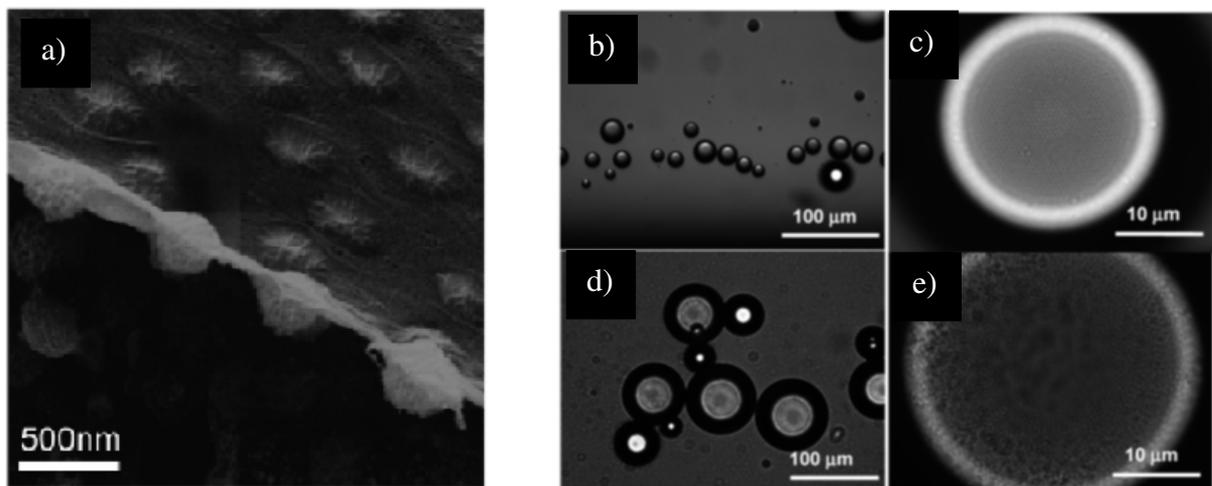


Figure 2: (a) Cryo-SEM image of a fracture water-decane interface populated by PNIPAM microgel particles [Reproduced with permission from Ref [19]]. (b-c) Toluene in water emulsion stabilized by PNIPAM microgel particles, (d-e) Toluene in water emulsion stabilized by PNIPAM microgel particles . [Reproduced with permission from Ref. [22]].

The extensive use of PNIPAM gels has been discussed in the recent years due to the toxicity of acrylamide residual monomers and the low biocompatibility of PNIPAM – like acrylamide, NIPAM is a suspected carcinogen and neurotoxin [24] — especially at a temperature above VPTT. Some of the best candidates for alternatives which present a VPTT close to human body temperature and of which biocompatibility for biomedical applications has been reported to be higher than the PNIPAM are microgels based on poly(*N*-vinylcaprolactam) (PVCL) [25-28]. Although no references have been found in the literature on Pickering emulsions using PVCL-based microgels, stable oil/water and air/water interfaces have been studied using PVCL [18] and VCL

copolymerized NIPAM and *N*-isopropylmethacrylamide (NIPMAM) microgels [29] where mechanical properties have been measured. In both works, a decrease of the interfacial tension was observed as the temperature increased below the VPTT while it was maintained constant above the transition temperature. In addition, the plateau above the VPTT, suggested that PVCL-based microgels presented a more efficient packing at the surface compared to PNIPAM-based ones, and therefore, a better resistance to aggregates formation above the VPTT [29]. With the aim of improving the properties of PVCL-based microgels as possible emulsion stabilizers, their amphiphilic character has been tune trough the copolymerization with hydrophobic comonomers such as 4-*tert*-butylcyclohexylacrylate (PTBCHA) [30]. It was observed that the increase of the TBCHA content in the microgel caused a gradual decrease in the size of the microgels in the swollen state, a change in the volume phase transition temperature to lower temperatures and a decrease in the general deformability [30]. Microgels with those properties can be of great interest for use in emulsion stabilization. Their controlled deformability brings these microgels closer to the behavior of the solid particles used in “usual” Pickering emulsions. Together with thermo-responsive microgels, pH-sensitive ones are the most studied microgels. Polyelectrolyte microgels, those formed from cross-linked polymers with a large number of ionizable groups, have a pH-dependent phase transition knows as VPTpH [31-32]. The swelling-deswelling of these microgels is due to the protonation/deprotonation of weakly acidic (-COOH) or basic (-NH<sub>2</sub>) groups present in the polymer chains, and is related to electrostatic repulsion between the charges within the microgel [33]. In fact, the alterations in the internal osmotic balance of the microgel brought about by changes in the ionic composition of the external solution are responsible of the swelling-deswelling behavior. The protonation/deprotonation of ionizable groups provokes the microgel swelling due to an increase in the osmotic pressure being this opposed by the inherent hydrophobicity of the microgel [32]. Anionic microgels collapse at pH values below *pKa* due to the absence of charges. On the other hand, in the case of cationic microgels, they collapse at pH values above *pKb*. So, VPTpH is correlated with the respective *pKa* or *pKb* values of the acid or basic groups but it may vary slightly depending on the structure of the microgel. Moreover, because the swelling/collapse mechanism is due to electrostatic repulsion between charges, it can be altered by pH, ionic strength or type of counter-ion in the medium [32]. In this regard, increasing the ionic strength, an electrostatic and osmotic screening is caused provoking the collapse of microgel particles. In addition, it has been observed that phosphate type counter-ions can bind to the amine-based polymer chains affecting the net charge and increasing the *pKa* of amine-groups [32]. Different types of anionic and cationic pH-sensitive microgels have been used to generate Pickering emulsions. Poly(2-(diethylamino)methacrylate) (PDEAMA) and poly(2-(tert-

butylamino)methacrylate) (PTBAEMA) [34] microgel particles acted as effective emulsifiers of Pickering for a wide variety of oils producing stable o/w emulsions in the case of doing the homogenization at a basic pH, well above the  $pK_a$  of the microgel. It was observed that the protonation of the tertiary amine groups of PTBAEMA microgel led to the spontaneous desorption of the highly cationic microgels from the surface of the emulsion droplets, which were then coalesced in a matter of seconds but could be reused for demulsification/emulsification cycles [35].

Recently the use of polyacrylamide (PAM) and poly(acrylamide-*co*-acrylic acid) (PAM-AA) anionic microgels with different cross-linkers and charge amounts have been reported for o/w Pickering emulsion stabilization [36]. By contrary, these microgels caused the emulsions to demulsify in alkaline solutions while showing a marked stability in salt and acidic conditions being necessary only a small amount of microgels and being able to control the size of the droplets [36].

pH-sensitive microgels have also been used to stabilize W/W emulsions and it has been shown that it is possible to stabilize or destabilize the emulsions by varying the pH [37]. It was observed that the pH range where the stability was given could be modified by adding a monovalent salt. Despite this success, emulsion stability could not be explained solely in terms of size change and the mechanical properties of the microgel layer could play a crucial role [37]. Another example are the studies with slightly cross-linked poly(4-vinylpyridine) sensitive microgels incorporating silica, both water-in-oil and oil-in-water microgels stabilized emulsions were obtained, but only under high pH conditions, *i.e.* when the microgels were completely collapsed [12,13].

Despite of the works published about the use of pH-sensitive microgels in Pickering emulsion, the most pH-sensitive microgels used as stabilizers or whose surface activity has been studied in detail, are in copolymerized systems with thermo-sensitive polymers [38,40]. In this sense, PNIPAM is the building block of a plethora of dual-sensitive microgels used for Pickering stabilization using as pH-sensitive comonomers acrylic acid (AA) [41,42] and methacrylic acid (MAA) [43,44].

The first report on emulsion stabilization by dual-sensitive microgels was achieved by Ngai *et al.* in 2005 [45]. Octanol in water emulsions were stabilized with pH- and temperature- sensitive microgels of PNIPAM copolymerized with methacrylic acid Poly(NIPAM-*co*-MAA). It was observed that the stability was dependent of the pH and temperature obtaining stable emulsion at high pH and low temperature and unstable ones at low pH or high temperature [45]. Under these last conditions, with differences in the particle attachment energy according to the oil but with a similar behavior [46], the microgels became more hydrophobic, collapsed and partially migrated into the oil phase, reducing the density of the particles at the interface (Figure 3) [4,15]. Several works have been published demonstrating the usefulness of PNIPAM-MAA microgels to stabilize

different O/W systems such as dodecane [23], hexadecane [39], toluene [18], hexane [47] and mostly heptane [15,48,49].

Brugger *et al.* observed that the synthesis method used for dual-sensitive microgels had an effect on their composition and therefore, on their ability to use as stimuli-sensitive stabilizers for emulsions [14]. Depending on the pH used during the synthesis, they found water soluble polymers (WSP) as residues from the synthesis process that had captured most of the methacrylic acid comonomer. These WSP presented surface activity and contributed significantly to emulsion stabilization, since purified microgels were ineffective in stabilizing emulsions [14]. Based on those results, they concluded that the presence of charges was a requirement for stabilization. However, in the same year 2008, Tsuji and coworkers reported the successful stabilization of different O/W-type emulsions using pure PNIPAM microgels [22]. Few years after, in 2011, it was determined that although the stabilization of emulsions does not depend on electrostatic repulsion, the presence and location of charges are relevant [9]. It was observed that charges enhanced the stabilization through the extent of swelling and deformability of microgel particles. In this way, emulsion stabilization is linked to the swelling and microgels structure at the oil-water interface, being those parameters dependent on the presence of charges together with solvent polarity and microgel morphology [9]. In the same way, Schmitt *et al.* concluded that the microgels are adsorbed at the interface without the need of charges and therefore the stabilization is not provided by electrostatic interactions [4].

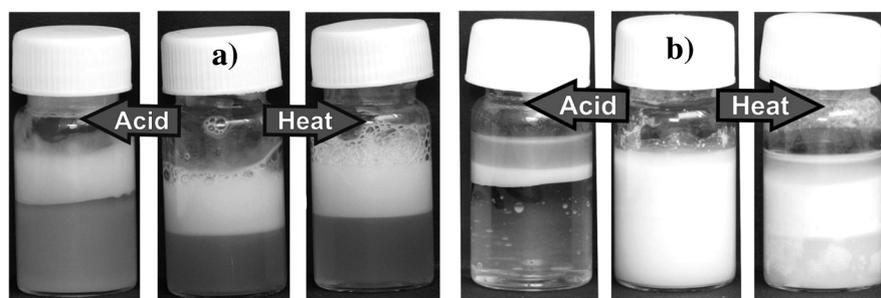


Figure 3: Pickering emulsions stabilized with PNIPAM-MAA microgels. a) Heptane/water emulsion after preparation (middle in left images) and no breaking of the emulsion was observed after addition of acid or heating. b) Octanol/water emulsions after preparation (middle in right images) and the emulsion decomposes after addition of acid. Decomposition is also observed after heating well above the VPTT. [Reproduced with permission from Ref. [15]].

As discussed above, the deformability of microgels plays an important role in the stabilization of emulsions. In this regard, recently Kwok and coworkers studied the effects of cross-linker content and PNIPAM microgel surface deformability on the corresponding Pickering emulsions [50]. It was found that less cross-linked and therefore, microgels with a higher swollen ratio improve

stabilization, while microgels with high cross-linking density and larger size in the swollen state favor bridging between emulsion drops and increases the emulsion flocculation [4,50].

From the point of view of biomedical applications, systems able to respond to chemical stimuli such as concentration change of a specific molecule are very promising. Among different systems, those responsive to glucose concentration have received a special attention due to the widely spread disease of diabetes. In this sense, PNIPAM microgels modified with phenylboronic acid (PBA) were used to stabilize Pickering emulsions [51]. The PBA binds to the diols of the saccharides to form a cyclic ester. At the same time PBA has a hydrophobic character, which can be changed to more hydrophilic by binding to sugar. This induces to exhibit two collapsed/swollen states in presence/absence of sugars. In addition, it was reported that under pH conditions close to the  $pK_a$  of the PBA derivative, the VPTT depends on the sugar concentration. In the absence of sugars these groups behaved as crosslinkers that increased the rigidity of the microgel in the compressed state. This unique structure resulted in interfacial behavior similar to that of non-deformable particles, leading to fragile and flocculated emulsions. However, the addition of sugar induced the swollen state of the microgel with a behavior similar to previous studied soft and deformable microgels. They were adsorbed more quickly making stable and less flocculated emulsions. Therefore, an effective method for emulsion control with these microgels was found [52].

While the possibility to use different types of microgel particles as Pickering stabilizers has been demonstrated, the mechanism and detail of the stabilization given by these soft particles is still an open question. Because of that, it is not only necessary to study the microgel and the macroscopic properties of the emulsion but also the mechanical properties of the interface.

### **Microgels at the interface**

As previously mentioned, most of the works referring to the use of microgels as emulsion stabilizers or describing their mechanical properties refer to PNIPAM microgels and/or microgels based on PNIPAM copolymerized with different pH-sensitive comonomers. In the following section, we will refer to them indistinctly and specify if another type of microgel is used. The different works referenced here use different techniques and interfaces, but since microgels can usually only be dispersed in the aqueous phase, the behavior and results are easily extrapolated.

***Adsorption process and interface profile.*** The microgels in the bulk of the dispersion have an isotropic three-dimensional structure, approximately spherical. In the presence of a concentration gradient they diffuse and when they arrive at the interface, as consequence of the amphiphilic nature, the microgels are spontaneously and almost irreversibly adsorbed [53,54]. However, unlike solid particles, when situated at this interface they deform and adopt a 2D anisotropic structural

conformation trying to extend along the surface [40]. This behavior is similar to the interfacial display of proteins where the reduction of free energy induces the denaturation of proteins [39,55].

The formation described above is known as "fried egg" and its causes and effects have been analyzed by different authors from the theoretical point of view [19, 56-60] – both numerically and analytically – as experimental on which we will focus. From those studies it has been deduced that the deformation of soft particles at the interface is produced to balance the energy gained during adsorption, *i.e.*, microgels deform and flatten in the interface due to the balance between surface tension and elasticity [61]. It is well known that the cross-linking density of the microgels is not usually homogeneous, being higher in the core than in the shell [21,24,27,28]. This cross-linking density inhomogeneity allows the flattening of the shell and the protrusion of the core, giving rise to a fried egg formation. In addition, the degree of stretching or deformation is closely related to the cross-linking density and cross-linker distribution in the microgel because of the deformation and interconnection is inversely dependent on its strength of the crosslinked bonds [4,39,60]. In this regard, Scotti and coworkers have recently described the limiting case of ultra-low cross-linked (ULC) PNIPAM microgels [62]. They showed that ULC microgels present an intermediate behavior between colloids and flexible polymers. In this way, at oil-water interfaces, their polymeric nature is dominant over their colloidal behavior presenting a pancake-like shape (all subchains are adsorbed) instead of fried egg formation due to the strong adsorption overcomes elasticity [62]. Therefore, it is necessary to study the density and distribution of the crosslinker within the microgel. In 2014, Destribats and coworkers studied the effect of PNIPAM microgels size on Pickering emulsions stability [63]. They concluded that although the smaller microgels may suffer less deformation, their size logically allows them to cover the water-oil interface more uniformly and with a higher density. The more homogeneous surface coverage, and the greater mobility at the interface, lets them rearrange in the film better, so these interfaces also withstand mechanical stresses very well [64].

As mentioned before, microgels adopt a peculiar conformation at interfaces and in the adsorbed conformation, the maximum diameter of the microgel on the surface can be much larger than the diameter in the dispersion or the diameter in the immersed part, as was described by Geisel *et al.* [40]. Recently, same authors went further in the study of the 2D phase behavior of microgels at fluid interfaces and determined that the microgel structure on both sides of the interface is not symmetrical so that it does not protrude equally in both media. Obviously because it depends on the solubility and surface activity of the microgel in each medium. The partial penetration on both sides of the theoretical flat interface occurs even if the microgel is not soluble in one of the media and the part of the microgel that is in the hydrophobic medium is hydrated. Therefore, the liquid-liquid interface is not flat and has roughness [40,58]. In Figure 4, it is possible to observe a scheme of this,

together to the packing structure of the microgels. At the "fried egg" conformation, the microgel is deformed and mainly submerged in the water, with a little part of the oil.

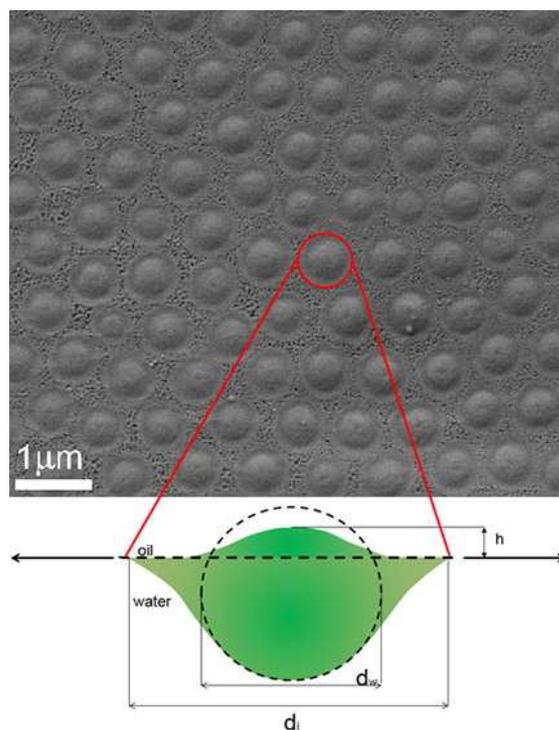


Figure 4: FreSCa cryo-SEM image of microgels and scheme of the microgel deformation at water/n-heptane interfaces. In the image, it is possible to observe the hexagonal packing of the microgels. [Reproduced with permission from Ref. [40]].

Few years ago, Ravaine's group studied the importance of charges on microgels adsorption at the oil-water interfaces of emulsions [4,64]. In this way, they reported that neither the number of charges nor their distribution in the microgel affect the way in which it adsorbs. The absence of charges, be it in neutral microgels or by shielding the charges by the presence of salts, makes the microgels more deformable [64]. Also, once the microgels are adsorbed, neither the size of the microgel at the interface nor the wetting — as protrusion heights or effective contact angles— is strongly dependent on the pH, although the total microgel size does it. The reason for this is that the part of the microgel that is immersed in the solution collapses [40]. As a result, emulsion stability is also not strongly dependent on pH, and charges are not needed to ensure emulsion stability [40,64].

**Deformation and packing.** As it has been discussed in previous sections, after the adsorption, microgel particles are extended along the surface of drops. During adsorption, the deformation of microgel particles favors the contact and the interconnection with the adjacent particles. That process results in the formation of a dense and elastic film-like structure that coats the droplets and

prevents coalescence [39]. In this sense, it has been observed that the time it takes to accommodate can even be the cause of the time dependence of the elasticity [55].

However, this process is not simple and is influenced by different parameters among which are the internal structure of the microgel - including the distribution and density of crosslinker and therefore the core-shell ratio - or the emulsion methods, as described by Destribats *et al.* [65].

Zielińska and coworkers reported the characterization of PNIPAM nanogels synthesized with different cross-linker amounts at air/water interface, using neutron reflectivity (NR), with isotopic contrast variation, and surface tension measurements [66]. They demonstrated that the degree of cross-linking has a deep effect on microgels adsorption kinetics, adsorbed amount and structure created. In this regard, as neutron reflectivity measures show, the transverse structure of the interface presents a film of microgels that can be represented by three different regions: a densely packed thpolymer with low water content in contact with air/oil, followed by a **fully solvated** and highly cross-linked region, and finally a region of polymer chains extending into the bulk aqueous solution. Finally, they reported that the degree of deformation diminishes as cross-linker concentration increases [66].

It is well documented that the cross-linker density is related to the amount of cross-linker during the synthesis, but also to the success in the cross-linking process and the formation of the microgel. On the latter depends the distribution of crosslinker inside the microgel. The use of different crosslinkers can lead to different distributions and can result in homogeneous microgels or a core-shell structure —with most of the links being on the inside (dense core, DC) or outside (dense shell, DS) part— [67,68].

Destribats *et al.* presented an extensive study with Poly(NIPAM-*co*-MAA) microgels that focused on their efficiency in terms of microgel deformability due to differences in crosslink density or the presence of external stimuli [39]. They found that the most deformable microgels are more efficient stabilizers. The explanation is that the deformability of the microgels on the surface induces the overlapping and the connectivity of the shells. The most stable emulsions are those with the highest shell overlapping capacity since this allows the formation of an elastic film that prevents coalescence. The same conclusion was later obtained also for pure PNIPAM microgels [69].

Brugger *et al.* observed that the microgels layer may not always be homogeneous and may have differences with the pH [48,49]. They found that the interface with PNIPAM-MAA microgels at low pH was homogeneous, while at high pH, it exhibits a structure of microgel clusters and voids where polymer chains are interconnected (Figure 5). This could be related to the deprotonation of the MAA chains that together with the specific and highly cooperative hydrogen bonds of the PNIPAM chains would help to the partial aggregation of microgels working like an additional crosslinker,

while, on the other hand, the interaction of the charges could induce the repulsion between clusters [48,49]. In the same line, are the results for other comonomers such as AA and VAA [64]. The behavior observed between neutral or charged microgels which has been screened by the addition of salt, is different from the microgels in which the carboxylic groups have been protonated by decreasing the pH. In the latter case, the emulsions are not stable. Consequently, the efficiency as a stabilizer is not due to the presence of charges but to the effect they have on the microgel structure and consequently in the deformability of the microgels or in the packing structure [65].

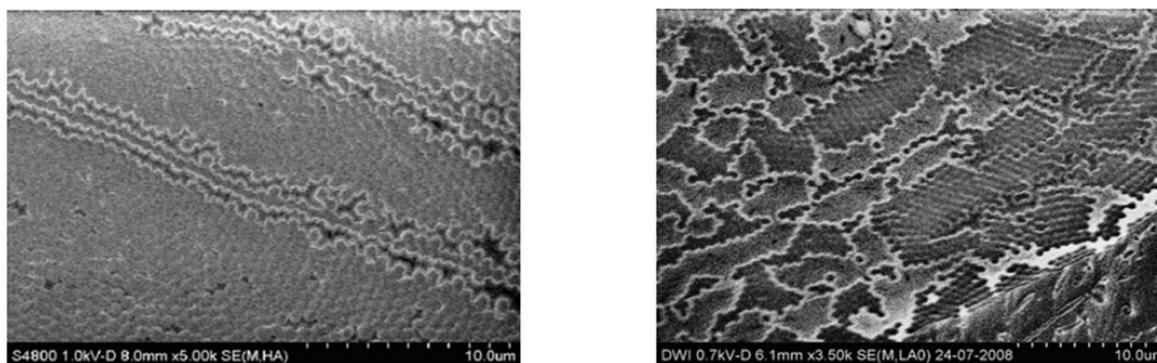


Figure 5: Cryo-SEM picture of a water/heptane interfacial microgel layer at pH 3 (left) and pH 9 (right). [Reproduced with permission from Ref. [49]].

**Hexagonal stable structure.** The structure of the microgels at the interface is also related to the density or concentration of microgels at the interface. In this way, for solid particles, they are almost irreversible adsorbed at the interface forming a dense monolayer or multilayers [7,70]. However, for microgels it differs when the particles are diluted or when they are hexagonal close packed *hcp* at the interfaces [40]. The *hcp* structure has been widely studied using mainly cryoSEM [40,69,71] and monolayer compression techniques [55,71,72]. Picard *et al.* reported that when the compression is low, the microgels spread covering the surface as much as the reticulation allows [72]. Bochenek and coworkers presented a sketch of PNIPAM microgel monolayers under compression below and above the VPTT (Figure 6) [58]. They observed that, at both temperatures, as the compression increases, the regular *hcp* structure takes form, as can be seen in Figure 6 when switching from regime I to regime II. In addition, Massé *et al.* described that the *hcp* structure, specifically the network parameter, is not sensitive to the presence of charges in the microgel or its sensitivity to pH but is determined by the specific characteristics of each microgel [64]. Recently, Gavrilov *et al.* reported contrary results to previous findings implying that the interfacial ordering can be controlled by pH using charged microgels [73]. They found that microgels with low fraction of

charged monomer units exhibited an almost ideal hexagonal packing, while uncharged microgel positions were completely random. Furthermore, differences have been found between poorly cross-linked microgels with a single network parameter and strongly cross-linked microgels with the coexistence of two hexagonal phases with different lattice parameters [72]. This lattice parameter is constant for any compression state within the domain until the compression limit is reached; and for high compressibility there is no difference in cross-linking. At the same time, Huang *et al.* reported that the distance between microgels does depend on the concentration of microgels [73]. In this regard, Zielińska and coworkers concluded that for the more cross-linked gels, the number of microgels packaged on the surface is higher, since these microgels spread less, so a greater amount is needed to cover the surface [66].

Contrary to those finding, Geisel *et al.* observed that it is not necessary to cover the interface completely with microgel particles to achieve stable droplets [74]. In addition, using transmission X-ray microscopy (TXM), they obtained three-dimensional representations that reveal a random arrangement of the microgels around the droplets with distances greater than the diameter of the microgel, *i.e.* not tightly packed [74].

***Compression and monolayer behavior.*** As Bochenek and coworkers reported through Langmuir's monolayer compression experiments, the compressibility of the interface, *i.e.* the lateral compressibility of the microgels, is practically independent of temperature, with the only difference being for high pressures [58]. This is because the change in volume has a more marked effect when the pressure is higher and a larger proportion of the microgel is in the water phase. In contrast, the isostructural phase transition that occurs when the microgel is compressed is different if the microgel immersed in the aqueous phase is swollen and compressible, or is collapsed and is not compressible [58].

In general, compression isotherms show similar results for pure and copolymerized PNIPAM microgels, both for oil/water [55] or air/water [72] interfaces and with different salt concentrations in the medium. As the monolayer is compressed, five regimes emerge, as can be seen in Figure 6. A first diluted regime (I) at zero surface pressure, where the monolayer behaves as a non-interacting particulate gas. The second regime (II) corresponds to a continuous increase of the surface pressure due to shell-shell contact. This regime is analogous to that of an expanded liquid. In a third regime (III), the pressure increases slowly and tends to become a plateau while the interfacial area decreases. In this regime the isostructural phase transition occurs where expanded and condensed microgels coexist and therefore two different network parameters can be appreciated [75]. For cases where two different network parameters cannot be appreciated by electron microscopy, it has also been proposed that all microgels are swollen but they are partially desorbed with some segments of

the microgel which are immersed in the sub-phase to keep the surface density constant [29,76]. In any case, the key is the deformation of the microgels. If the compression keeps increasing, a second sharp increase is observed (IV) due to the core-core contact, followed by a plateau (V). This plateau is attributed to the collapse of the microgel forming the film [55,70,72].

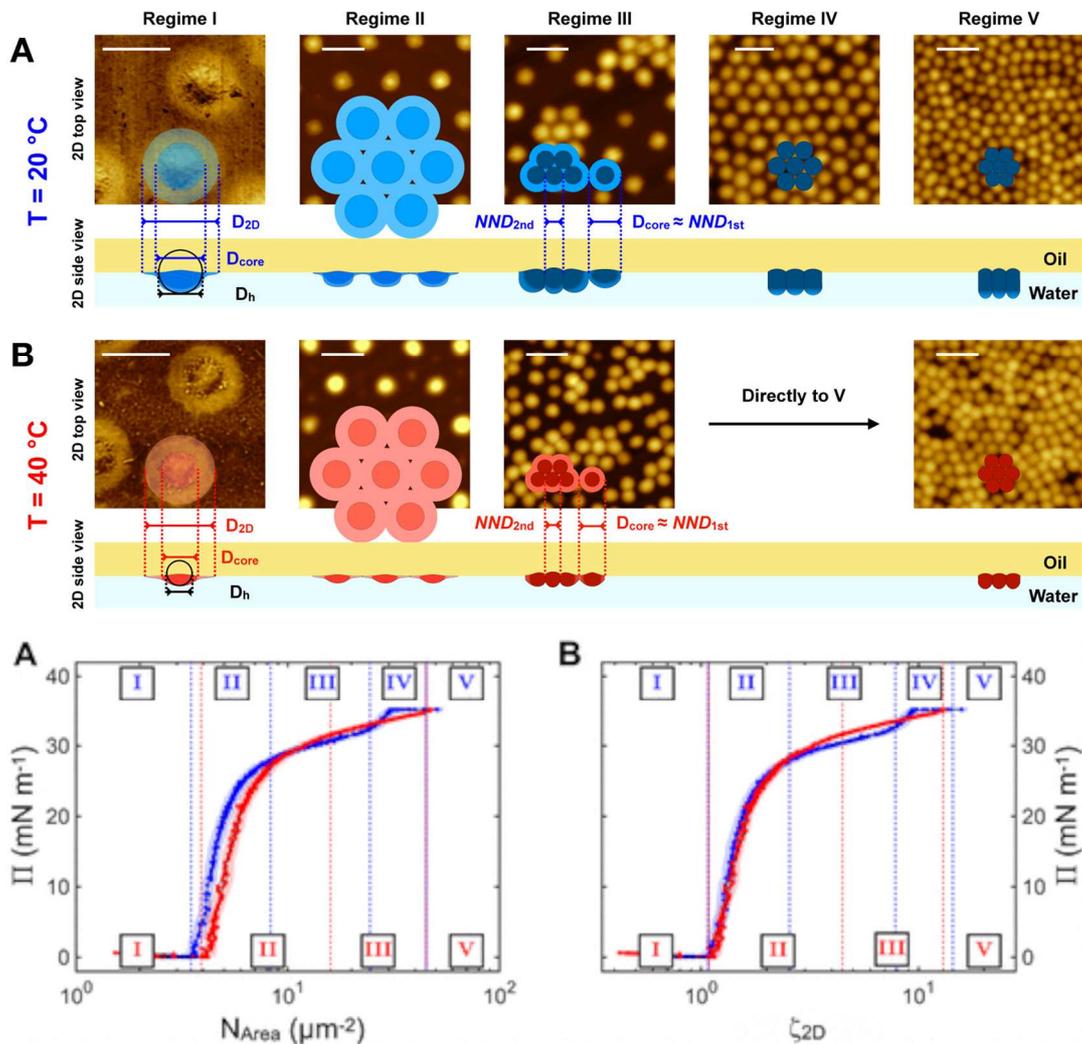


Figure 6: (Up) Compression isotherms,  $\Pi$  vs number of microgels per unit area,  $N_{\text{Area}}$ . and compression isotherms,  $\Pi$  vs area fraction,  $\zeta_{2D}$ , of the microgels. Blue for  $T = 20\text{ }^{\circ}\text{C}$  and red for  $T = 40\text{ }^{\circ}\text{C}$ . (Down) Atomic force micrographs images and sketch of the microgel monolayers under each compression regimes for  $T$  under and over VPTT. [Reproduced with permission from Ref. [58]].

As previously discussed, the charge density and thus the electrostatic interactions influence on the adsorption and structuring of the microgels at the interface has been discussed controversially in the literature publishing inconsistent results. In this sense, in some works with PNIPAM-MAA microgels, small differences have been found that indicate that the charged gels can be compressed more than the non-charged ones [40,71,72,77]. In the same direction, Brugger *et al.* reported how

the addition of acid reduces the particle charges and therefore also increases the compressibility of the particle layer [49]. Recently, Schmidt *et al.* extended previous studies of Geisel *et al.* [71] and Picard *et al.* [72] combining compressing isotherms, atomic force microscopy imaging, and computer simulations [78]. They showed that the compressibility of the microgels is governed by in-plane and/or out-of-plane electrostatic interactions, depending on the degree of compression. In addition, they found that the size of the charged microgels plays a key role on their interfacial properties. In this regard, the effect of the charges on compressibility was observed at low compressions only in the case of small microgels, while no effect of the size was observed at high compressions [78]. Nevertheless, it is widely accepted that charges do not act directly through electrostatic repulsion only indirectly by changing the internal structure of the microgel which becomes more easily or hardly compressible and interpenetrated [40,71]. For the same reason, the density and distribution of the cross-linker has a strong impact on compression and behavior of the microgels at the interface, and surface elasticity increased by decreasing the density of crosslinkers [55,72]. Therefore, the best stabilizers are those that are poorly crosslinked and with a higher swollen ratio microgels [10,72].

For PVCL microgels, Maldonado-Valderrama *et al.* presented a detailed study obtaining the progressive decrease of the surface tension when the temperature increases below the VPTT and maintaining constant when the VPTT is exceeded. This indicates that the surface accommodates a greater number of particles and a tighter packing density as the microgel collapses, resulting in a more compact surface layer. Constant values above the VPTT contrast with the minimum found for PNIPAM and suggest a more compact packing [29]. Likewise, the monolayer of PVCL microgels under forced compression show two different behaviors depending on whether the system is above or below the VPTT. For the swollen state, the behavior of PVCL microgels is similar to the regimes observed for PNIPAM and can be explained in the same terms. For the collapsed state, the behavior only presents two regimes similar to those (I) and (IV) of the other state [29].

### **Mechanical properties of the interface.**

The work of Schmitt *et al.* concludes that the microgels are adsorbed at the interface, and due to their soft nature, they deform at the interface and interconnect [4,7,63,64]. This behavior is what provides the interfacial elasticity due to the high deformation state of microgels. The phenomena of absorption, deformation and packing are expressed in mechanical properties - tension, elasticity and viscosity - which can be quantified and measured. This one is more complex than characterization with a single technique, however, using shear and dilatational rheology, we can get a pretty detailed idea of the behavior [79].

The dilatational modulus  $E$  is a complex quantity that contains a real and an imaginary parts, respectively called the storage modulus  $E'$ , which coincides with the dilatational interfacial elasticity ( $\varepsilon$ ), and the loss modulus  $E''$ , which is related to the dilatational interfacial viscosity ( $\eta$ ) and  $\nu$  is the angular frequency of the applied oscillation. We will use the letter  $G$  to refer to the same concepts of elasticity in shear rheology.

The correlation between high modulus of elasticity and emulsion stability has been examined in the literature [80-83]. In this sense, high elasticity and low loss modulus of an interfacial layer have been found to help emulsion stability [84].

In O/W emulsions stabilized with PNIPAM-*co*-MAA microgels, interfacial dilatational rheology has demonstrated that at low temperature and high pH, the interface is highly elastic and therefore stabilizes the emulsion. The addition of acid reduces Coulomb repulsion,  $G'$  decreases further, but the main actor in the stability of the emulsion is the drastic increase of the loss modulus  $G''$  in  $T > VPTT$ . The stabilization of the PNIPAM-*co*-MAA microgels clearly depends on the viscoelasticity of the interfacial microgel layer [15].

**Surface tension and rheology.** Like conventional surfactants, PNIPAM microgels decrease the surface tension of the water [85]. However, their internal structure is more complex and the hydrophilic and hydrophobic regions are unevenly distributed within the microgel. As has been discussed before, the structure at the interface has not been completely resolved, which makes the explanation of the mechanical properties more complex than in the case of conventional surfactants [66]. This does not prevent the quantification of its effect on macroscopic mechanical properties. In addition, compared to other Pickering emulsions, for solid particles there are hardly any significant changes in interfacial tension [18,86,87].

In the case of microgels, interfacial tension between two mediums is not independent of them, neither is the surface tension  $\gamma$  at the equilibrium when PNIPAM microgels are adsorbed. The interfacial tension values reported by different authors are around 45mN/m (mJ/m<sup>2</sup>) for in air/water interfaces [54], around 17mN/m for dodecane/water [23,55], 15 mN/m for heptane/water [23], or 5-9 mN/m for toluene/water [18]. In fact, it would be more correct to talk about surface pressure  $\Pi = \gamma_o - \gamma$ , where  $\gamma_o$  is the interfacial tension before the microgels adsorption, for example 72,8 mN/m for air/water at 20°C, because in this way it is not necessary to consider the value of tension with the pure interface without microgels. In most cases, these interfacial tension values correspond to an interfacial pressure around 30-35 mN/m. In general, it has been well document that no marked different exists with the structure of the polymers, therefore no effect if it is a polymer solution [20,54,88] or microgels [15,20,53] .

In the case of thermo-responsive microgels, the interfacial/surface tension is temperature-dependent, in the same way as for small molecular surfactants, polymers and colloidal particles [18,85,88,89]. The study of different authors about the effect of temperature on the behavior of PNIPAM microgels at different interfaces revealed that, below VPTT, temperature mainly influences the rate of diffusion and results to faster interface adsorption of the dispersed substances. However, when temperature is above VPTT and because of the reducing deformability of microgel particles, the interface behavior of microgels is not diffuse-controlled mechanism being the interface adsorption of microgel slower than at  $T < VPTT$  [18]. Moreover, as it has been discussed, temperature plays an important role in the deformation capacity of microgels and therefore, in the ability of them to cover surfaces [18,23,90,91]. In this regard, Richtering *et al.* recorded the temperature dependence of the heptane-water dynamic interfacial tension using PNIPAM microgels to cover the interface (Figure 7). It was observed that PNIPAM microgels approach to three different states at oil-water interface depending on the temperature being differences between temperatures below, around and above the VPTT [91]. As mentioned before, below VPTT, microgels deformability dynamically dominates their spreading at the interface. By contrast, above VPTT, the final static equilibrium states are dominated by microgels packing and interactions [91].

Regarding the equilibrium value of the interfacial tension for PNIPAM microgel, a V-shaped behavior is observed with a minimum around the LCST/VPTT at the equilibrium with oil/water interfaces [18,23,91]. In the case of air/water interfaces, different behavior was reported by Cohin and coworkers [53]. It was observed that the interfacial tension decreases when  $T < VPTT$  and remains constant or even decreases even a little more for  $T > VPTT$  in air/water interfaces [53]. However, the temperature effect at air/water interface has not been studied in such detail. By contrast, for PVCL microgels, different groups reported that the behaviors at both interfaces (air/water and oil/water) are similar to that observed for PNIPAM microgels at air/water interface having interfacial tension values between 42 and 52 mN/m [18,29].

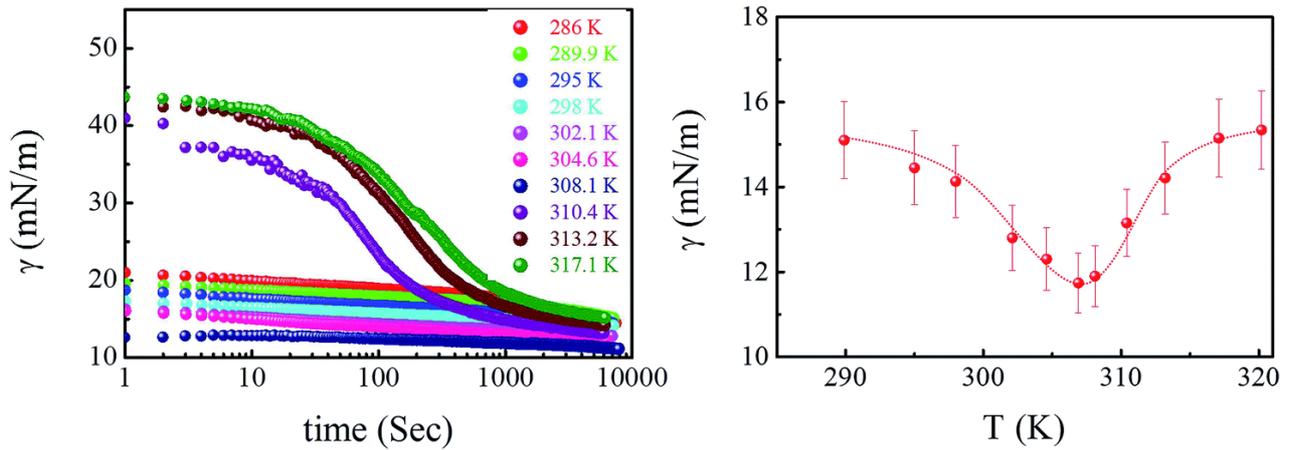


Figure 7: The dynamic interfacial tension  $\gamma_t$  of the heptane-water interface in the presence of PNIPAM microgels at various temperatures and value equilibrium interfacial tension,  $\gamma_m$ , for each temperature. [Reproduced with permission from Ref. [91]].

Regarding the time needed to reach the equilibrium interfacial tension, it has been observed an influence of the microgel concentration on it, *i.e.*, the time to reach equilibrium interfacial tension decreases with increasing microgel concentration [18,77]. By contrast, as observed by Pinaud *et al.*, the final tension value when the microgels are absorbed, does not seem to be affected by the concentration [55]. As an infinite time limit case, PNIPAM microgels and polymer solutions have a concentration threshold value, which changes with temperature, for which microgels are absorbed at the interface in sufficient quantity to exhibit surface activity [55,85,90,92]. The time to reach equilibrium is also affected by the microstructure of the microgel and increases as the amount of crosslinker increases, which strongly supports the deformation controlled interfacial behavior of microgels [18]. As explained before, the softness of microgels is crucial in their interfacial behavior. Therefore, microgels with low cross-linking density, which are softer, need less time to reach the equilibrium interfacial tension.

Regarding the other mechanical properties of the PNIPAM microgels dispersions, they exhibit a strong dependency on frequency, and in the case of elasticity, also on temperature; as it is verified with the typical rheology studies [49,93], as well as dilatation rheology experiments [49]. Le Kiminta and Lencan concluded that the elasticity – or elastic modulus – is proportional to the frequency, while the viscosity – modulus of loss divided by frequency – depends inversely on the frequency; with typical frequency values between 0.01 and 1 Hz [93].

For dual-sensitive microgels, the main references are limited to PNIPAM-MAA microgels and it is important to note that the properties of other systems may change. In this sense, it has been observed

that the effect of pH is more pronounced than that of temperature being a constant decrease of the surface tension under acidic conditions [15]. In addition, it seems that the size of the microgels has no direct effect on the surface tension either above or below the VPTT [18] neither the type/amount of cross-linker [55].

Brugger *et al.* found a strong dependence of the mechanical properties with the pH of PNIPAM-MAA microgel solutions at heptane/water interface through the study of the elastic modulus in relation to the shear stress and dilatation (Figure 8) [15,49]. As can be seen in Figure 8, the interfacial shear rheology experiments show a clear viscoelastic linear behavior at pH 9, characterized by the independence of  $G'$  and  $G''$  from shear amplitude, with prevalence of the elastic behavior before entering the non-linear zone. By contrast at pH 3, it was not possible to complete the measurements of  $G'$  before its value fell without even reaching the small yield stress and the value of  $G''$  was several orders of magnitude lower. This indicates that at acidic conditions the interface breaks and flows like a viscous fluid. For the stable interface at pH 9, the values of  $G'$  and  $G''$  in the linear regime were found around 0.5 mN/m and 0.2 mN/m, respectively [49].

Although the linear viscoelastic behavior still appeared in interfacial dilatational rheology experiments, the profile obtained for these measures was similar for both pHs, independent of strain and with slightly higher values in the case of elasticity for higher pHs. The values of  $E'$  are of the order of 2 and 4 mN/m for pH 2.8 and 9.2 respectively; and those of  $E''$ , of 0.3 for both pHs. The measurements carried out in whole pH range show that the shear modulus and the dilatation modulus are fundamentally different depending on the microstructure and inter-particle interactions; as well as that the layer supports perpendicular stresses better. Finally, the dependence on pH was also observed in greater compressibility at low pH. These properties can be explained considering the microgels microstructure at each pH. At low pH, PNIPAM-MAA microgels are organized as a dense and crystalline layer, which would be brittle, while at high pH as microgel particles are swollen, they are articulated by the interconnection of polymer chains being more elastic [49].

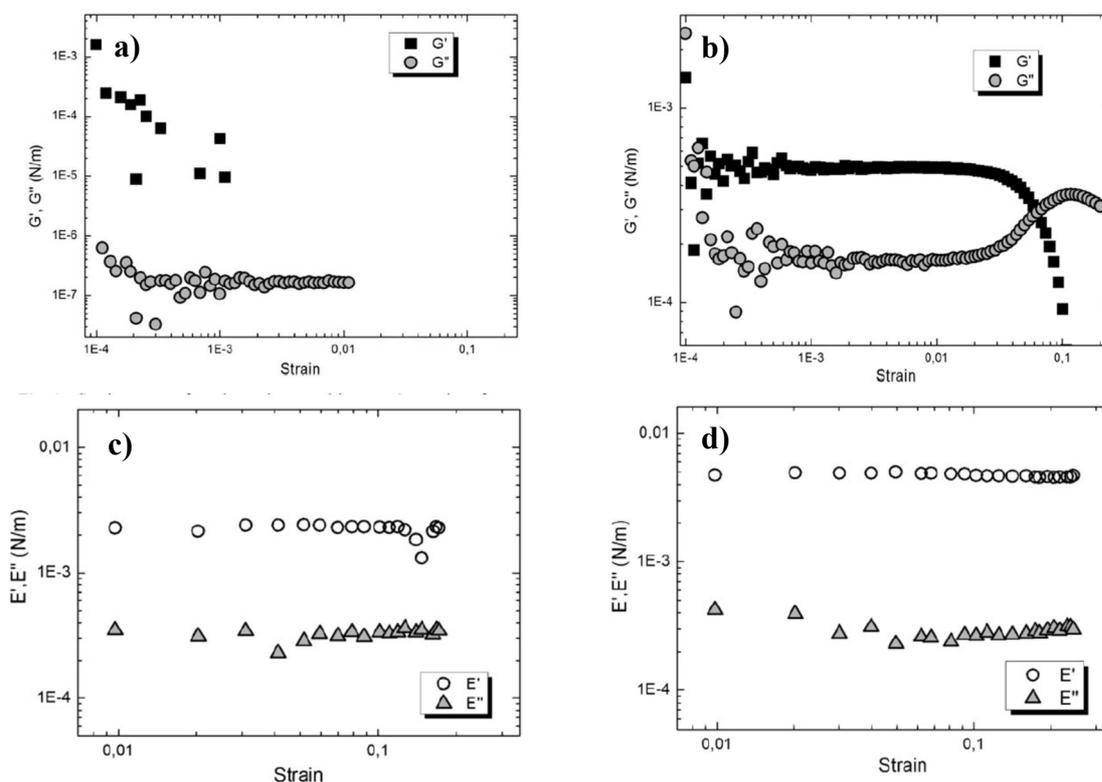


Figure 8: Strain sweep of a microgel covered heptane/water interface at pH 3 and 9 and a frequency of 0.5 Hz (a and b respectively); and as measured by dilatational rheology at pH 2.8 and 9.2 (c and d respectively). [Reproduced with permission from Ref. [49]].

The effects of temperature and pH on mechanical properties were studied by the same group [15]. They reported the decrease of the value of the elastic module  $G'$  with temperature around one unit (mN/m) for all pHs in an approximately linear way. Moreover, it was obtained a low value of loss modulus ( $G''$ ) for pHs between 4 and 9 without dependence on temperature, except for a large increase for pH 3 above VPTT. It is important to point out that all these results were in accordance with the macroscopic appearance of the emulsions and their stability [15].

Some years after, Cohin and coworkers published the values of the elastic modules for PNIPAM microgels and values between 5 and 8 mN/m for all temperatures were obtained, which were almost not significantly higher than the residual measurement obtained for a pure air-water interface of the order of 1 to 3 mN/m [53]. These results are in accordance with those obtained by Brugger *et al.* for PNIPAM-MAA microgels at the air-water interface [49] and one order of magnitude lower than that obtained for the linear PNIPAM chains around the LCST [94]. When the elastic modulus as a function of surface pressure for microgels was studied by Pinaud and coworkers, a maximum was observed for an interfacial pressure equivalent to the flattened conformation of the microgels (regime II) [55].

For PVCL microgels, similar mechanical properties to those of PNIPAM microgels have been obtained by Maldonado-Valderrama *et al.* [29]. They observed that in the whole temperature range,  $E'$  is higher than  $E''$ , which implies a solid-like behavior, with an elasticity between 2 and 4 mN/m independent of temperature, little higher than the air/water elasticity which indicates the formation of a very loose adsorbed layer with low cohesiveness between the polymer chains [29]. The similar results obtained by PVCL microgels opens the possibility of using thermo-responsive microgels for stabilizing emulsions for bio-applications thanks to the good biocompatibility of PVCL microgels [24,27,28].

### Summary and Future perspectives

Pickering emulsions stabilized with thermo-, pH- or dual-sensitive microgels have proven to be a successful strategy to design emulsions that can evolve under the effect of an external stimulus. However, the stabilization of Pickering emulsions using microgels is a more complex matter than stabilization using solid particles. The concept of contact angle or electrical charge no longer makes sense since the microgels are deformed at the interface and are interconnected with much greater importance of cross-linking, swelling or compression. Nevertheless, the behavior of different types of microgels at the interface and the influence of different microgel parameters such as charge or cross-linker distribution has been well studied [10,15,39,63,65]. In the same way, the mechanical properties of the interface such as tension, elasticity and viscosity have been measured using shear and dilatational rheology [18,23,29,54,91]. However, despite the increasing number of studies on the use of microgels as Pickering stabilizer reported in the literature, the properties of the adsorbed state and its relation with the emulsion stability are not well understood yet opening the door for further investigations. In this sense, it is not yet clear the role of electrostatics on the interfacial properties of charged microgels [73,78]. In the same way, the effect of the size of microgels has been discussed controversially in the literature [18,64]. Therefore, from all those studies the complexity of the subject is deduced and therefore, it is necessary to study each particular system not only macroscopically but also from the interface mechanical properties point of view.

After several decades of research, even in the knowledge about the use of microgels as Pickering stabilizers has been considerably improved, some questions remain open, as mentioned above. As far as it has been found, the literature is reduced to the use of PNIPAM microgels which are not completely suitable for bio-applications due to its lack of biocompatibility [24]. It is therefore necessary to propose more biocompatible alternatives. In this context, the use of PVCL microgels can be proposed, whose mechanical properties at the interface have already been studied [29].

Recently, a new family of biocompatible[95-98] and multi-responsive microgels[99,100] based on oligo(ethylene glycol) has attracted attention thanks to their interesting properties [101-105]. It has

been demonstrated that these novel microgels are able to encapsulate an unexpected high content of preformed magnetic NPs (up to 33 wt% of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> versus microgels) and different types of active molecules (up to 1 mg/mg<sub>microgel</sub>) while maintaining simultaneously perfect colloidal stability, sharp thermo-responsiveness, intense collapse-to-swelling behavior and their film formation ability [101,103] (Figure 9).

These properties together with the fact that it has been proven that by using different crosslinkers a different distribution inside the microgel is obtained [101], and such microgels present the strong ability to be overlapped and form spontaneously cohesive and stretchable films [102,104,106] what could have interesting properties in the deformation, make them strong candidates for emulsion stabilizers.

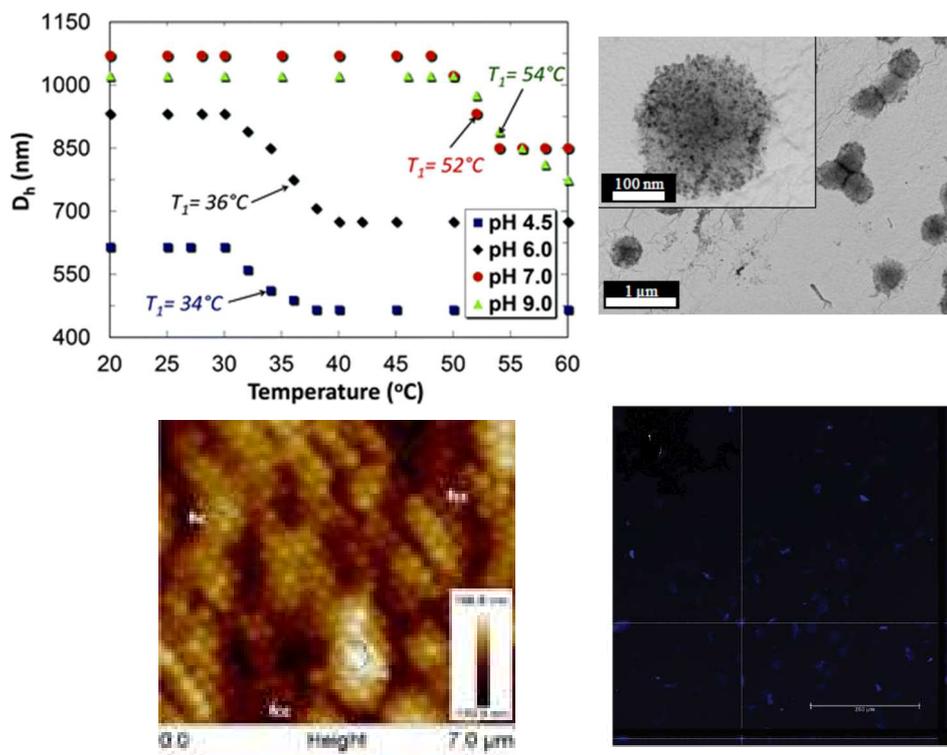


Figure 9: (a) Hydrodynamic diameter  $D_h$  (nm) of OEGDA-crosslinked P(MEO2MA-co-OEGMA-co-MAA) microgels versus temperature for different pH values; (b) Transmission electron micrographs of 33 wt%  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>-P(MeO<sub>2</sub>MA-co-OEGMA-co-MAA) hybrid microgels; (c) AFM micrograph of the surface of self-assembled microgels film from the same by water evaporation without any chemical treatment; (d) Cross-sectional confocal images of Salicylic acid-loaded film. [Reproduced with permission from Ref. [101,102,104]].

### Conflicts of interest

There are no conflicts to declare.

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# Microgels Self-assembly at Liquid/Liquid Interface as Stabilizers of Emulsion : Past, Present & Future

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## Graphical abstract

