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Temperature-responsive Pickering Emulsions Stabilized by Poly(Ethylene Glycol)-Functionalized Silica Particles

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Abstract

A series of PEG-functionalized silica nanoparticles with various molecular weight (MW 200, 400, 550, 2000, 5000 g.mol⁻¹) have been prepared through a one-step synthesis and further used for the elaboration of temperature-responsive Pickering. The physicochemical properties of the nanoparticles were determined by TEM, TGA, DLS, surface tension and zeta potential measurements and the formed emulsions have been characterized by optical microscopy. The ability of SiO₂@mPEG 550 to form temperature-responsive emulsions with oils of different nature has been explained by the hydrophilic/hydrophobic balance of the PEG/mPEG chains. The emulsions stabilized with PEG-functionalized SiO₂ NPs undergo a clear temperature-triggered destabilization from room temperature to 80 °C due to the modification of the distribution of the PEG/mPEG chain at the oil-water interface.

Keywords. Pickering emulsion; PEG; Functionalized silica; Temperature-responsive nanoparticles

1. Introduction

Emulsions are metastable mixtures of two immiscible liquid phases - a dispersed phase and a continuous phase, *e.g.* oil and water - that is stabilized either by surfactant or by solid particles [1,2]. Particle-stabilized emulsions, also called Pickering emulsions, are more stable than conventional emulsions. Pickering emulsions may be useful for reducing the surfactants amount and so, the risk for health and environment [3]. Although a long-term stability is generally the final aim of a formulation process for food, cosmetics, paints, etc., a transitory stability (*i.e.* on demand destabilization) might be wanted for other applications such as emulsions polymerization[4], oil recovery [5] or catalyst recovery [6] in order to collect the product of interest. In these cases, additional disruption mechanisms need to be introduced to achieve the destabilization of the system, which may increase the costs and the energy consumption.

Bare hydrophilic silica nanoparticles (NPs) can stabilize water/polar oil emulsions without any surface functionalization even if they are partially wet by these oils [7,8]. Although the use of bare silica NPs is costless and timeless compared to surface functionalized NP, it may be appropriate to functionalize the silica NPs surface for preparing emulsions with other types of oils and giving them additional functionalities. The grafting of silanes with specific functional groups is well known and controlled [9,10] and permits to enhance the wetting properties. The grafting of other types of materials is also possible, *e.g.* inorganic species (alumina, metals...) [11,12] or polymers [13–15] which allows the preparation of different types of emulsions.

The surface functionalization can limit the desorption of particles from interface, for instance, but also allows to add stimuli-responsive properties to the emulsions. Developing amphiphilic particles and changing their surface properties, in other words their wettability, in response to a stimulus is very promising. As a result, stimuli-responsive Pickering emulsions have gained increased amounts of attention in recent years. Thus, various trigger-responsive materials have been prepared leading to Pickering emulsions being responsive itself to the trigger such as

temperature, pH, light, magnetic field [2,16–18]. Using temperature change for emulsion destabilization is one of the less invasive method to set up, compared to the addition of chemicals or change of the pH of the system. In addition, it can be reversible.

Polyethylene glycol (PEG), also called polyethylene oxide (PEO), and PEG methyl ether (mPEG) are water-soluble and temperature-responsive polymers [19]. The temperature increase induces a modification of the conformation of the polyoxoethylene chains (from polar to nonpolar due to dehydration of the ethylene oxide units) and emulsions stabilized with PEG-based surfactants can undergo a phase separation or a phase inversion (from oil-in-water to water-in-oil). [14,20–22] Surface active particles are more attractive than surfactants since they form much more stable emulsions [23]. One approach to obtain a synergetic effect of a PEG-based surfactant and the highest stability provided by silica NPs has been studied by Yue Zhu *et al.* [24]. By combining silica NPs and polyoxyethylene monodecyl ethers ($C_{10}E_n$), which adsorbs on the silica surface, they could obtain the formation of stable emulsions which are destabilized with temperature. However, the use of PEG adsorbed onto the silica surface may induce the release of some PEG molecules in one of the two phases when the emulsion is destabilized.

One way to overcome this issue is to covalently bind the PEG onto the silica NPs. [21,25,26] Although temperature-responsive Pickering emulsions prepared with PEG-functionalized silica particles has been reported in the literature [14,27], the preparation of the particles is a multi-step and time-consuming process - synthesis of NPs followed by the grafting of the different functional silanes.

Herein, we report on the elaboration and characterization of temperature-responsive Pickering emulsions stabilized with PEG-functionalized silica particles ($SiO_2@PEG$). The particles were prepared through a one-step synthesis based on the hydrolysis and condensation of the silica precursor in the presence of PEG with various molecular weight (MW 200, 400, 550, 2000,

5000 g.mol⁻¹). The physicochemical properties of the NPs have been thoroughly characterized before the preparation of emulsions. We find that SiO₂@mPEG 550 NPs form temperature-responsive Pickering emulsions with oils of different nature. These emulsions undergo a clear temperature-triggered destabilization when heated from room temperature to 80°C while no destabilization has been observed for emulsions stabilized with longer PEG chains (MW 2000 and 5000 g.mol⁻¹). This work provides an interesting and easy approach to prepare temperature-responsive Pickering emulsions with PEG-modified silica particles that are synthesized via a one pot synthesis. Moreover, it demonstrates the possibility to stabilize emulsions without the presence of hydrophobic silanes on the silica surface.

2. Materials and Methods

2.1. Chemicals

All chemicals were used as purchased. Tetraethyl orthosilicate (TEOS) (98 wt.%, Sigma-Aldrich), ammonia (25 wt.%, Chem Lab), absolute ethanol (VWR), poly(ethylene glycol) 200 (Sigma-Aldrich), poly(ethylene glycol) 400 (Sigma-Aldrich), poly(ethylene glycol) 1500 (Acros organics), poly(ethylene glycol)mono methyl ether 550 (Sigma-Aldrich), poly(ethylene glycol)mono methyl ether 2000 (Sigma-Aldrich), poly(ethylene glycol)mono methyl ether 5000 (Sigma-Aldrich), cyclopentyl methyl ether ($\geq 99.9\%$, Sigma Aldrich), toluene (99.85%, Acros Organics), heptane (Analytical reagent grade, Fischer Scientific), isopropyl myristate (Sigma Aldrich), paraffin oil (Cooper), squalane (99%, Acros Organics). D₂O (99.9%) was purchased from Euriso-top (France). All aqueous solutions were prepared with ultrapure water obtained from a Thermo Scientific system (12.2 M Ω .cm, Millipore AG).

2.2. Synthesis of bare silica nanoparticles

The silica particles were synthesized following procedure reported in the literature [28]. 13.5 mL of ultrapure water, 184 mL of absolute ethanol, and 41 mL of NH₄OH were mixed in a 500

mL round-bottom flask and stirred at 300 rpm at 40 °C. 11 mL of TEOS was added at once to the mixture. It was left stirring for 1 hour with a reflux cooling. The particles suspension was purified by several cycles of centrifugation and redispersion.

2.3. One-pot synthesis of polyethylene glycol silica nanoparticles (SiO₂@PEG)

The SiO₂@PEG NPs were synthesized according to a protocol adapted from [29]. 6 mL of TEOS and 72 mL of ethanol were mixed under vigorous stirring for 5 min at 65 °C. 17.1 mL of water and 3.8 mL of ammonia were added. 3 g of PEG (or mPEG) dissolved in ethanol are added dropwise within 5 min. The mixture was stirred for one hour with reflux cooling. The particles were washed by centrifugation and transferred into ultrapure water.

2.4. Dynamic Light Scattering (DLS)

Dynamic light scattering (DLS) experiments were carried out using a light scattering goniometer instrument from LS Instruments (3D LS Spectrometer, Switzerland) equipped with a 25 mW He-Ne laser light source (JDS Uniphase) operating at $\lambda = 632.8$ nm. The scattering spectrum was measured using two single-mode fiber detections and two high-sensitivity APD detectors (SPCM-AQR-13-FC, PerkinElmer). The samples were filled into cylindrical tubes with a diameter of 7.5 mm and placed in the temperature-controlled index matching bath, where the temperature was fixed at 25 °C. Measurements were performed at scattering angles of 90°. The average hydrodynamic radius was obtained through a second order cumulant analysis.

2.5. ¹H NMR spectroscopy

The ¹H NMR spectra were recorded on a Bruker Avance 300 at 300 MHz (Bruker, USA). D₂O was used as solvent for the analysis. Chemical shifts were given in ppm and were measured relative to the TMS.

2.6. Transmission Electron Microscopy

The transmission electron microscopy (TEM) micrographs were obtained on a TECNAI G2-20 Twin microscope (FEI, USA), equipped with a LaB6 filament operating at 200 kV. Two drops

of nanoparticles suspension were deposited on a carbon–copper grid (CF200-Cu, Electron Microscopy Sciences, USA).

2.7. Thermogravimetric analysis (TGA)

Thermogravimetric analyses (TGA) were performed using a Q500 instruments (TA Instruments, USA). In a typical analysis, 10-15 mg product was placed in a Pt crucible. The sample was at first equilibrated at 120 °C, and then heated at 10 °C/min to 900 °C, under nitrogen.

2.8. Surface tension measurement

The surface tension measurements of sample were performed with a Krüss K100 tensiometer. In a typical experiment, the rod was immersed in the liquid studied at a rate of 10 mm.min⁻¹ and an immersion depth of 2 mm. Calibration with ultrapure water was carried out. For each measurement, the surface tension values were sampled every 3 s until the standard deviation was below 0.1 mN.m⁻¹. Three measurements were taken in a row for each sample. No temperature correction was made to the previous measured values, since the observed deviations - between 0.1 and 0.7 mN.m⁻¹ - were larger than the temperature corrections, expected to be below 0.2 mN.m⁻¹.

The measurements of the surface tension as a function of temperature were performed with 10 mL aqueous suspension of nanoparticles at 1 wt. % between 25 °C and 80 °C. An equilibrium time of 25 min was applied between the temperature increase and the measurement.

2.9. Optical Microscopy

Optical micrographs were acquired with a VHX-900 microscope from Keyence. The measurement of the droplets diameter size was performed with the Keyence software 1.6.1.0. The distribution function (log-normal) of emulsion droplets diameters was obtained by treatment of at least 200 individual measurements using Origin 9.1® (OriginLab corporation, US) according to Eq. 1:

$$y = \frac{A}{\sqrt{2\pi\omega}\phi} \exp\left[-\frac{\left(\ln\frac{\phi}{\phi_m}\right)^2}{2\omega^2}\right] \quad (1)$$

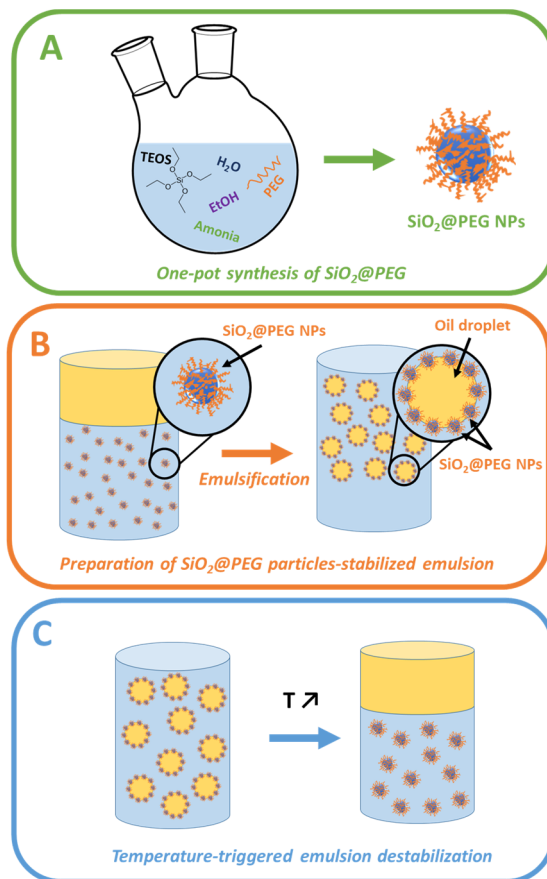
where y is the probability for having droplets of diameter (ϕ), ω is an asymmetric factor (*i.e.* measure of width), the peak will be approximately symmetric when ω is small, ϕ_m is the median droplets diameter (ϕ_m corresponds to the peak center when the log-normal is approximately symmetric), and A is the amplitude and corresponds to the area under the curve. The ϕ_m , ω , and A are parameters characterizing the size distribution of the droplets.

2.10. ζ -Potential measurements

The ζ -potential of the particles was measured on a Zetasizer Nano-ZS ZEN 3600 (Malvern Instruments, UK) at 25 °C. 20 mg of particles were dispersed in 1 mL of aqueous solutions.

2.11. Temperature-responsive behavior of the emulsions

The temperature-responsive behavior of the emulsions was tested by heating the vials in a water bath a gentle stirring at 100 rpm up to 80 °C.



Scheme 1. Schematic illustration of the method of A) one pot synthesis of the $\text{SiO}_2\text{@PEG}$ NPs, B) Preparation of the emulsions stabilized by the $\text{SiO}_2\text{@PEG}$ NPs and C) Temperature-induced destabilization of the emulsion.

2.12. Particle-stabilized emulsions preparation

The emulsions were prepared using water phase containing the silica nanoparticles (1.5 mL) and different oils (1.5 mL). The emulsification was performed with an Ultraturrax T10 basic (IKA Works, Inc., Germany) for 60 s at 11500 rpm at room temperature.

3. Results and Discussion

The morphology and the size of the SiO₂@PEG NPs were studied by TEM (**Figure 1**). They present a rough surface unlike the bare silica NPs (**Figure SI-2**). It is noteworthy the presence of small particles that are linked as a pearl necklace extending out the particles for SiO₂@PEG 400 and SiO₂@mPEG 550 (**Figure 1a-b**). These small particles in such branch-like structure were not observed in previous studies [29]. The formation of such particles may be due to the condensation of silica onto the PEG chains extending out the main silica particles. The presence of small NPs (~ 20 nm) around and attached to the core make the particle rough and may help the stabilization of emulsions as it has been demonstrated by San Miguel et al. [30]

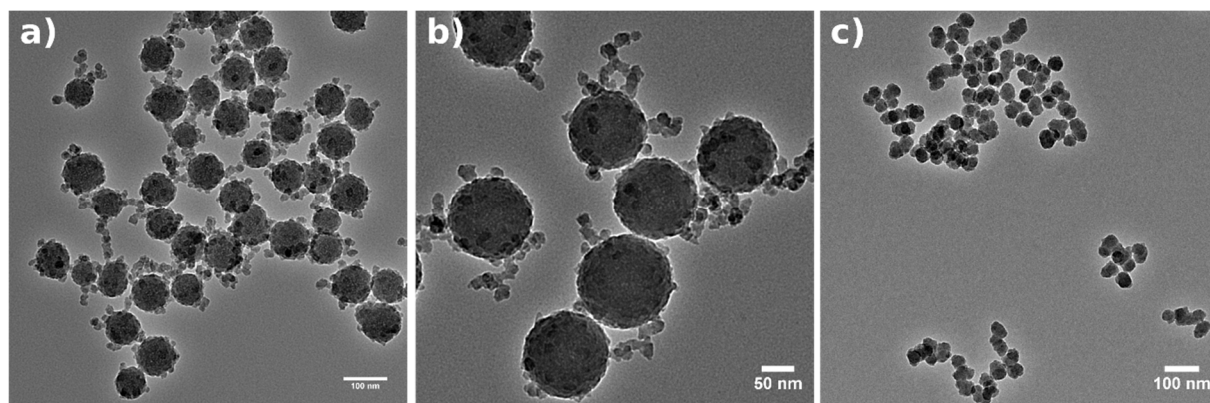


Figure 1. TEM images of a) SiO₂@PEG 400, b) SiO₂@mPEG 550 and c) SiO₂@mPEG 5000 NPs synthesized by the one-step method.

The size of the particles has also been measured by DLS (**Table 1**). As for TEM results, no clear trend has been observed as a function of PEG molecular weight. While for low molecular weight (200 to 550), PEG and mPEG gives the same range of size, *i.e.* 150-180 nm, for bigger PEG (or mPEG), a smaller size has been observed. It may be explained by the formation of much more silica nuclei on the PEG with longer chain (more ether groups) and thus, the final size of silica particles is low compared to other batches. However, the sizes measured by DLS are close to the sizes of the NPs (core + branches) measured on TEM pictures, particularly for SiO₂@PEG 400 (125 nm measured on TEM), SiO₂@mPEG 550 (200 nm measured on TEM)

and SiO₂@PEG 5000 (77 nm measured on TEM). It indicates that the chains of NPs are attached to the core.

In order to verify the presence of PEG onto the surface of silica particles, several characterizations have been performed. First, the ζ -potential values of the NPs were measured as a function of the PEG (or mPEG) weight (**Table 1**). Short chain lengths have surface charges comparable to bare silica. NPs functionalized with bigger PEG show a higher reduction of surface charge. Hence, short PEG chains extend less out of the surface of the NPs, which may explain values close to the ζ -potential of silica. The increase of MW of PEG, which is a nonionic polymer, decreases the surface charge of the NPs.[31]

Table 1. Size hydrodynamic diameter measured in DLS and ζ potential of bare silica NPs and SiO₂@PEG NPs dispersed in ultrapure water.

Particles	Hydrodynamic diameter (nm)	Zeta potential (mV)
Bare silica	110	- 55
SiO ₂ @PEG ₂₀₀	180	- 59
SiO ₂ @PEG ₄₀₀	150	- 59.7
SiO ₂ @mPEG ₅₅₀	180	- 46
SiO ₂ @mPEG ₂₀₀₀	320	- 29.1
SiO ₂ @mPEG ₅₀₀₀	80	- 31.6

The presence of PEG on the surface of the NPs was investigated by ¹H NMR spectroscopy. (**Figure SI-5**) ¹H NMR spectrum of SiO₂@mPEG 550 NPs was compared to the spectrum of silica NPs functionalized with mPEG 500 through the two-step protocol proposed by Björkegren *et al.* [14] were measured. Both spectra show peak that corresponds to the presence of PEG (3.6 ppm). This result suggests that the peak of SiO₂@mPEG 5000 is less intense than

the peak of the silica NPs functionalized through the two-step method.[32] The nature of interaction between silica and PEG is different for the two types of NPs. Particles grafted with a coupling agent have the PEG molecules covalently attached to their surface, which puts all these molecules in a similar environment resulting in a sharp peak. On the other hand, the broad peak of the SiO₂@mPEG 550 particles prepared with one-pot method suggests that the molecules of PEG are in different environments, *i.e.* a part of the PEG is inside the SiO₂ core and the other part is outside of the core. The synthesis of SiO₂@PEG consists in a modified Stöber synthesis of silica in presence of PEG developed by Akbari et al [29]. According to Xu *et al.* [33], the hydrolysis step of the sol-gel process of the silica precursor competes with the transesterification between the PEG and silica precursor (TEOS) before the condensation. This method allows to entrap the PEG by a covalent binding, within the silica NPs but also onto the surface.

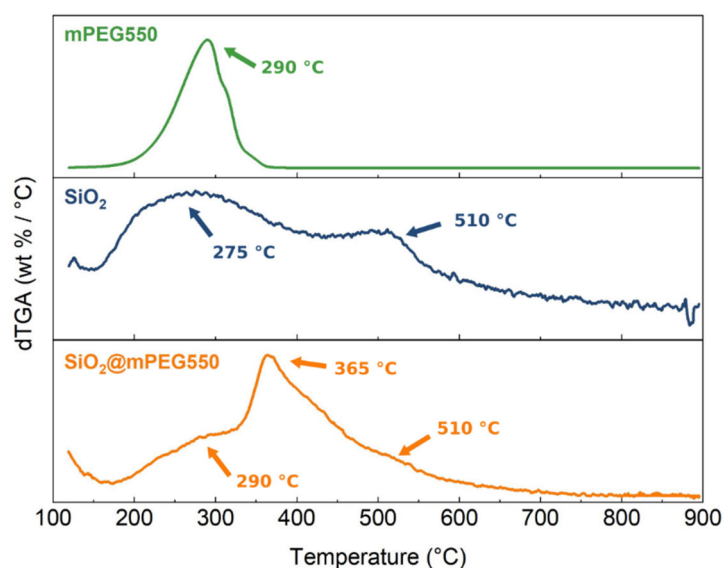


Figure 2. dTGA curves of mPEG 550, bare silica NPs and SiO₂@mPEG 550 NPs. Experiments were conducted at 10 °C/min to 900 °C, under nitrogen.

The SiO₂@PEG NPs were characterized with TGA measurements (**Figure 2**). First, the dTGA curve of the SiO₂@mPEG 550 shows a main peak at 365 °C and two shoulders at 290 °C and

510 °C. While the signal at 290 °C corresponds to the PEG degradation (as measured for pure mPEG 550, figure SI-4) and silica dehydroxylation, the signal at 510 °C can be attributed to the dehydroxylation of isolated hydroxyl groups like it was measured for the bare silica NPs. [34] The main peak of the dTGA of SiO₂@mPEG 550 at 365 °C can be attributed to the degradation of grafted PEG species.[35] A peak at around 275 °C is also visible in the dTGA curve of the silica NPs that can be attributed to the dihydroxylation of some hydroxyl groups. The peak at 365 °C of dTGA curve of SiO₂@mPEG 550 is similar to the peak of SiO₂@GPTMS@PEG 2000. These results may suggest that the mPEG 550 is covalently attached to the NPs.

In order to check that the presence of PEG in the samples is not due to the residual PEG molecule – not attached on silica network – the NPs have been centrifuged and redispersed in water several times. ¹H NMR spectra of two supernatants have been performed to control the absence of free PEG in the suspension (**Figure SI-6**). The ¹H NMR spectra of two supernatants have been performed after 3 and 5 washing cycles. While after three washing step, some free PEG molecules are still present, after five washing steps no more free PEG molecule are present (peak reduced to noise level). This result proves that the washing steps were effective to remove free PEG molecules.

The surface tension of the NPs was measured in order to compare the surface activity of the SiO₂@PEG with bare silica NPs. The surface tension of aqueous suspension of bare silica NPs is known to be around 72 mN.m⁻¹ whatever the concentration which indicates the negligible effect of their presence. [36,37]. Surprisingly, at room temperature, the surface tension of the aqueous suspension of SiO₂@mPEG 550 NPs is at the same order, around 71 mN.m⁻¹ whatever the different concentrations measured (**Figure SI-7**). Surface tensions of aqueous suspensions of SiO₂@mPEG 5000 and SiO₂@GPTMS@mPEG 2000 are 10 % lower at around 65 mN.m⁻¹. These results would indicate that the short length of mPEG (MW 550) does not modify enough the surface tension of silica dispersion at room temperature. Hence, longer chain PEGs are more

capable of reducing the surface tension with better steric stabilization on the surface once adsorbed. No significant change in surface tension has been observed by increasing the concentration of the NPs from 0.5 to 2.5 wt. %, whatever the nature of the NPs.

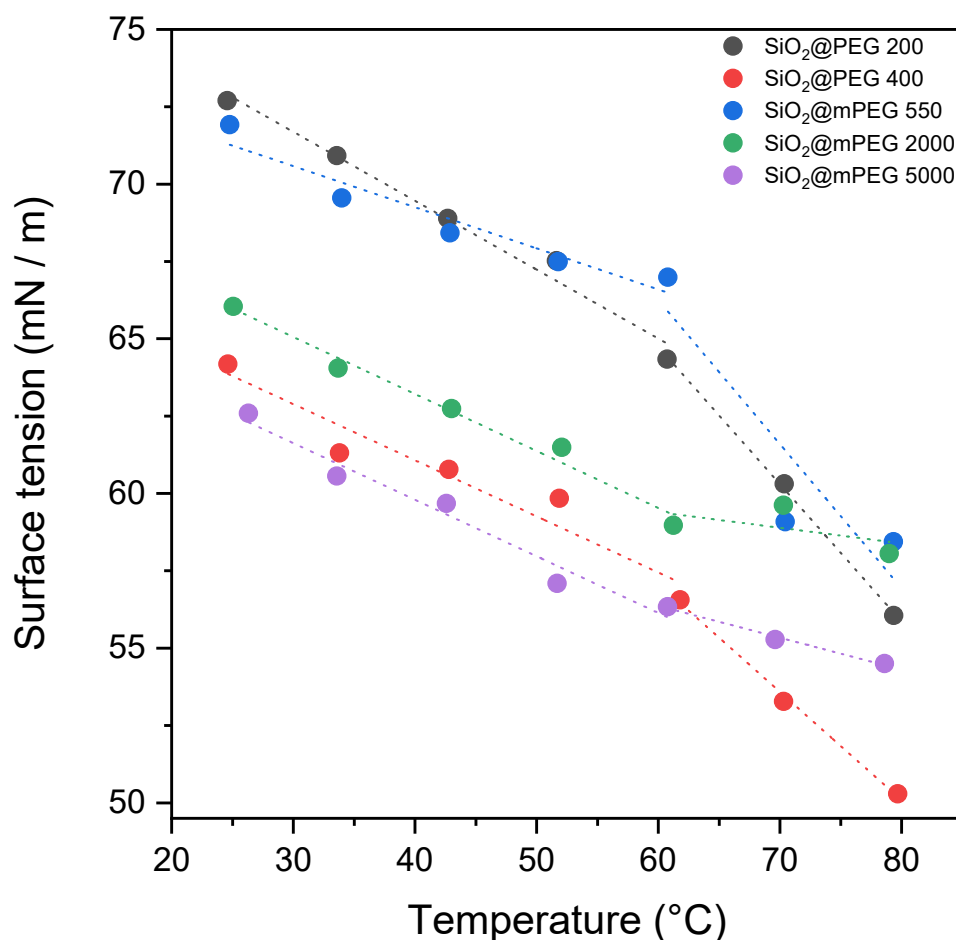


Figure 3. Surface tension as a function of temperature of aqueous suspensions of the different SiO₂@PEG NPs. Concentration (1 wt. %).

The surface tension of the aqueous suspensions of purified PEG-functionalized NPs has been also measured as a function of the temperature in order to determine the temperature-responsive behavior of the NPs. (**Figure 3**) The measurements have been performed at a fixed NPs concentration (1 wt. %). Two groups of data can be observed. In one hand, the SiO₂@PEG200 and SiO₂@mPEG550 with a surface tension at around 72 mN.m⁻¹ that corresponds to the surface tension of water. The NPs have no or very small effects on the surface tension at room

temperature. In the other hand, SiO₂@PEG400, SiO₂@mPEG2000 and SiO₂@mPEG5000 have a surface tension decreased at around 65 mN.m⁻¹ at room temperature, indicating they are surface active. Unlike the SiO₂@PEG200 and SiO₂@mPEG550, they should provide better stabilization for emulsions. These results may indicate that the NPs are surface active when the surface coverage of PEG is high enough [14]. The presence of PEG chains may be indeed more important onto the surface of the particles when using mPEG 2000 and mPEG 5000, with long chains.

When the temperature is increased up to 60 °C, the surface tensions of the dispersions decrease linearly and a break of the slope appears for higher temperatures. The surface tension of NPs functionalized with short chains of PEG (PEG 200, PEG 400 and mPEG 550) decreases faster for temperature higher than 60 °C while the surface tension of NPs functionalized with long chains of PEG is stabilized (mPEG 2000) or decreases slower (mPEG 5000). According to these results, the temperature-responsive behavior of Pickering emulsion were investigated at room temperature and at 80 °C, clearly above the temperature of change of behavior, *i.e.* T = 60 °C.

Water / toluene emulsions (50/50) have been prepared with the SiO₂@PEG NPs (**Figure 4**). As expected, particles grafted with small PEG, *i.e.* PEG 200, were poor stabilizers while O/W emulsion phase could be obtained with particles grafted with PEG of MW ≥ 400. [38]. The emulsions have been observed under optical microscope (**Figure 4**). The mean size of the droplets has been determined from the size distribution, obtained from the statistical analysis of the optical micrograph. It is around 35 μm for the emulsions stabilized with SiO₂@PEG 400 and SiO₂@mPEG 550 while smaller size of droplets for the emulsion stabilized with SiO₂@mPEG 2000 and SiO₂@mPEG 5000 has been measured.

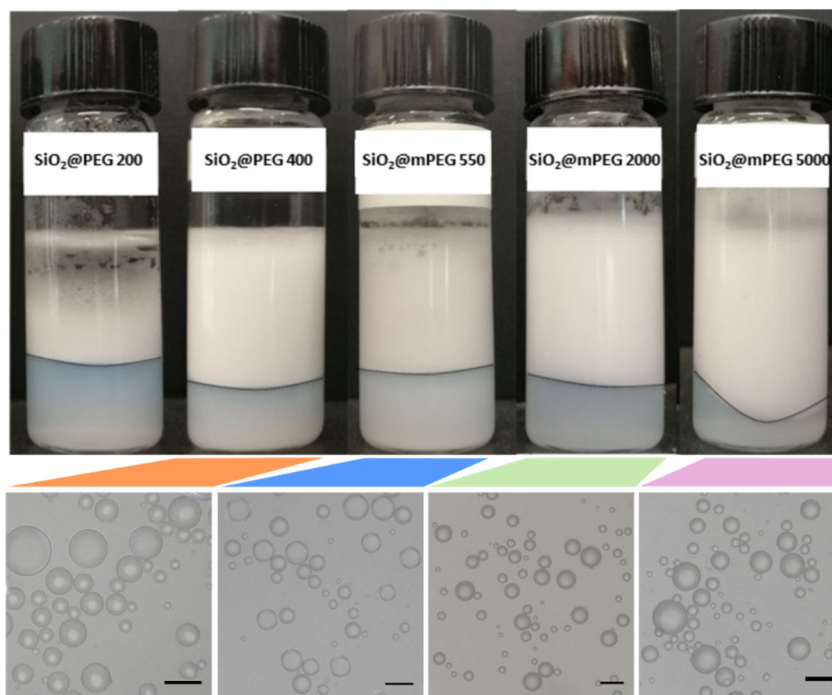


Figure 4. Appearance of the toluene/water (1:1 v/v) emulsions stabilized by silica NPs (1 wt.%) grafted with different types of PEG (top); Optical microscope pictures of the droplets for the corresponding emulsions (bottom). Scale bars: 50 μ m.

The temperature-responsive behavior of SiO₂@PEG NPs-stabilized emulsions has been tested by applying an increase of temperature from 25 to 80 °C (**Figure 5**). Shorter chains of PEG are expected to have a better temperature-responsive behavior than long PEG chain according to the measurements of the surface tension (**Figure 3**). They require less energy to dehydrate compared to longer chains. SiO₂@PEG 200 could not stabilize emulsion, hence it can be considered as unsuitable for the following. Both SiO₂@PEG 400 and SiO₂@mPEG 550 gave emulsions at room temperature and have presented a temperature-responsive behavior with temperature increase, *i.e.* a clear phase separation. Despite having stable emulsions, the particles with longer chains of PEG have almost no temperature-responsive behavior when heated (SiO₂@mPEG 2000), as expected. Moreover, the emulsion stabilized by SiO₂@mPEG5000 maintains stable. The temperature responsive behavior or the PEG-

functionalized silica particles can be attributed to the hydrophilic/hydrophobic balance of the PEG/mPEG chains. At low temperature, the balance between the ether oxygen of EO chain-water interaction and carbon-carbon backbones of PEG is enough to let the SiO₂@PEG particles stabilizing emulsions [39]. With the increase of temperature, the hydrogen bonds between the EO chain and water become weaker [40]. At high temperature, the distribution of the PEG/mPEG chain at the oil-water interface is modified which results in the destabilization of the emulsion [41]. Especially, the SiO₂@PEG particles become more hydrophilic with the increase of the chain length, improving the ability of EO units to form more hydrogen bonds with water. In this way, the increase in the chain length of the PEG also increases the energy required to break the hydrogen bonds between EO units and water molecules. According to these results and the previous characterizations, SiO₂@mPEG550 NPs are the most suitable particles for stabilizing water / toluene emulsions and giving them a temperature-responsive behavior.

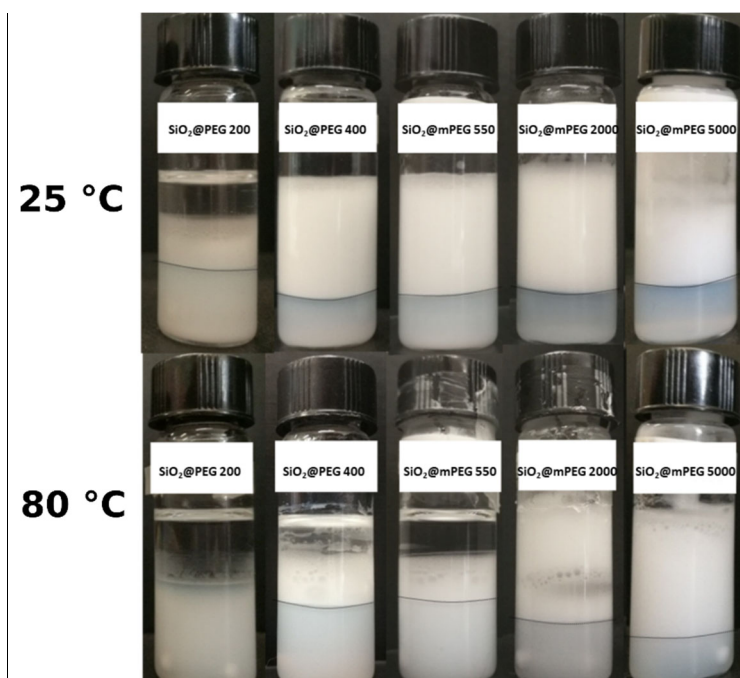


Figure 5. Pictures of the toluene/water (1:1 v/v) emulsions stabilized with silica particles (1 wt.%) grafted with different length of PEG, at 25 °C and 80 °C.

In order to verify the ability of SiO₂@mPEG 550 NPs to stabilize emulsion with other oils, several emulsions have been prepared with different oils: toluene, heptane, paraffin oil, isopropyl myristate, CPME and squalane. (**Figure SI-8-13**) The influence of the nature and polarity of the oils on the final properties of the emulsions and their temperature-responsiveness have been investigated. The emulsions have been compared to emulsions prepared with bare silica NPs, pure mPEG 550 and a mixture of bare silica NPs and mPEG 550 (**Figure 6**). As expected, emulsions could be obtained with paraffin oil, isopropyl myristate, CPME and squalane.[42] A destabilization occurs when the temperature increases but it could be explained by the gentle stirring used to homogenize the temperature that may accelerate the natural destabilization of the emulsions. Pure mPEG 550 molecules stabilize emulsions with almost all oils (except isopropyl myristate, probably due to the poor solubility of mPEG in this oil). A temperature-triggered destabilization occurs except for toluene. Stable emulsions were obtained with the mixture silica NPs and mPEG 550 was used whatever the nature of the oil. A weak temperature-triggered destabilization happens except for emulsion prepared with squalane. Hence, oils with higher polarity (*e.g.* heptane) are more favorable to obtain Pickering emulsions with bare silica and pure PEG [42,43]. When SiO₂@mPEG 550 NPs were used, stable emulsions were obtained at room temperature and a clear destabilization occurs at 80 °C. Here, the results show that the SiO₂@mPEG 550 NPs can form stable and temperature-responsive emulsions with oils of different nature.

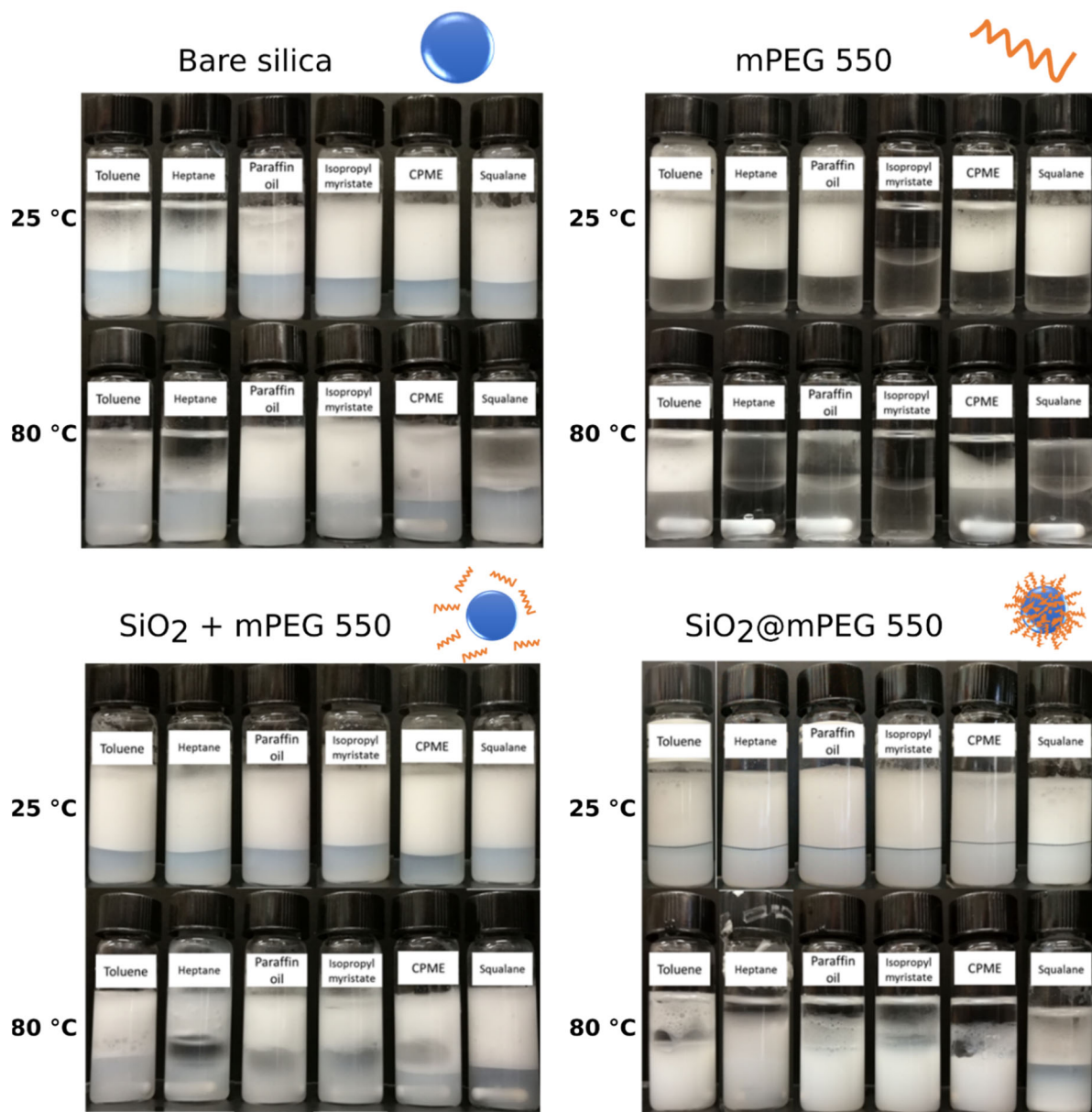


Figure 6. Appearance of the oil/water (1:1 v/v, different nature of oil) emulsions stabilized with bare silica (1 wt.%), mPEG 550 (0.07 wt.%), a mixture of bare silica and mPEG 550 (11:1 ratio, 1 wt.%) and silica particles (1 wt.%) grafted with type of PEG at 25 and 80 °C.

4. Conclusion

A series of PEG-functionalized-SiO₂ NPs have been prepared *via* a one-step method and were used for the elaboration of temperature-responsive Pickering emulsions. The physicochemical properties of the NPs as well as the presence of PEG molecules anchored on the particles have

been thoroughly studied. A drop of the surface tension has been observed near 60 °C for three length of PEG (MW 200, 400 and 550). Stable Pickering emulsions, obtained with several oils of different polarity, were stabilized with NPs functionalized different PEG length (except with the shortest, 200 g.mol⁻¹). Emulsions stabilized with SiO₂@mPEG 550 NPs underwent a clear destabilization with temperature (from room temperature to 80 °C) whatever the nature of the oil compared to the other PEG lengths studied and bare silica NPs, mPEG 550 and their mixture. Further investigations are currently conducted, including the grafting of polyoxometalates onto the poly(ethylene glycol)-functionalized silica particles for catalytic applications. Polyoxometalates, which are used as catalysts, tend to spontaneously adsorb onto hydrophilic surface (such as PEG or polyethoxylated surfactant) through a self-assembly[44,45]. After a completed reaction, the catalyst is usually collected by filtration or centrifugation which are time and energy consuming techniques and not suitable for industrial process. The use of SiO₂@PEG NPs as support for polyoxometalates would help to recover the catalysts and the products after a temperature-trigger destabilization.

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