



## Supramolecular organization of protonated aminosilicones in water

Hugo Petitjean, Pierre Guiglion, Martin In, Janice R Aldrich-Wright, Patrice Castignolles, Francois Ganachaud, Marianne Gaborieau

### ► To cite this version:

Hugo Petitjean, Pierre Guiglion, Martin In, Janice R Aldrich-Wright, Patrice Castignolles, et al.. Supramolecular organization of protonated aminosilicones in water. Journal of Colloid and Interface Science, 2013, 408, pp.87 - 93. 10.1016/j.jcis.2013.07.010 . hal-04082274

**HAL Id: hal-04082274**

**<https://hal.science/hal-04082274>**

Submitted on 26 Apr 2023

**HAL** is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.



Distributed under a Creative Commons Attribution - NonCommercial - NoDerivatives 4.0 International License

# Supramolecular Organization of Protonated Aminosilicones in Water

Hugo Petitjean,<sup>a,ε</sup> Pierre Guiglion,<sup>b,c,¥</sup> Martin In,<sup>d</sup> Janice R. Aldrich-Wright,<sup>b</sup>

Patrice Castignolles,<sup>c</sup> François Ganachaud,<sup>\*a,e,f</sup> Marianne Gaborieau<sup>b</sup>

<sup>a</sup> *Laboratoire de Chimie des Polymères UMR7610 CNRS/ Université Pierre et Marie Curie 3 rue Galilée 94200 Ivry, France*

<sup>b</sup> *University of Western Sydney, Nanoscale Organisation and Dynamics Group, School of Science and Health, Locked Bag 1797, Penrith NSW 2751, Australia*

<sup>c</sup> *University of Western Sydney, School of Science and Health, Australian Centre for Research on Separation Science (ACROSS), Parramatta Campus, Locked Bag 1797, Penrith NSW 2751, Australia*

<sup>d</sup> *Laboratoire Charles Coulomb UMR5221 CNRS/ Université Montpellier 2 Place Eugène Bataillon 34095 Montpellier Cedex 5, France*

<sup>e</sup> *Université de Lyon, F-69003, France*

<sup>f</sup> *INSA-Lyon, IMP, UMR5223, F-69621 Villeurbanne, France. Fax: (33) 4 72 43 85 27. Tel: (33) 4 72 43 E-mail : francois.ganachaud@insa-lyon.fr*

<sup>ε</sup> *Current address: CNRS ENSCM UM1 UM2, UMR 5253, Institut Charles Gerhardt, MACS, F-34296 Montpellier 5, France*

<sup>¥</sup> *Current address: Department of Chemistry, University College London, 20 Gordon Street WC1H 0AJ London*

## Abstract

This study deals with the ionically-driven self-assembly of oligomeric aminosilicones, judiciously protonated with a variety of organic acids. Depending on the length of the silicone and the strength of the associated acids, (inverse) water-in-silicone emulsions, small nanoparticles or catanionic vesicles were prepared and characterized by conventional (TEM) or original (DIC optical microscopy, DOSY NMR) techniques. For chains longer than about 40 units, a specific PEG-based sulfonic acid was synthesized and used in a view to generate a supramolecular blocky-like copolymer and ensure fast and efficient emulsification. In all instances, a simple impulse such as pH rising allows to phase-separate the colloidal objects.

## <sup>10</sup> Keywords

Aminosilicone; ionic pairs; self-assembly; colloids; nanoparticles; inverse emulsions; reversible association.

## Introduction

Silicones or polydimethylsiloxanes (PDMS) are non-hazardous polymers with remarkable properties, which make them popular in a number of applications close to life science e.g. cosmetics, drugs vectorization, tracers for magnetic resonance imaging (MRI).<sup>1</sup> For personal care applications, for instance, silicones are generally formulated, together with numerous components, in water. Aqueous silicone dispersions are mostly prepared by ring-opening polymerization of cyclosiloxane<sup>2</sup> and/or polycondensation of bis-silanol silicone oligomers,<sup>3</sup> but both techniques require highly basic or acidic surfactant catalysts. Introducing polar functional groups in the PDMS chains remains a challenge in ROP carried out in diphasic conditions.<sup>4</sup> Surfactant-free ring-opening copolymerization of cyclosiloxanes of different polarities was never successful in our hands, most presumably because the initiation step does not proceed in the water phase (as it does in radical copolymerization of monomers of different polarities).<sup>5</sup>

Another alternative consists in emulsifying silicone chains bearing either non-ionic moieties such as polyethyleneglycol (PEG), or ionic groups (sulfonate, ammoniums, carboxylates). Among the former family, particular configurations called « trisiloxanes » are commercialized by various silicone companies and have been extensively studied.<sup>6</sup> Phase diagrams in water of these siloxane surfactants in combination with non-ionic surfactants, were produced. In addition, their « super-wetting » properties were otherwise correlated to the formation of vesicles over a large range of concentrations.<sup>7</sup>

Amino-functionalized silicone polymers (also denominated ‘amodimethicones’ by the cosmetics industry) are particularly used in textile, cosmetics, healthcare or coatings industries. They adhere to naturally negatively-charged supports, such as hair, teeth, or fibers.<sup>8</sup> Amino groups are furthermore reactive, which make them useful for crosslinking reactions with other chains bearing epoxide,<sup>9</sup> isocyanate<sup>10</sup> or acrylate<sup>11</sup> functions. To our knowledge however, almost no reports have been published in the academic literature on their surface activity,<sup>12</sup> except for the phase diagram of

water/aminosilicone/non-ionic surfactant where a microemulsion zone is clearly seen.<sup>13</sup> Protonating the amino groups by acetic acid clearly decreased the size of the emulsion, but this effect was visibly not further considered. Recent papers in the open literature also showed the possibility to prepare (micro)emulsions from aminosilicone, but always in the presence of a strong excess of non-ionic surfactants.<sup>14</sup> Vesicles and gels were also claimed in a patent<sup>9</sup> to be produced from a reaction between aminosilicones and epoxidised PEG chains, the obtained network presumably mimicking trisiloxane structure. D<sub>5</sub> (cyclosiloxane with 5 dimethylsiloxy units) emulsions stabilized by different types of aminosilicone surfactants were also described.<sup>15</sup> Low molar mass telechelic aminosilicones quaternized by alkyl halogen molecules exhibit bolaform surfactant features,<sup>16</sup> otherwise claimed to give vesicles without further details.<sup>6</sup>

Ionic self-assembly, in the bulk, in solution or in water dispersion is an elegant, easy way to organized into supramolecular networks simple synthons such as surfactants.<sup>17</sup> The off-stoichiometry pairing of polyelectrolytes and surfactants in water is known for long (e.g. <sup>18</sup>), whereas the pairing of ionic surfactants with hydrophobic counter-ions, which allows tuning the morphologies of the self-assemblies, e.g. worm-like micelles or vesicles, is more recent.<sup>19</sup> In particular, the aqueous emulsification of fatty amines via their protonation with different organic acids has been the subject of several studies, where precise phase diagrams were derived for any stoichiometry of both reactants.<sup>20</sup> On the other hand, supramolecular self-assembly of protonated aminosilicone was, to our knowledge, presented only once, in the bulk and using exclusively perfluorinated carboxylic acids.<sup>21</sup> This article thus aims at presenting a platform of colloid nano-objects obtained from aminosilicones of increasing chain-lengths selectively protonated by various organic acids in water. We will particularly show that the structure and rigidity of the nano-objects are controlled not only by the nature of the organic counter-ion, but also by the degree of aggregation of supramolecular electrostatic complexes. Particles, vesicles and gels that could be useful in cosmetics or vectorization applications are presented.

## Experimental part

### Materials

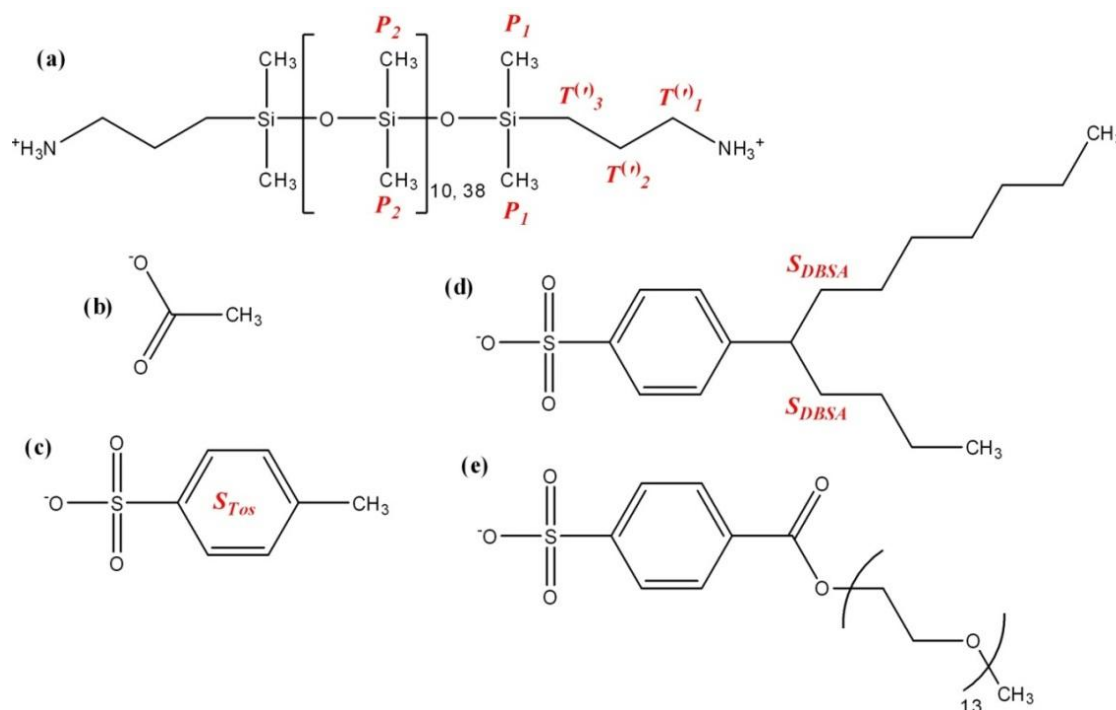
All products used in this study are plotted Scheme 1.  $\alpha,\omega$ -amino functionalized polydimethylsiloxanes of various molar masses (DMS-A11,  $M_n \approx 900 \text{ g.mol}^{-1}$ , DMS-A15,  $M_n \approx 3000 \text{ g.mol}^{-1}$ ) were purchased from ABCR or directly donated by the Wacker company. Their structure was checked by quantitative  $^1\text{H}$  NMR in solution in methanol- $\text{d}_4$  (note that it aggregates in chloroform- $\text{d}$ ); the number-average number of dimethylsiloxane units  $-\text{O}-\text{Si}(\text{CH}_3)_2-$ ,  $\text{DP}_n$ , was typically found to be  $12.73 \pm 0.01$  and  $40.56 \pm 0.03$  per chain for DMS-A11 and DMS-A13, respectively. Monomethylated PEG, trifluoroacetic acid and tosylic acid, all from ACROS, were used without further purification. Dodecylbenzene sulfonic acid (DBSA) was purchased from Janssen (for most visual observations, particle size measurements and microscopy) and Aldrich (for NMR studies). Both were used as received. Various solvents used here are of analytical grade and were provided by PROLABO, as well as potassium carbonate. *o*-sulfobenzoic anhydride (ALDRICH) is 99% purum. Methanol- $\text{d}_4$  was purchased from Aldrich. All water was from MilliQ (Millipore) quality. Absolute ethanol (purity > 99.5%) was from Sigma-Aldrich and used as received.

### Synthesis of *o*-PEG benzosulfonic acid.

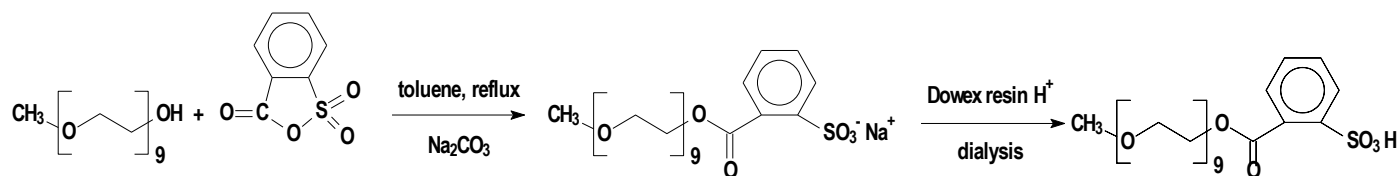
The reaction pathway is given in Scheme 2. In a beaker (50 mL) monomethylated-PEG (1 g) is homogenised in toluene (20 mL) with stirring. Then potassium carbonate (500 mg, 2 eq. compared to PEG) and *o*-sulfobenzoic anhydride (368 mg, 1.1 eq. compared to PEG) are added and stirring under reflux for 2 hours. The  $\text{K}_2\text{CO}_3$  powder, initially insoluble, rapidly disappears whereas the solution rapidly becomes troubled. After solvent is evaporated, the sulfonated PEG is precipitated with dichloromethane (20 mL), filtrated and dried under vacuum. A viscous translucent oil (1.6 g) is dissolved in distilled water (50 mL), dialyzed with a  $1000 \text{ g.mol}^{-1}$  cut membrane with distilled water

(4 L). The purified surfactant is acidified with a ion-exchange Amberlite IR120-H<sup>+</sup> resin (2.5 g , 6 eq. of protons) to produce the final product (yield 1.18 g, 61%), again a translucent viscous oil.

<sup>1</sup>H NMR (in D<sub>2</sub>O) δ : 8-7.6 (m, 3.2H, aromatic) ; 4.46 (m, 1.22H, CH<sub>2</sub> adjacent to COO) ; 3.85 (m, 1.26H, CH<sub>2</sub> on β position of COO) ; 3.66 (m, 49.4H, CH<sub>2</sub> in PEG) ; 3.34 (s, 3H, CH<sub>3</sub> on the extremity of PEG).



**Scheme 1** Cationized telechelic α,ω-amino PDMS (a) using various acids, namely (b) acetic acid, (c) tosylic acid, (d) dodecylbenzene sulfonic acid, and (e) PEG-benzene sulfonic acid (the latter, non-commercial, was synthesized in this study, see main text). Note that HCl and perfluoroacetic acid were also tested, but the results are not systematically presented in this work. Also denominated in red are the protons that were followed by conventional (*P* and *T* signals, where the prime of the latter applies to complexes) and diffusion (*S* signals, protons from the tosylate ring or methylene groups the closest from the DBSA ring) NMR to characterize the state of the various dispersions (see text for details).



**Scheme 2** Synthesis of PEG-BSA by addition of a monofunctional PEG on sulfobenzoic anhydride and further acidification using ion-exchange resins.

## Methods

Particle size measurements were done by PCS on a Malvern Zeta Sizer 4 apparatus equipped with a helium-neon laser (633 nm) and a thermoregulated cell set at 25°C. Samples to be measured are prepared by diluting 5  $\mu$ L of emulsion in 5 mL of distilled water. The CONTIN autocorrelation function was applied to measure the particle size distribution. Observations of the emulsions were carried out with an optical direct microscope Leica DMR with transmitted light illumination under phase or differential interference contrast (DIC). Few drops of the colloidal dispersions were sandwiched between two glass slides and visualized directly. Transmission electron microscopy measurements were processed on a JEM100CXII UHR microscope from GEOL, with a 100kV acceleration tension. One drop of the colloidal dispersion was deposited on a carbon-coated grid and allowed to evaporate, without the need for staining or cryopreparation.

All  $^1\text{H}$  diffusion Nuclear Magnetic Resonance (NMR) experiments were performed at exactly 25 °C using a Bruker Avance 400 NMR spectrometer equipped with a 5 mm BBO probe and operating at a Larmor frequency of 400 MHz for  $^1\text{H}$ , and with 18  $\mu$ s 90° pulse. A combined duration of acquisition and relaxation delay of 2 s was sufficient to ensure full relaxation between scans (it was checked with one-dimensional  $T_1$  inversion-recovery experiments). The WATERGATE sequence (water suppression through gradient tailored excitation) was used for solvent (HO) signal suppression, with a 38  $\mu$ s pulse length. For measurements with DBSA, a duration of the applied magnetic field gradient pulse  $\delta$  of 3 ms was used, with a diffusion delay  $\Delta$  of 300 ms, and the gradient strength was increased from 1 % to 99 % of its maximal strength of 55.3 G $\cdot$ cm $^{-1}$ , by steps of 2 %. For measurements with tosylic acid, a duration of the applied magnetic field gradient pulse  $\delta$  of 2 ms was used, with a diffusion delay  $\Delta$  of 100 ms, and the gradient strength was increased from 1 % to 44.5 % by steps of 1.5 %. Spectra were recorded with 40 scans for pure acid solutions in water (blanks), with 64 scans for aminosilicones aggregates with tosylic acid, and with 128 scans for aminosilicones aggregates with



DBSA. Data acquisition with various diffusion times, phase correction and integration were carried out via Bruker Topspin NMR 1.3 and 2.1 software, the rest of the data processing was done using Origin 8.5.1 software. For each signal, the attenuation of the signal integral  $A$  with increasing field gradient magnitude  $g$  was fitted using equation (E-1) to determine the self-diffusion coefficient  $D$ :<sup>2,3</sup>

5

–

(E-1)

where  $A_0$  is the peak's surface area without field gradient,  $\delta$  is the duration of the applied magnetic field gradient pulse,  $\gamma$  is the magnetogyric ratio of the measured nucleus (here  $^1\text{H}$ ),  $g$  is the gradient strength, and  $\Delta$  is the diffusion delay. Self-diffusion coefficients were determined for the aminosilicone signals (Table 1) and for the counter ion signals when using tosylic acid and DBSA (see  
10 main text).

## Results and discussion

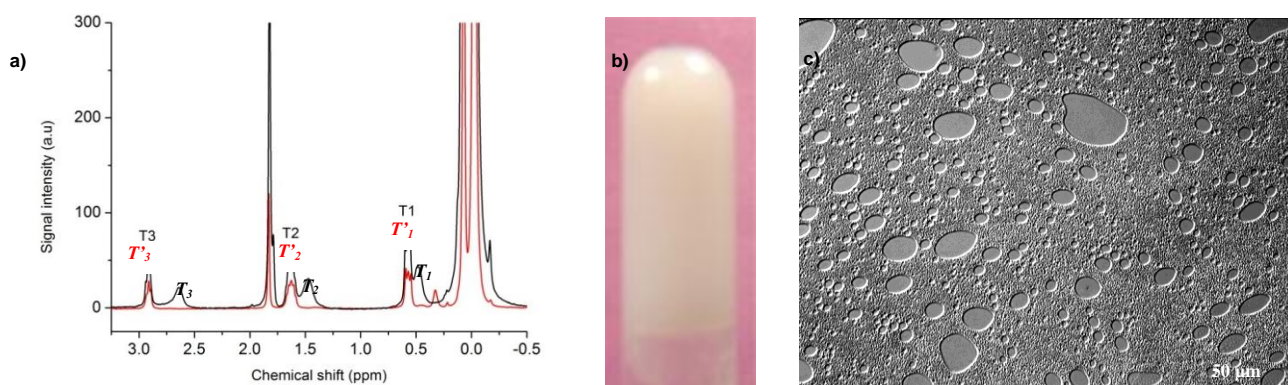
In this work, aminated telechelic silicones with two different molar masses (of around 12 and 40 repeating dimethylsiloxy units, see Scheme 1) were protonated mainly by organic, strong acids (apart from acetic acid), to ensure an efficient ion-pairing between the protonated amino group and the  
15 counter-ion. Note that the shortest commercially available aminosilicone (structure in Scheme 1 with only 2 silicon atoms) was found to give systemically transparent mixtures while protonating it and was thus not further studied here (not shown). The mixing procedure is very simple: an acid solution in water of the desired concentration (typically  $5 \cdot 10^{-2} \text{ mol.L}^{-1}$ ) is first prepared in plastic test tubes, to which the aminosilicone oil is then introduced through a pipette and dispersed using a simple vortex.  
20 To avoid acid-catalyzed silicone chain depolymerization, a stoichiometric ratio of 0.8 eq. of acid per eq. of amine was chosen.<sup>1</sup>

---

<sup>1</sup> This off-stoichiometry ratio is also preferred to generate nano-objects on the full volume, like in e.g. catanionic vesicles (see below).

## Protonation with carboxylic acids

The shortest aminosilicone with  $DP_n \approx 12$  was used first. While protonating it with acetic acid, the dispersion first remained heterogeneous and messy and took several days to equilibrate. The freshly prepared samples exhibited in  $^1\text{H}$  NMR the three methylene signals of original, non-protonated aminosilicone (signals  $T$  in Figure 1a) in addition to those of the aminosilicone complexes (signals  $T'$  in Figure 1a). After the sample was given enough time to evolve into a “frozen state” (typically several days), the additional shifted signals finally disappeared and the resolved signals of protonated aminosilicone only remained (Figures 1a and 1b). We tentatively explain this behavior by the fact that carboxylic acids slowly protonate amine in this heterogeneous, viscous medium. A phase-contrast optical microscope analysis allowed showing the generation of an inverse emulsion, i.e. water droplets embedded into a silicone matrix (Figure 1c). Despite the polydispersity of droplet sizes, a typical low value of 1  $\mu\text{m}$  or less could be measured on the micrographs.



**Fig. 1** Short aminosilicone ( $DP_n \approx 12$ ) protonated with acetic acid (see conditions of preparation in the main text); a)  $^1\text{H}$  NMR spectra of acetic acid/aminosilicone complexes freshly prepared (in black) and aged for 1 week (red) (letters used for the peak assignment referred to the formula shown in Scheme 1); b) Photograph showing the dense, non-creeping, gel formed after resting for several days; c) differential interferometry contrast optical micrograph of the gel, showing the percolated water droplets (magnification:  $\times 100$ ).

20

The fact that this jammed emulsion does not flow for several days while turning it upside down can be explained by a fraction of non-protonated aminosilicone bridging the vesicles together and gelling

the system. This is remarkable when considering that only 5wt.% of active organic matter is used here. Similar gels were prepared using perfluoroacetic acid in place of acetic acid (not shown); this tends to demonstrate that rather than the  $pK_a$ , it is the nature of carboxylate/amino complexes that impose an inverse water-in-silicone dispersion.<sup>2</sup>

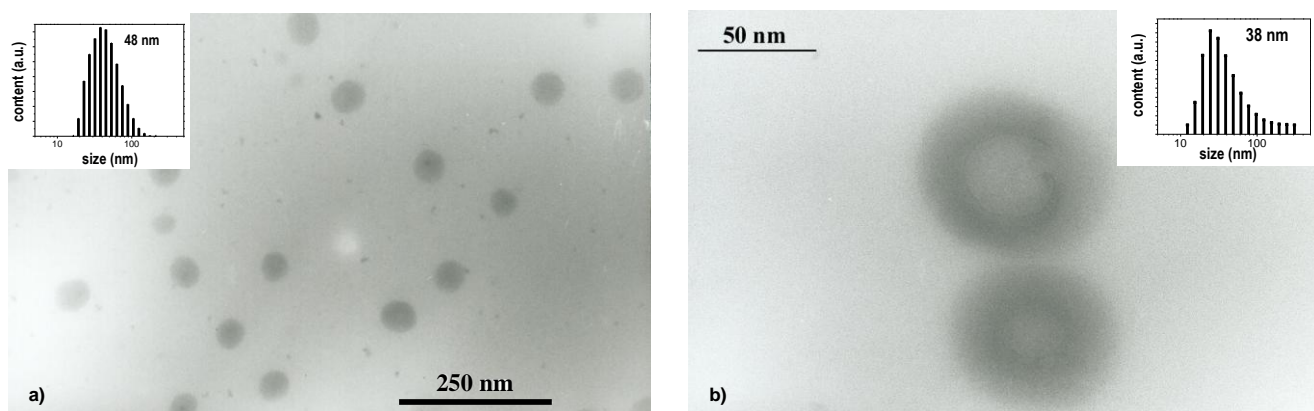
## 5 Protonation with organic and surface-active sulfonic acids

Sulfoaromatic acids were then tested, namely tosylic and dodecyl benzene sulfonic (DBSA) acids (see structure Scheme 1) again with the shortest aminosilicone ( $DP_n \approx 12$ ). After mixing and vortexing, both samples generate homogeneous translucent dispersions which were specifically characterized by PCS and conventional (non-cryo) transmission electron microscopy (Figure 2). Whereas tosylic acid  
10 protonation generates round, apparently hard particles, colloids from DBSA were much softer with an appearance of core-shell structuration. In both cases, colloids were rather monodisperse with sizes averaging 40 to 50 nm, as measured by both PCS and TEM techniques. Different simple trials were done to discriminate the state of colloidal objects (nanoparticles versus nanocapsules). Ultracentrifugation is a nice, easy way to separate most polymer nanoparticles, which sit at the bottom,  
15 from vesicles that are filled with water, thus creaming under the centrifuge force. However, the nano-objects have such small sizes (typically below 50 nm, see Figure 2) and density close from those of water (silicone density = 0.965<sup>22</sup>) that both samples did not migrate even at high centrifugation force (typically 20,000×g). We also tried to compare the hydrodynamic and gyration radii of both samples, since their ratio varies from particles to capsules, but again without success.<sup>3</sup>

---

<sup>2</sup> Measuring the surface tension of these gels by tensiometry could not be done on these too viscous gel dispersions; contact angle measurements were not possible either since the water droplets sunk into the material once deposited.

<sup>3</sup> Hydrodynamic radius measured in PCS is related to the drag coefficient of a particule moving in a viscous medium; it is the same for a hollow sphere and a filled sphere if they have the same outer radius. On the contrary, the radius of gyration is related to the inertia moment of the particle and will be different for a hollow sphere ( ) as compare to a filled sphere ( ) (see e.g., Tanford, C. *Physical Chemistry of Macromolecules*, Wiley NY (1963)). However, because this characterization requires several dilutions which can change the state of the supramolecular objects, we did not conclude from these results (not shown).



**Fig. 2** TEM micrographs and PCS particle size distribution (insets) of colloidal objects prepared by protonation of short aminosilicone with (a) tosylic acid and (b) DBSA. Micrographs on different locations of the grid showed similar, homogeneous object dispersions.

5

To discriminate the state of the two structures, we thus turned to a powerful technique, i.e. diffusion proton NMR (also known as DOSY for Diffusion-Ordered Spectroscopy).<sup>23</sup> The coefficient of self-diffusion ( $D$ ) tells about the hydrodynamic properties of molecules, here typically depending on the aggregation state of our ionic self-assemblies. The principle and theory of the technique is given in the experimental part. The aggregates diffusion was measured in water and not deuterated water ( $D_2O$ ), to avoid the possible influence of the deuteration on the aggregation behaviour.<sup>24</sup> In order to set-up the technique, we determined self-diffusion coefficients of different aminosilicone complexes (namely with acetic acid and tosylic acid) (Table 1). The closer an entity is to the end of the aminosilicone chain, the faster it diffuses ( $D > 6 \times 10^{-10} \text{ m}^2 \cdot \text{s}^{-1}$ ). For entities that are far away from the aminosilicone chain ends, typically the methyl groups borne by silicon atoms inside the chains ( $P_2$  in Scheme 1), self-diffusion coefficients range between  $10^{-11}$  to  $10^{-12} \text{ m}^2 \cdot \text{s}^{-1}$ , i.e. are 10 to 100 times lower. These observations tend to show that aggregates composed of aminosilicone chains are entangled, while the charged amino end-groups that cover the surface have a higher degree of liberty.

15

**Table 1:** Self- diffusion coefficients  $D$  ( $\times 10^{10} \text{ m}^2.\text{s}^{-1}$ ) for the different groups (see scheme 1 in the main text for the assignment of  $T$  and  $P$  groups) of aminosilicone/acetic acid and aminosilicone/tosylic acid complexes prepared at two dilutions in water. The first two columns using acetic acid show the reproducibility of the measurements.

	<b>Acetic acid</b>		<b>Acetic acid</b>	<b>Tosylic acid</b>	<b>Tosylic acid</b>
	<b>0.1%</b>		<b>1%</b>	<b>0.1%</b>	<b>1%</b>
<b>T'<sub>1</sub></b>	<b>6.80</b>	<b>6.94</b>	<b>6.58</b>	<b>7.54</b>	<b>7.19</b>
<b>T'<sub>2</sub></b>	<b>7.20</b>	<b>7.32</b>	<b>7.08</b>	<b>6.78</b>	<b>7.22</b>
<b>T'<sub>3</sub></b>	<b>7.67</b>	<b>7.63</b>	<b>7.27</b>	<b>9.28</b>	<b>8.28</b>
<b>P<sub>1</sub></b>	<b>7.51</b>	<b>6.82</b>	<b>6.03</b>	<b>5.58</b>	<b>5.24</b>
<b>P<sub>2</sub></b>	<b>-</b>	<b>0.03</b>	<b>0.12</b>	<b>0.03</b>	<b>0.03</b>

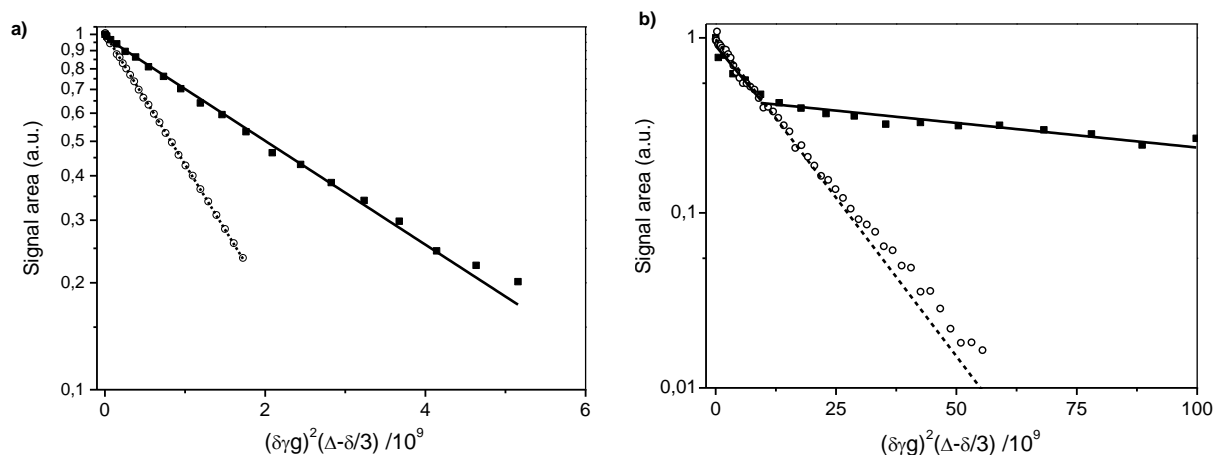
5

To unravel the structure of tosylate and DBSA complexes, protons on the two counter-ions were then chosen as probes for diffusion NMR experiments (see  $S$  assignation in Scheme 1). Plots showing the signal attenuation with increased gradient strengths yield, after exponential regression of diffusion NMR experimental data, linear straight lines on a logarithmic scale (Figure 3). These are representative of the self-diffusion coefficients of the probed protons. Clearly, the aminosilicone sample protonated with TsOH yields a straight line, which slope varies from the blank experiment (tosylic acid alone in water). This shows that all the tosylate ions from the complexes have the same self-diffusion coefficient, typically  $3.4 \pm 0.05 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ , about twice smaller than tosylic acid molecules free in water ( $8.5 \pm 0.02 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$ ). Since all tosylate ions exhibit the same signal, then they are all located at the interface of (plain) aggregates. On the other hand, the aminosilicone/DBSA sample gives two distinct straight lines, with one slope very close from the self-diffusion coefficient of the blank experiment (composed of DBSA micelles) and one of much lower value. From exponential regressions,  $7 \pm 1 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$  for ‘fast-diffusing’ entities (to be compared to  $8.3 \pm 0.1 \times 10^{-10} \text{ m}^2.\text{s}^{-1}$  for free micelles), and  $6.5 \pm 0.7 \times 10^{-12} \text{ m}^2.\text{s}^{-1}$  for ‘slow-diffusing’ entities were found. DBSA counter-ions

20

outside the vesicular membrane diffuse quickly but slightly more slowly than to those engaged in micelles (ions are free in solution) while those inside the vesicles diffuse significantly less rapidly (counter-ions trapped in the aggregates). We can therefore conclude and confirm that the supramolecular structures formed by DBSA protonation of the aminosilicone are vesicles.

5 The fact that short aminosilicone/tosylic acid complexes form nanoparticles is to be compared to the behaviour of dipeptide phenylalanine sequences in water reported by the group of Gazit.<sup>25</sup> These aggregates build up both through stacking interactions of the aromatic rings, and via amine/acid ionic pairing. These supramolecular interactions wrap these oligomers into nanoparticles, of about the same size as those observed here. Note that Gazit's team recently showed<sup>26</sup> that these aggregates are  
10 extremely stiff (in the order of 430 N/m), which may explain in our case that the particles also sustain their shape under the very hot microscope laser. Concerning the complexes with DBSA, it is acknowledged that thermodynamically stable unilamellar vesicles in the nanometer range form spontaneously by mixing judicious contents of anionic and cationic surfactants of similar or close alkyl chain sizes (catanionic vesicles).<sup>27</sup> These latter interact specifically in water, thus forming a strong ion-  
15 pair of similar nature as those studied here, and aggregate into vesicles, because the resulting complex resembles a double-tail lipidic structure. Picking the right telechelic aminofunctional silicone, which average molar mass is about twice that of dodecylbenzene sulfonic acid ( $M_{n,PDMS} \approx 900 \text{ g.mol}^{-1}$  against  $M_{n,DBSA} \approx 330 \text{ g.mol}^{-1}$ ), produces a supramolecular bolaform surfactant that spontaneously arranges into a bilayer structure. Note that our technique is much simpler than previous reports on silicone  
20 vesicle preparation, which aggregated non-spontaneously and into complex non-mastered distributions (formation of onion or bilamellar phases in addition of vesicles).<sup>28</sup>

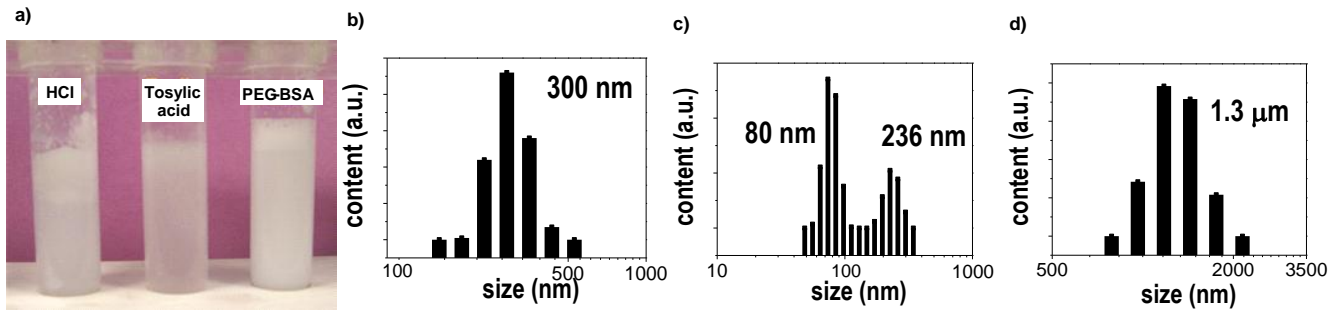


**Fig. 3** Decay of the counter ion's signal in diffusion NMR experiments of aggregates of aminosilicone (black squares) and blank acid aqueous solutions (open circles); (a) monoexponential decay with tosylate counter ion, (b) bi-exponential decay with dodecylbenzene sulfonate counter ion. Best exponential fits are also shown for blank (dashed lines) and complexes (plain lines) experiments. Note the difference in  $x$  axis scale between the two plots.

### The case of long aminosilicone chains

The ability of longer telechelic amino PDMS chains ( $DP_n \approx 40$ ) to generate particles while being protonated and emulsified in water was then tested. None of the usual counter-ion, e.g. chloride, acetate or tosylate, reached stable dispersions but instead caused partial or total gelation and phase separation (see Fig. 4a). These results prompted us to prepare an organic acid that could provide a steric stabilization to the aggregates. Indeed, the cationization of the amino groups with a PEG-functionalized benzenesulfonic acid or PEG-BSA (Scheme 1) in water led to a spontaneous emulsification with the generation of a stable suspension. PEG-BSA was prepared in two steps with a final yield of about 60% (see Scheme 2 and supporting information for precise protocol and characterization of the product). After mixing and vortexing, particles of typically 300 nm in diameter are sterically stabilized by PEG chains reversibly tethered to the surface through the sulfonate/amine ion pair (Fig. 4b). Sonicating the sample during three minutes produces nanoparticles of much lower diameter (about 80 nm for the smallest distribution of size, Fig. 4c), but the sample comes back to its original 300 nm size after resting for a week. This can be an indication that the pseudo-triblock formed

here has generated nanoparticles at equilibrium in these particular conditions. Raising the ionic strength by adding excess NaCl does not coalesce the suspension, but particle diameter increases noticeably (at about an average diameter of 1.3  $\mu\text{m}$ , Fig. 4d). This salt does not compete in terms of ion exchanging with the strong ion pairs generated here. Finally (and this is the case also for all other colloids prepared here), raising the pH to about 11 by adding few drops of concentrated NaOH aqueous solution broke the emulsion. We chose the term of “*toupée* particles” to describe these latter surfactant-free suspensions, by analogy with the well-known “*hairy* particles” that exhibit covalently-linked hydrophilic polymer chains on their surfaces. Indeed, the hairs at the interface of the present dispersions are only physically bound, and can thus be removed (like a wig) by changing the external conditions (here pH).



**Fig. 4** suspensions of aminoPDMS with long chains ( $\text{DP}_n \approx 40$ ) and bearing various counter-ions. Partial or total gelations are observed in all tubes but the third one, where a stable suspension spontaneously forms when using a PEG-functionalized acid (a). Size distributions as obtained from QELS: original mixture (b), dispersion after 3 minutes sonication (c), and dispersion after addition of 1 equivalent of NaCl (d).

## Conclusion

We showed in this study that tailoring the protonation of simple telechelic aminosilicone chains allows one to produce at will gels, nanoparticles, vesicles with tunable sizes never achieved before with amphiphilic silicones.<sup>6</sup> In addition, these objects were prepared in absence of surfactants, a fair improvement compared to previous studies dealing with (amino-) functionalized polymer protonation.<sup>17,20</sup> Thanks to that simple but tailored protonation process, raising the pH provokes a rapid



demixing of the silicone chains, whatever the acid chosen, whether these are solubilized in water (acetic acid, tosylic acid, PEG-sulfonate) or easily micellized (DBSA). The fact that any of the counter-ions is easily removable by cleaning with basic water may find important prospects in various coatings or cosmetic applications,<sup>6</sup> where surfactants are prohibited since they accumulate and change the properties of the final films.

The next step of our investigations is to embed the different colloids with a cyclosiloxane and to proceed to its ring opening polymerization within the supramolecular assemblies, while maintaining their colloidal states, as this was done before uniquely with conventional catanionic vesicular templates.<sup>29</sup> The advantage of this would be to generate stable colloidal dispersions upon dilution, surfactant addition or temperature, i.e. in real life applications.

## Acknowledgements

PC and MG thank the UWS School of Natural Sciences equipment funding, Alison Maniego for preparing the dispersions and discussions, Dr Allan Torres and Scott Willis (UWS) for discussion on diffusion NMR and help with these experiments. FG thanks Patricia Beaunier for TEM measurements and Chantal Larpent for having told us in the first place about the existence of *o*-sulfobenzoic anhydride.

## References

- 1 See for instance, a recent e-book produced by the society Dow Corning on their website (2008).  
[http://www4.dowcorning.com/content/publishedlit/silicones\\_in\\_industrial\\_applications\\_internet\\_version\\_080325.pdf](http://www4.dowcorning.com/content/publishedlit/silicones_in_industrial_applications_internet_version_080325.pdf).
- 2 See for instance some papers from our group: a) M. Barrère, F. Ganachaud, D. Bendejacq, M. A. Dourges, C. Maitre, P. Hémerly, *Polymer*, 2001, **42**, 7239; b) C. Ivanenko, C. Maitre, F. Ganachaud, P. Hémerly, *e-polymers*, 2003, **n°10**; c) B. Yactine, F. Ganachaud, O. Senhaji, B. Boutevin, *Macromolecules*, 2005, **38**, 2230.

- 3 Among the most relevant studies, see: a) J.C. Saam, D.J. Huebner, *J. Polym. Sci: Polym. Chem. Ed.*, 1982, **20**, 3351; b) M. Barrère, C. Maitre, F. Ganachaud, P. Hémary, *Macromol. Symp.*, 2000, **151**, 359; c) S. Dong, F.J. Traver, J.F. Warrenchak, US Patent 6,232,396 (2001); d) R.P. Gee, B.M. Wrolson, US Patent 6,235,834 (2001).
- 4 A comprehensive review on the ROP of cyclosiloxanes, including the mechanism involved in (mini)emulsion, can be found here: F. Ganachaud, S. Boileau, 'Siloxane-containing monomers' in *Handbook of Ring Opening Polymerization*, P. Dubois, O. Coulembier, J.-M. Raquez Ed. Wiley-VCH, p. 65-95 (2009).
- 5 See, for instance: D.E. Ganeva, E. Sprong, H. de Bruyn, G.G. Warr, C.H. Such, B.S. Hawzett, *Macromolecules*, 2007, **40**, 6181
- 6 A book has been entirely devoted to this class of surfactants, see : 'Silicones Surfactants' *Surf. Sci. Series*, 1999, **86** (edited by R. Hill).
- 7 R.M. Hill, *Curr. Opin. Coll. Interface Sci.*, 2002, **7**, 255.
- 8 See, for instance : a) J. Jachowicz, M.D. Berthiaume, *J. Coll. Interface Sci.*, 1989, **133**, 118; b) J. Jachowicz, M.D. Berthiaume, *J. Coll. Interface Sci.*, 1991, **141**, 299.
- 9 M. Ferritto, L. Zuchen, W. Schulz, WO 02/083759 (2003).
- 10 H. Chen, Q. Fan, D. Chen, X. Yu, *J. Appl. Polym. Sci.*, 2001, **79**, 295.
- 11 P.Y.K. Lo, M.J. Ziemelis, European Patent 0,267,003 (1988).
- 12 To the best of our knowledge, only one review summarizes the preparation and some basic physicochemical properties of telechelic aminosilicones, see : G. Schmaucks, *Surf. Sci. Series*, 1999, **86**, 65.
- 13 a) R.P. Gee, US Patent 4,620,878 (1986); b) M.Ozaki, I. Ona, US patent 5,073,593 (1991); c) H. Katayam, T. Tagawa, H. Kunedia, *J. Coll. Interface Sci.*, 1992, **153**, 429; d) I. Ona, M. Ozaki, US Patent 5,110,865 (1992); e) J.H. Merrifield, R.J. Thimineur, F.J. Traver, US patent 5,244,598 (1993); f) R.P. Gee, *Colloids Surf. Part A*, 1998, **137**, 91.
- 14 See, e.g.: a) Z.H. Luo, X.L. Zhan, P.Y. Yu, *Chin. Chem. Letters*, 2004, **15**, 1101; b) D. Gräbner, L. Xin, H. Hoffmann, M. Drechsler, O. Schneider, *J. Colloid Interf. Sci.*, 2010, **350**, 516; c) D. Gräbner, L. Xin, H. Hoffmann, M. Dreschsler, O. Schneider, *J. Coll. Interface Sci.*, 2010, **350**, 516.

- 15 S. C. Mehta, P. Somasundaran, *Langmuir*, 2008, **24**, 4558.
- 16 R.M. Hill, S.A. Snow, U.S. Patent 5,235,082 (1993).
- 17 For an excellent review on the field, see : C.F.J. Faul, M. Antonietti, *Adv. Mater.*, 2003, **15**, 673.
- 18 a) E. D. Goddard, *Colloids Surf.*, 19, 255 (1986); b) E. D. Goddard, *Colloids Surf.*, 19, 301 (1986).
- 19 A review presents some striking examples of this: R. Abdel-Rahem, *Adv. Colloid Interf. Sci.*, 2008, **141**, 24.
- 20 Among the most recent papers (including references therein), see : a) S. Karlsson, S. Backlund, R. Friman, *Colloid Polym. Sci.*, 2000, **278**, 8; b) S. Karlsson, R. Frima, M.Bjoerqvist, S. Backlund, *Langmuir*, 2001, **17**, 3573; c) S. Karlsson, R. Friman, B. Lindstroem, S. Backlund, *J. Colloid Interf. Sci.*, 2001, **243**, 241; d) P.C. Hartmann, P. Dieudonné, R.D. Sanderson, *J. Colloid Interf. Sci.*, 2005, **284**, 289.
- 21 A. F. Thünemann, R.H. Kublickas, *J. Mater. Chem.*, 2001, **11**, 381.
- 22 A.C.M. Cuo, “Poly(dimethylsiloxane)” in *Polymer Data Handbook 2<sup>nd</sup> Edition*, Mark, J. E. Ed, Oxford University Press (2009).
- 23 a) W.S. Price, *Concepts In Magnetic Resonance*, 1997, **9**, 299; b) W.S. Price, *NMR Studies of Translational Motion: Principles and Applications*. 1st ed., Cambridge University Press (2009).
- 24 D.V. Fenby, Z.S. Kooner, J.R. Khurma, *Fluid Phase Equilibria*, 1981, **7**, 327.
- 25 M. Reches, E. Gazit, **2004**, *Nano Lett.* **4**, 581.
- 26 L. Adler-Abramovich, N. Kol, I. Yanai, D. Barlam, R.Z. Shneck, E. Gazit, I. Rouso, *Angew. Chem. Int. Ed.*, 2010, **49**, 9939.
- 27 a) W. R. Hargreaves, D. W. Deamer, *Biochemistry*, 1978, **17**, 3759; (b) E.W. Kaler, A.K. Murthy, B.E. Rodriguez, J.A.N. Zasadzinski, *Science*, 1989, **24**, 1371. See also the following reviews: (c) C. Tondre, C. Caillet, *Adv. Coll. Interf. Sci.*, 2001, **93**, 115; (d) E.F. Marques, O. Regev, A. Khan, B. Lindman, *Adv. Coll. Interf. Sci.*, 2003, **100-102**, 83.
- 28 a) Z. Lin, R.M. Hill, H.T. Davis, L.E. Scriven, Y. Talmon, *Langmuir*, 1994, **10**, 1008; b) R.M. Hill, S.A. Snow, US Patent 5364633, 1994; c) A.R. Ekeland, R.M. Hill, Eur. Patent 724876, 1996.
- 29 a) M. Kepczynski, F. Ganachaud, P. Hémerly, *Advanced Materials*, 2004, **16**, 1861; b) M. Kepczynski, J. Lewandowska, M. Romek, S. Zapotoczny, F. Ganachaud, M. Nowakowska, *Langmuir*, 2007, **23**, 7314.

## Graphical abstract



## Highlights

- “Portrait gallery” of soft matter from supramolecular silicone colloidal dispersions.
- Gels, vesicles, and nanoparticles from ionic self-assembly of protonated aminosilicones.
- New concept of “toupée particles”, i.e., which hair can be removed by tuning the pH.

# Supporting information for

## Supramolecular Organization of Protonated Aminosilicones in Water

*By H. Petitjean, P. Guiglion, M. In, J. R. Aldrich-Wright, P. Castignolles, F. Ganachaud\*, M.*

*Gaborieau*

### EXPERIMENTAL PART

#### **Materials**

$\alpha,\omega$ -amino functionalized polydimethylsiloxanes of various molar masses (DMS-A11,  $M_n \approx 900$  g.mol<sup>-1</sup>, DMS-A15,  $M_n \approx 3000$  g.mol<sup>-1</sup>) were purchased from ABCR or directly donated by the Wacker company. Their structure was checked by quantitative <sup>1</sup>H NMR in solution in methanol-d<sub>4</sub> (note that it aggregates in chloroform-d); the number-average number of dimethylsiloxane units -O-Si(CH<sub>3</sub>)<sub>2</sub>-, DP<sub>n</sub>, was typically found to be  $12.73 \pm 0.01$  and  $40.56 \pm 0.03$  per chain for DMS-A11 and DMS-A13, respectively. Monomethylated PEG, trifluoroacetic acid and tosylic acid, all from ACROS, were used without further purification. Dodecylbenzene sulfonic acid (DBSA) was purchased from Janssen (most visual observations, particle size measurements and microscopy) and Aldrich (for NMR studies). Both were used as received. Various solvents used here are of analytical grade and were provided by PROLABO, as well as potassium carbonate. o-sulfobenzoic anhydride (ALDRICH) is 99% purum. Methanol-d<sub>4</sub> was purchased from Aldrich. All water was from MilliQ (Millipore) quality. Absolute ethanol (purity > 99.5%) was from Sigma-Aldrich and used as received.

### Synthesis of o-PEG benzosulfonic acid.

In a beaker (50 mL) monomethylated-PEG (1 g) is homogenised in toluene (20 mL) with stirring. Then potassium carbonate (500 mg, 2 eq. compared to PEG) and o-sulfobenzoic anhydride (368 mg, 1.1 eq. compared to PEG) are added and stirring under reflux for 2 hours. The  $K_2CO_3$  powder, initially insoluble, rapidly disappears whereas the solution rapidly becomes troubled. After solvent is evaporated, the sulfonated PEG is precipitated with dichloromethane (20 mL), filtrated and dried under vacuum. A viscous translucent oil (1.6 g) is dissolved in distilled water (50 mL), dialyzed with a 1000 g.mol<sup>-1</sup> cut membrane with distilled water (4 L). The purified surfactant is acidified with a ion-exchange Amberlite IR120-H<sup>+</sup> resin (2.5 g, 6 eq. of protons) to produce the final product (yield 1.18 g, 61%), again a translucent viscous oil.

<sup>1</sup>H NMR (in D<sub>2</sub>O)  $\delta$  : 8-7,6 (m, 3.2H, aromatic) ; 4,46 (m, 1.22H, CH<sub>2</sub> adjacent to COO) ; 3,85 (m, 1.26H, CH<sub>2</sub> on  $\beta$  position of COO) ; 3,66 (m, 49.4H, CH<sub>2</sub> in PEG) ; 3,34 (s, 3H, CH<sub>3</sub> on the extremity of PEG).

### Methods

Particle size measurements were done by PCS on a Malvern Zeta Sizer 4 apparatus equipped with a helium-neon laser (633 nm) and a thermoregulated cell set at 25°C. Samples to be measured are prepared by diluting 5  $\mu$ L of emulsion in 5 mL of distilled water. The CONTIN autocorrelation function was applied to measure the particle size distribution. Transmission electron microscopy measurements were processed on a JEM100CXII UHR microscope from GEOL, with a 100kV acceleration tension. One drop of the colloidal dispersion was deposited on a carbon-coated grid and allowed to evaporate, without the need for staining or cryopreparation.

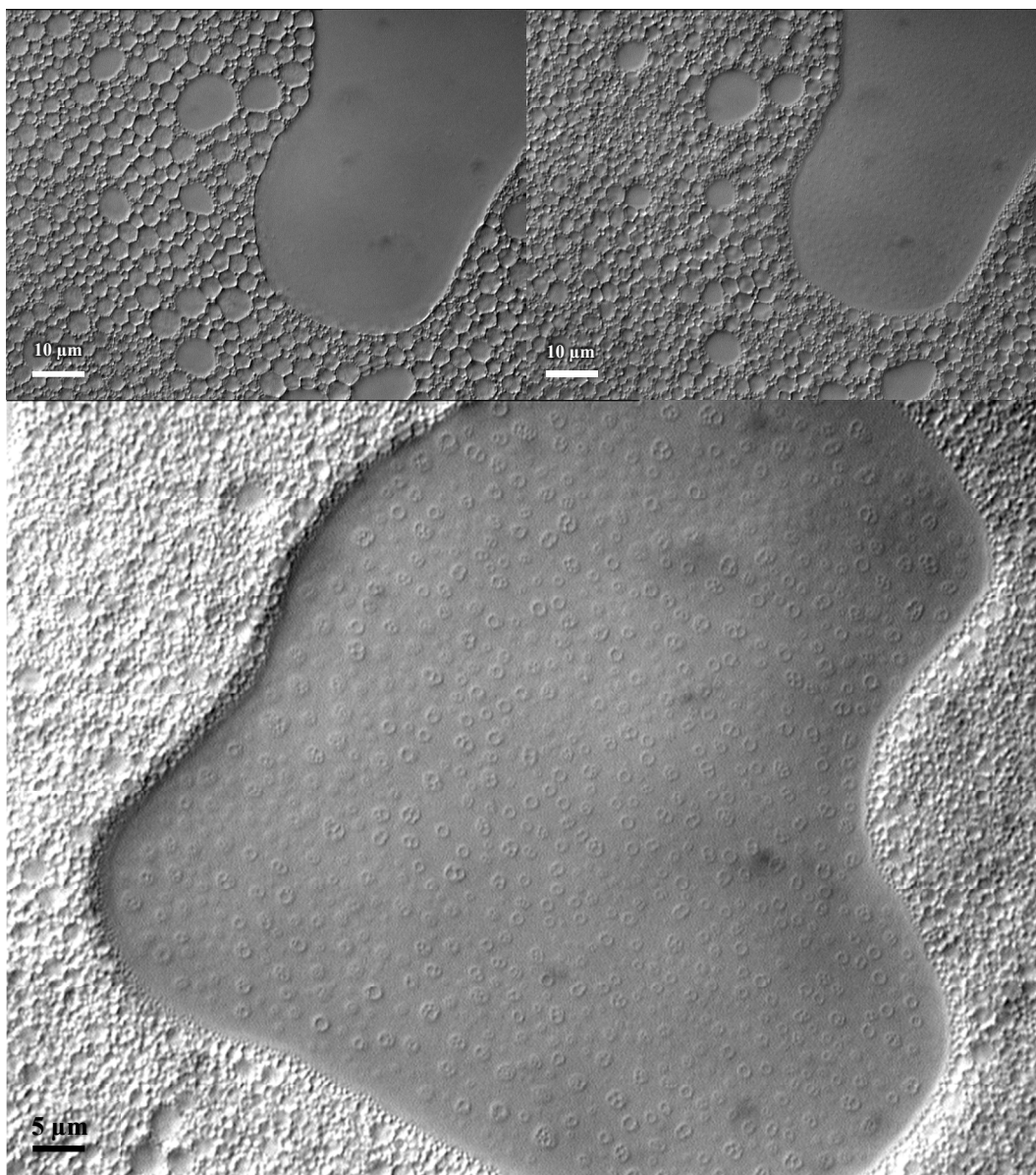
All <sup>1</sup>H diffusion Nuclear Magnetic Resonance (NMR) experiments were performed at exactly 25 °C using a Bruker Avance 400 NMR spectrometer equipped with a 5 mm BBO probe and operating at a Larmor frequency of 400 MHz for <sup>1</sup>H, and with 18  $\mu$ s 90° pulse. A combined duration of acquisition

and relaxation delay of 2 s was sufficient to ensure full relaxation between scans (it was checked with one-dimensional  $T_1$  inversion-recovery experiments). The WATERGATE sequence (water suppression through gradient tailored excitation) was used for solvent (HO) signal suppression, with a 38  $\mu$ s pulse length. For measurements with DBSA, a duration of the applied magnetic field gradient pulse  $\delta$  of 3 ms was used, with a diffusion delay  $\Delta$  of 300 ms, and the gradient strength was increased from 1 % to 99 % of its maximal strength of 55.3 G·cm<sup>-1</sup>, by steps of 2 %. For measurements with tosylic acid, a duration of the applied magnetic field gradient pulse  $\delta$  of 2 ms was used, with a diffusion delay  $\Delta$  of 100 ms, and the gradient strength was increased from 1 % to 44.5 % by steps of 1.5 %. Spectra were recorded with 40 scans for pure acid solutions in water (blanks), with 64 scans for aminosilicones aggregates with tosylic acid, and with 128 scans for aminosilicones aggregates with DBSA. Data acquisition with various diffusion times, phase correction and integration were carried out via Bruker Topspin NMR 1.3 and 2.1 software, the rest of the data processing was done using Origin 8.5.1 software.

For each signal, the attenuation of the signal integral  $A$  with increasing field gradient magnitude  $g$  was fitted using equation (S1) to determine the self-diffusion coefficient  $D$ :<sup>2,3</sup>

$$A = A_0 \exp \left[ -D (\delta \gamma g)^2 \left( \Delta - \frac{\delta}{3} \right) \right] \quad (\text{S1})$$

where  $A_0$  is the peak's surface area without field gradient,  $\delta$  is the duration of the applied magnetic field gradient pulse,  $\gamma$  is the magnetogyric ratio of the measured nucleus (here <sup>1</sup>H),  $g$  is the gradient strength, and  $\Delta$  is the diffusion delay. Self-diffusion coefficients were determined for the aminosilicone signals (Table S1) and for the counter ion signals when using tosylic acid and DBSA (see main text).



**Figure S1:** Phase contrast micrographs of gels obtained with the aminosilicone/acetic acid complex. Two images (top) focused on different plans of the samples show the very large polydispersity of the size of the droplets of water-in-silicone generated here. Zooming on a “water pocket” (bottom), one can specifically observe the small droplets trapped beneath the pool: some shows complex, multivesicle-like shapes.



**Table S1:** Self- diffusion coefficients  $D$  ( $\times 10^{10} \text{ m}^2.\text{s}^{-1}$ ) for the different groups (see scheme 1 in the main text for the assignment of  $T$  and  $P$  groups) of aminosilicone/acetic acid and aminosilicone/tosylic acid complexes prepared at two dilutions in water. The

	<b>Acetic acid</b>		<b>Acetic acid</b>	<b>Tosylic acid</b>	<b>Tosylic acid</b>
	<b>0.1%</b>		<b>1%</b>	<b>0.1%</b>	<b>1%</b>
<b>T'<sub>1</sub></b>	<b>6.80</b>	<b>6.94</b>	<b>6.58</b>	<b>7.54</b>	<b>7.19</b>
<b>T'<sub>2</sub></b>	<b>7.20</b>	<b>7.32</b>	<b>7.08</b>	<b>6.78</b>	<b>7.22</b>
<b>T'<sub>3</sub></b>	<b>7.67</b>	<b>7.63</b>	<b>7.27</b>	<b>9.28</b>	<b>8.28</b>
<b>P<sub>1</sub></b>	<b>7.51</b>	<b>6.82</b>	<b>6.03</b>	<b>5.58</b>	<b>5.24</b>
<b>P<sub>2</sub></b>	<b>-</b>	<b>0.03</b>	<b>0.12</b>	<b>0.03</b>	<b>0.03</b>