Colloid Polym Sci (2009) 287:461–470
DOI 10.1007/s00396-008-1991-y

ORIGINAL CONTRIBUTION

On the feasibility of chemical reactions in the presence of siloxane-based surfactants

Carmen Racles · Maria Cazacu · Gabriela Hitruc · Thierry Hamaide

Received: 22 October 2008 / Accepted: 16 December 2008 / Published online: 23 January 2009

Abstract Siloxane-containing surfactants have been tested as stabilizers for the preparation of polymer nanoparticles by three types of chemical reactions. Two crosslinking reactions were used to obtain silicone elastomers particles: one involved HO-terminated polydimethylsiloxane and tetraethoxysilane, while the other one was a crosslinking via polyhydrosilylation. The third reaction was a linear polycondensation between a diamine and a siloxane dialdehyde. The monitoring of the reactions has been made by infrared spectroscopy and the resulting particles have been analyzed in dispersion by light scattering and in dry state by electron microscopy and atomic force microscopy. The particles size was of hundreds of nanometers and their spherical shape was generally maintained after drying. The spectral and microscopy data proved efficient stabilization, which allowed the reactions to evolve after the formation of the particles.

Keywords Siloxane · Surfactants · Nanoparticles · Crosslinking · Polycondensation

Introduction

In the scientific world, there is an increasing interest for nanotechnologies and, in particular, for the preparation of nanoparticles. This is due to the dramatic change in any material's properties which occurs when it is reduced to nanoscale. Polymer nanoparticles are more and more investigated and one of their most spectacular applications is in the medical field, where they are largely used for encapsulation of drugs [1]. For such a purpose, the polymers have to be biodegradable, biocompatible, or bioresorbable [1–3]. One direction for the preparation of polymer nanoparticles is based on the use of surfactants for their formation and stabilization, in physical processes as well as in chemical reactions. Another approach is based on self-assembling of block copolymers in selective solvents, when polymeric micelles are formed. The resulting nanoparticles are used in bionanotechnology as drug carriers for anticancer drugs, nonviral gene vectors, bioreactors, and diagnostic tools [4]. Crosslinking of the core or corona stabilize the micelle structure and thus further extends the possibilities for functional materials [5–9].

Polysiloxanes are nontoxic materials, with physiological inertness [10], and have many medical applications [11–13]. On the other hand, they have a rare combination of properties that makes them unique: they are hydrophobic and soluble in nonpolar solvents; they have very high chain flexibility; very low T_g; low cohesive energy; and very low surface tension, good thermal stability, and resistance to UV radiations and to ozone. These properties have been exploited for a long time already, and silicone-based materials are present in our lives in many forms, from sealants and foam stabilizers to coatings, adhesives, cosmetic additives, medical devices, and implants. They would probably be good candidates for applications like the encapsulation of

C. Racles (✉) · M. Cazacu · G. Hitruc
"Petru Poni" Institute of Macromolecular Chemistry,
Aleea Gr. Ghica Voda 41A,
Iasi 700487, Romania
e-mail: raclesc@icmpp.ro

T. Hamaide
LMPB–IMP, Université de Lyon,
15, Boulevard Latarjet,
69622 Villeurbanne Cedex, France

hydrophobic drugs into nanoparticles, but their liquid state at room temperature could be a drawback for their colloidal stability. Some of our experiments showed that polydimethylsiloxane (PDMS) nanoparticles obtained by nanoprecipitation collapse after drying, although they may show a relative stability in water dispersion [14]. This behavior may lead, for example, to hydrophobic coatings obtained from waterborne formulations. But for other applications, silicone particles with better stability may be requested. The applicative potential of polysiloxanes and the increasing environment concerns motivate us to find new ways or formulas to manipulate them in water.

The preparation of PDMS latexes by cationic and anionic polymerizations of cyclosiloxane in emulsion have been known for a long time in industry and, more recently, the miniemulsion, microemulsion, and suspension polymerization have also been investigated [15]. The synthesis of colloidal silicone resins has been reported extensively, due to their applications in industry and to their interesting and complex morphology ([15, 16] and references therein). For example, poly(organosiloxane) nanospheres with different morphologies and amphiphilicities have been synthesized by sequential condensation of tri- and difunctional silanes, in aqueous dispersion in the presence of surfactant [17]. Hollow silicone resin particles of controlled diameter have been synthesized using catanionic vesicles as templates for the polycondensation/polymerization processes of 1,3,5,7-tetramethylcyclotetrasiloxane within their membranes [18]. Thiol-functionalized organosilica microspheres were synthesized by a surfactant-free emulsion-based method [19].

Our approach in this study is based on the principles of nanoprecipitation. This process was described for the first time by Fessi et al.; they showed that the use of only one solvent with unlimited water miscibility (acetone, ethanol, or tetrahydrofuran (THF)) can lead to the spontaneous formation of nanoparticulate pseudolatex dispersions [20–22]. In nanoprecipitation, the polymer solution, which possibly also contains other additives, is mixed with the aqueous protective colloid solution. An important requirement for particle formation is that the resulting water/solvent mixture is nonsolubilizing for the polymer [23].

Since the core polymers have polysiloxane backbone, the use of siloxane-containing surfactants as particles stabilizers seemed the best choice, in order to increase the compatibility. We have previously reported on some new surfactants and their ability to stabilize different polymeric nanoparticles [14, 24]. Siloxane-based surfactants usually have the ability to substantially lower the water surface tension, even when used in very small amounts, and they proved their efficiency in many applications [9, 25–30].

Three chemical reactions have been chosen for this investigation, based on the properties of the resulting materials. Two of them are crosslinking reactions, since one way to increase the nanoparticles stability is to crosslink the core. The third one is a linear polycondensation, which yields a polyazomethine with positive T_g [31], since the thermomechanical properties of the polymer cores play an important role for the stability of the nanoparticles [14, 32]. Besides considering the feasibility of such reactions in the presence of siloxane surfactants, the resulting materials may exhibit interesting applicative potential. For example, different materials, like magnetic nanopowders, liquid crystals, or drugs, can be encapsulated in the silicone elastomers particles, in a one-step process. Also, such particles—including liquid crystalline (LC) polymers like the polyazomethine taken as an example—can serve as disperse phase in nanocomposites. Our preliminary tests showed encouraging results.

Here, we report our first results on the feasibility of these reactions inside the surfactants aggregates, in dilute aqueous solutions and very mild conditions. More detailed investigations on the morphology, properties, and possible applications of the resulted particles are in progress.

Experimental

Materials

Tetraethoxysilane (TEOS), divinyltetramethyldisiloxane (DV), octamethylcyclotetrasiloxane (D4), tetramethylcyclotetrasiloxane ($D4^H$), dibutyltin dilaurate (DBTDL), platinum divinyltetramethyldisiloxane complex (Pt(dvs)) solution in xylenes, *p*-phenylenediamine, THF, and ethyl alcohol were high purity commercial products and were used as such. The tested surfactants (S1–S3) were obtained by us, and their critical micelle concentration (CMC) and equilibrium surface tension (γ) were determined by tensiometry. Pentamethylsebacomethyldisiloxane potassium salt (S1) has been obtained according to [14]: CMC=0.087 g/l and γ=39.6 mN/m. Pentamethylpenta(propyloxyethylene-glucoside) cyclosiloxane (S2) has been synthesized following the method described in [14] for similar cyclotetrasiloxanes: CMC=0.134 g/l and γ=37.1 mN/m. Bis[3-(trihydroxymethylene-methane-amino)-2-hydroxypropylene-oxypropylene]-1,3-disiloxane (S3) was obtained by reacting bis-glycidoxipropyl tetramethyl disiloxane with trihydroxymethylaminomethane: CMC=0.127 g/l and γ=28.6 mN/m. Details will be given in a forthcoming paper.

OH-terminated polydimethylsiloxane with average Mn of 40,000 has been obtained by cation exchange catalyzed ring-opening polymerization of D4, according to [33]. Dimethyl–methylhydrogen siloxane copolymer (PHMS) with 30% D^H units has been prepared by cationic copolymerization of D4 and $D4^H$, following the procedure described in [24]. Bis(formyl-*p*-phenoxymethyl)disiloxane (SDA) has been synthesized as described in [31].

Methods

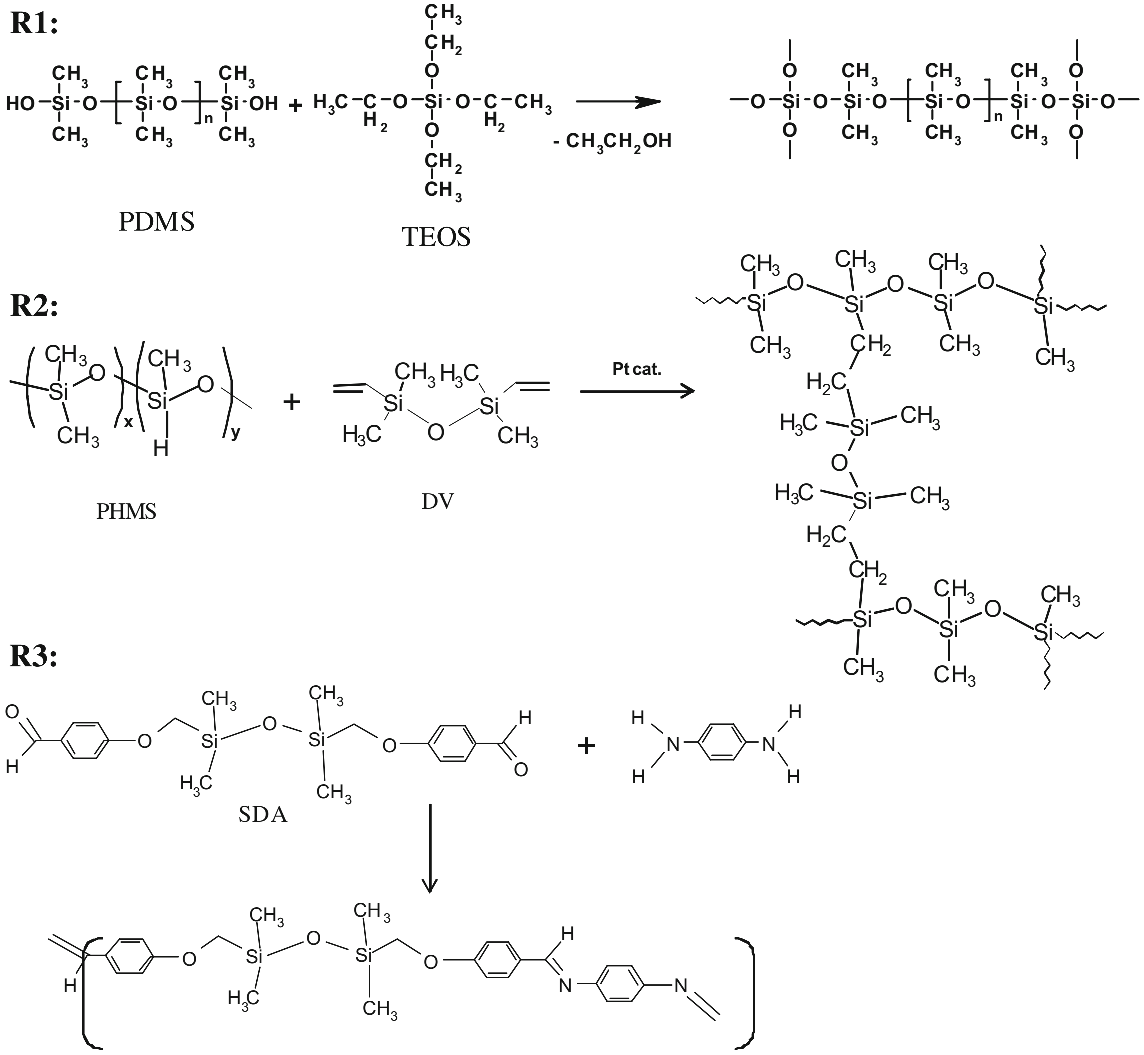
Surface tensions and critical micelle concentration were measured with an automatic tensiometer, Sigma700 from KSV, using the Wilhelmy plate method, adequate software, and external dosing for CMC detection. The infrared (IR) spectra were registered on a Bruker Vertex 70 FT-IR instrument, in transmission mode, in the 300–4,000 cm^{-1} range (resolution 2 cm^{-1}, 32 scans), at ambient temperature.

Transmission electron microscopy (TEM) observations, scanning electron microscopy (SEM), atomic force microscopy (AFM) measurements; were made on TESLA BS 513A transmission electron microscope, at an acceleration tension of 80 kV. The samples were prepared on copper grids of 200 mesh size, coated with a collodium film and carbon; microdrops of the concentrated dispersions were placed on the grids, then the water was removed in saturated atmosphere, and the samples were vacuum dried.

Scanning electron microscope (SEM) observations were made on a TESLA BS 301 microscope operating at 15 kV, with secondary electrons. The samples were deposed on glass slides, which were fixed on copper supports, then covered with a thin layer of carbon-gold.

The atomic force microscope (AFM) measurements were made on a Solver Pro-M platform (NT-MDT, Russia), in semicontact mode. Drops of the particles dispersion were placed on glass slides and slowly dried at room temperature.

Particles size and distribution were determined by dynamic light scattering (DLS) on a Malvern Zetasizer NS (Malvern Instruments, UK). The concentrated dispersions of nanoparticles were measured without further dilution and multimodal analysis mode (CONTIN analysis) was used for size distribution by intensity.



Scheme 1 Three model reactions: *R1* crosslinking of OH-terminated PDMS, *R2* crosslinking of dimethyl–methylhydrogen siloxane copolymer, and *R3* linear polycondensation

Crosslinking of OH-terminated PDMS (R1)

In a typical example, 10 ml of a 1% THF solution containing PDMS and TEOS 5/1 by weight was prepared and stored for 1 day. Then two microdrops of DBTDL were added and the solution was injected via a syringe into 20 ml of 1 g/l aqueous solution of surfactant, under mild stirring, at room temperature. After 15 min, the stirring was stopped for another 30 min, then the THF and an amount of water were removed on rotatory evaporator. The resulting water dispersions containing approximately 3% silicone particles were stored at 4 °C.

Crosslinking of dimethyl–methylhydrogen siloxane copolymer (R2)

PHMS (0.11 g) and DV (0.03 g) were dissolved in 13 ml of THF. One microdrop of Pt(dvs) catalyst was added and the solution was immediately injected into 25 ml of a 1 g/l aqueous solution of S1, under mild stirring. The mixture was heated at 45 °C for 1 h, then the solvent was distilled as described above.

Linear polycondensation (R3)

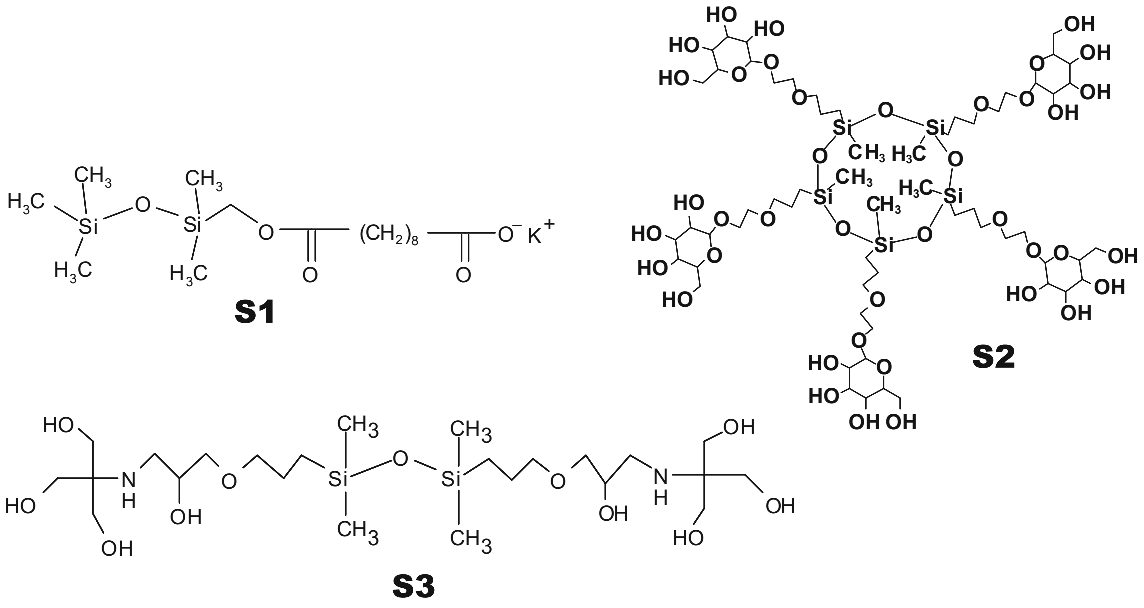
SDA and *p*-phenylene diamine, 0.0252 and 0.0068 g, respectively, were dissolved in 3 ml absolute ethanol, prior to injection into 6 ml aqueous solution of S1 (1 g/l). The resulted nanodispersion was processed as in example R1.

Results and discussion

We have chosen three model reactions (Scheme 1, R1–R3) and carried them out following in general terms the principles of nanoprecipitation. In each case, the organic solvent is miscible with water and has a lower boiling point than water. The reagents solution was injected under pressure in an aqueous solution of a siloxane-based surfactant, then the organic solvent was stripped off by vacuum distillation. The remaining water dispersion was stored for months in the refrigerator and no deposit was observed.

An anionic low molar mass surfactant was used for all the reactions, while for R1 two siloxane-based nonionic surfactants (Scheme 2) were also tested. In all cases, the same concentration of surfactant solutions was used (1 g/l) that is higher than their measured CMC. We chose an unique testing concentration in this stage, in order to compare the results in terms of “formulation” efficiency.

The results of our previous attempts to prepare polymer nanoparticles by nanoprecipitation [14, 24] showed that for the same surfactant and experimental parameters, there are differences in the size and size distribution from one polymer to another, and especially the stability after drying (estimated by electron microscopy) was greatly influenced by the thermomechanical properties of the polymer core. For example, well-defined spherical nanoparticles were obtained from polysulfone (polymer with high T_g), a tendency of agglomeration was observed for polycaprolactone (negative T_g, but positive T_m), while the PDMS



Scheme 2 The tested surfactants: *S1* pentamethylsebacomethyldisiloxane potassium salt, *S2* pentamethylpenta(propyloxyethylene-glucoside) cyclosiloxane, and *S3* Bis[3-(trihydroxymethylenemethane-amino)-2-hydroxypropylene-oxypropylene]-1,3-disiloxane

nanoparticles (both T_g and T_m negative) collapsed. Nevertheless, due to the valuable properties of PDMS, which are preserved after crosslinking, we are trying to obtain stable nanoparticles with silicone elastomer as the core.

In this purpose, we first tested reaction R1 in the presence of surfactant S1. This reaction have previously been studied in bulk, aiming to obtain siloxane–silica nanocomposites with improved optical and mechanical properties, due to in situ generation of silica [33]. Here, we have chosen a different ratio of the reagents, in order to avoid excessive reinforcing with silica, and we did not use a catalyst in the first experiments, in order to slow down the reaction for kinetics investigations. In the crosslinking process, there are two types of reactions going on: the hydrolysis of TEOS and the polycondensation of the resulted –OH groups with those from PDMS extremities, as well as between them [34, 35].

It is worth mentioning that, as expected, no particles what so ever are formed when the THF solution of PDMS/TEOS is poured into pure water. In this case, a massive (“macro”-) precipitation occurs, due to the extremely nonpolar nature of the high molecular weight PDMS.

In the presence of surfactants, a turbidity appears instantaneously, when the miscible organic and aqueous phases are mixed and no “macro”-precipitation was observed during the process, but only the opalescence characteristic to nanoparticles dispersion. The surface tension of the nanoparticles dispersion was practically equal to that of the surfactant solution, which means that no additional PDMS was present at the surface, as it should have if the polymer was not encapsulated, and also that the amount of surfactant was enough to maintain the saturated surface monolayer. These aspects show in essence the effectiveness of the surfactant in stabilization of the colloidal dispersion.

On the other hand, we investigated the reaction evolution in three different media: in water, in air, and in surfactant solution, knowing that water plays an important role in the reaction, for the hydrolysis of TEOS [36]. For each of these cases, the reagents mixture was prepared in THF and either added into distilled water, or stored in an open vessel, or injected to the surfactant solution. The organic solvent was removed, then aliquots were assayed and dried prior to IR analysis.

In the IR spectra, we followed the change in the intensity of the band at 865 cm^{-1}, assigned to Si–OH group [37], considering as reference the Si–CH_3 band at 1,260 cm^{-1}. In this way, we observed that the most rapid reaction occurred in water, while the slowest was in the surfactant solution (Fig. 1a). This means that the reagents were protected from water by the adsorbed surfactant molecules. Otherwise, we should have observed the same reaction kinetics in the stabilized systems as in pure water. In normal conditions, the sol–gel reaction is viewed as a two-step network-forming polymerization process. In the first step, silicon alkoxide is hydrolyzed to generate intermediary species of silicon hydroxide. Then, the species undergo a stepwise polycondensation reaction to form a three-dimensional network [36, 38, 39]. However, it is known that, once the hydrolysis begins, the condensation reactions simultaneously occur. As Si–OH group’s content decreases, the probability to self-condense also decreases due to the molecular movements restrictions imposed by the network structure on the one hand and to the diffusion importance increasing on the other hand [36]. These have as an effect the limitation of the Si–OH groups’ consumption.

In all our cases, the curves obtained from the IR spectra show a decrease of the OH absorption, followed by a plateau. Based on the established mechanism of this reaction [36, 38, 39] and on our results, we may assume that the process—i.e., mainly hydrolysis—starts in the reagents solution, in the presence of traces of water (a “sol” state), then, after the removal of the organic solvent, the reagents continue to react in bulk (forming the “gel” state), where

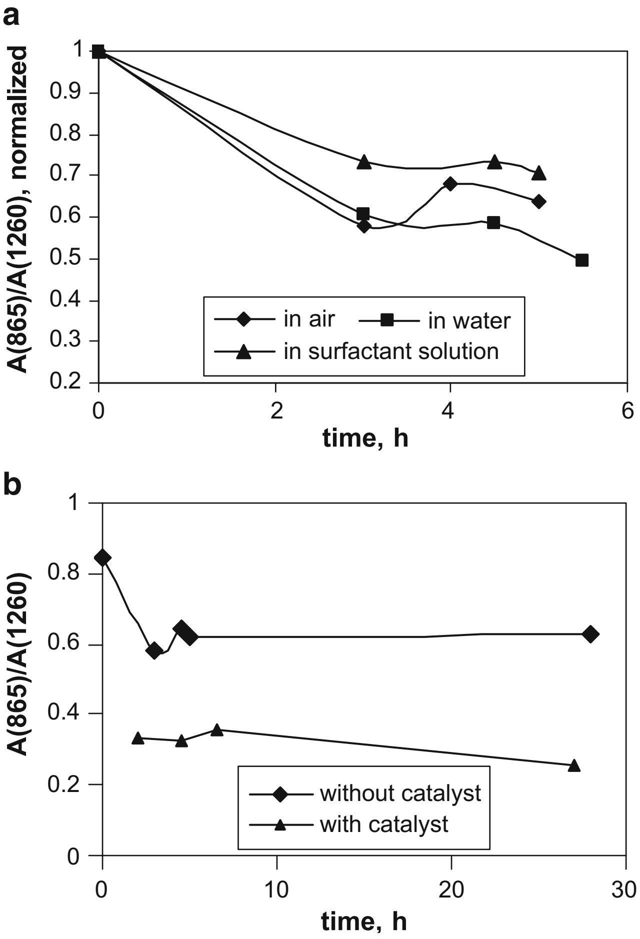


Fig. 1 The variation of the absorption band at 865 cm^{-1} in reaction R1: **a** in three media (normalized values); **b** in nanoparticles, with and without catalyst

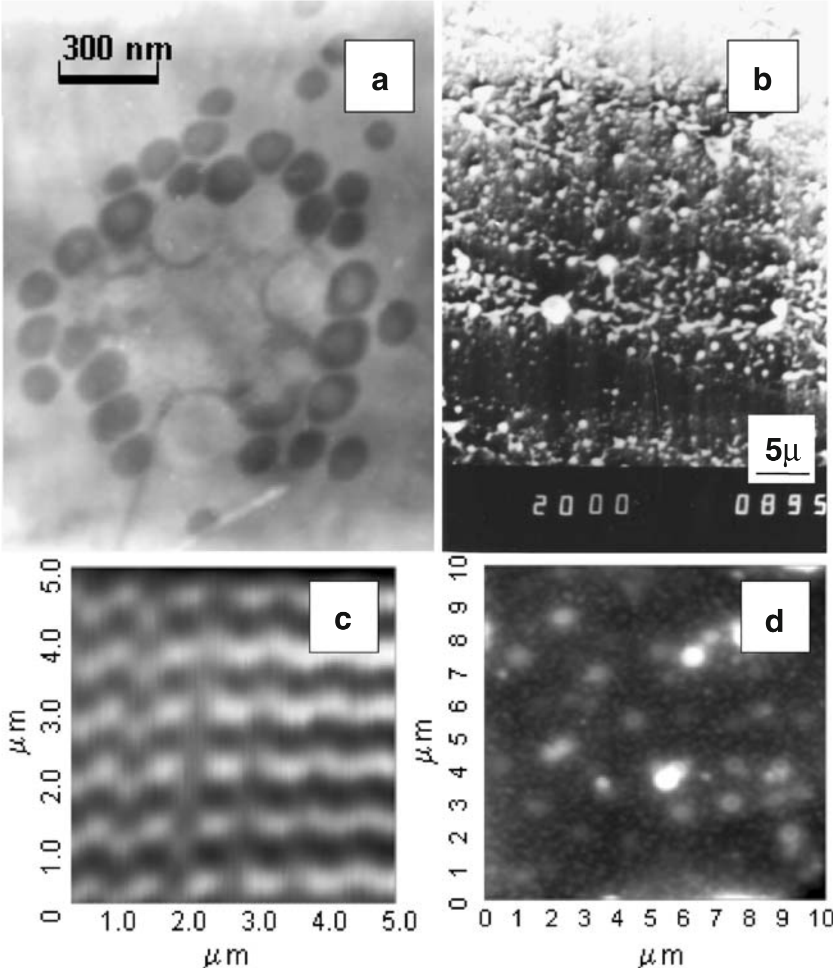


Fig. 2 Silicone elastomer particles resulted in reaction R1, in different conditions: **a** with surfactant S1, without catalyst (TEM image); **b** with surfactant S1 and DBTDL catalyst (SEM image); **c** with surfactant S1 and catalyst (AFM image); and **d** with surfactant S2 and catalyst (AFM)

the condensation predominates, till the process significantly slows down, due to drastic decrease of the system mobility. This is a complex process and is out of our purpose to discuss it in detail here. The reason for showing these results is to demonstrate that the reaction goes on after the formation of the particles (since the particles form in the first fractions of a second after the mixing) and that its kinetics is different in the stabilized particles than in pure water or in the atmosphere. In other words, even if the reaction started before the phase mixing, it continues in the formed particles. The DBTDL catalyst speeds up the reaction, as can be observed in Fig. 1b.

The obtained particles preserved their spherical shape after drying, due to crosslinking, unlike in the case of the linear PDMS that we have previously observed [14], although this is still a soft material (T_g around −120 °C) [33]. In Fig. 2, representative microscopy images were collected.

In TEM, particles around 200 nm were observed for the weakly crosslinked PDMS—reaction without catalyst (Fig. 2a)—which is in agreement with the DLS measurements (Table 1). Coalescence occurred at some degree, after a long time of storage. The particles obtained with DBTDL as catalyst were larger, as measured by DLS and observed by SEM and AFM (Fig. 2b, c). This result may be due to the fact that the condensation starts in solution and advances much faster before the injection into the surfactant solution.

Table 1 DLS results for the three tested reactions

Reaction	Surfactant	Z_{ave} (nm)[a]	PDI
R1 without catalyst	S1	235	0.302
R1 without catalyst, after 6 months	S1	362	0.327
R1 with catalyst	S1	536	0.305
R1 with catalyst	S2	552	0.486
R1 with catalyst	S3	385	0.380
R2	S1	239	0.316
R3	S1	169	0.207

PDI polydispersity index

[a] Average diameter, by intensity

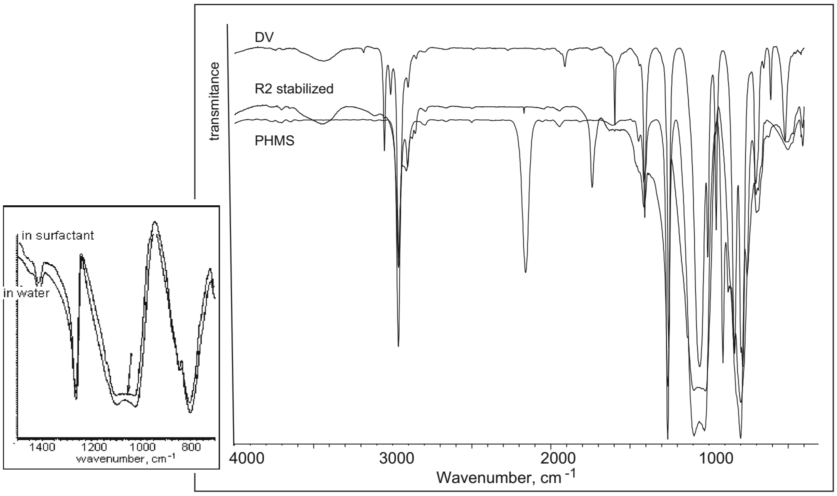


Fig. 3 IR spectrum of the cross-linked polysiloxane (reaction R2), in comparison with the starting reagents; *detail*: the same reaction in water and in surfactant solution

The particles obtained with surfactant S2 showed a tendency to agglomerate (Fig. 2d), probably due to the strong intermolecular bonds that may form between the numerous OH groups of the carbohydrate-containing surfactant molecules. This explains the DLS result, which was obtained on undiluted sample. In the case of S1, a rather compact arrangement of particles have been observed, although some difficulties were encountered in obtaining good AFM images in semicontact mode (Fig. 2c).

The second reaction that we investigated is a polyhydrosilylation, occurring in the presence of a Pt catalyst. The crosslinking reaction was confirmed by IR spectroscopy. After 1 h, the disappearance of both reagents absorption bands, at 2,160 cm^{-1} (Si–H) and 3,050, 1,596, 1,008, and 955 cm^{-1} ($CH = CH_2$) was observed. Besides the usual polysiloxane bands at 1,022 and 1,095 cm^{-1}, an additional one at 1,048 cm^{-1} was observed in the particles spectrum; this band could be assigned to the ethylene–disiloxane bridge between the polysiloxane chains [40]. The IR spectra of the resulting material and the starting reagents are shown in Fig. 3. Further verifications confirmed that the system behaves differently in surfactant solution than in pure water. The same reaction mixture was poured into water, then the solvents were removed in the same conditions and the resulting material was analyzed by IR spectroscopy. In this case, no additional peak was observed between the two bands characteristic to polysiloxane bonds, while the reagents characteristic bands disappeared and the polysiloxane region (at 1,000–1,100 cm^{-1}) was broader (detail in Fig. 3). The most likely explanation is that the Si–H groups hydrolyzed and subsequently autocondensed, while the unreacted divinyldisiloxane was removed in the drying process (this aspect was verified separately). So, based on the available information, we may assume that, in the presence of surfactant, the reaction occurs as shown in Scheme 1, the reagents being thus protected from water. An AFM image of the obtained particles is presented in Fig. 4a, exhibiting small particles, as well as larger aggregates.

Both these reactions allow the tailoring of the cross-linking density by proper choice of the functional polysiloxane (polysiloxane chain length or copolymer composition, respectively). Also, by using different siloxane surfactants, the resulted particles have differently functionalized shells. The particles concentrated dispersions resulted in both R1 and R2 were stable in time, as can be observed in the picture taken after 3 months of storage (Fig. 4b).

In the case of silicone elastomers, due to the soft nature of the materials, we encountered some difficulties in their characterization, especially related to the shape preservation during microscopy observations. In order to further test the feasibility of chemical reactions in the presence of a siloxane surfactant and also to verify the observation that the thermomechanical properties of the polymer strongly influence the shape stability of the particles, we chose as a

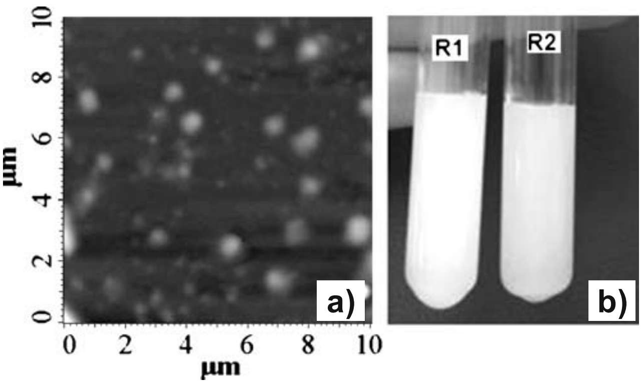


Fig. 4 a Nanoparticles obtained in reaction R2—AFM image; **b** concentrated water dispersions of silicone elastomers resulted in reactions R1 and R2, after 3 months of storage

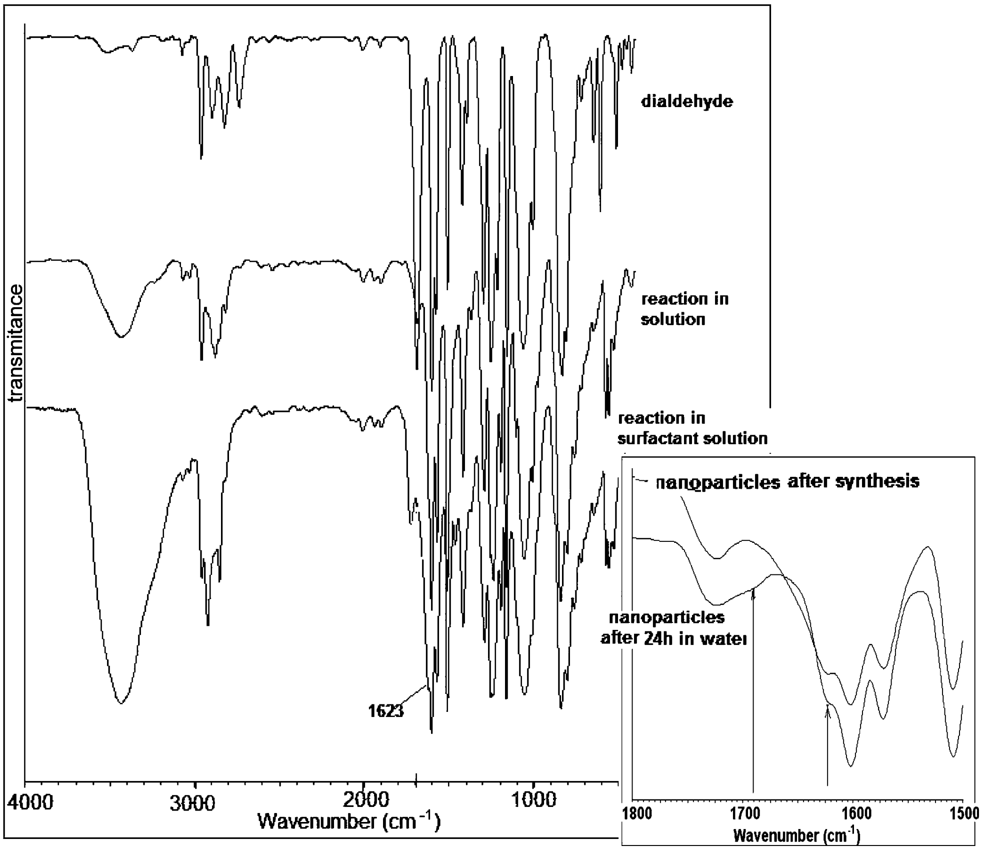


Fig. 5 IR spectrum of the starting dialdehyde and the polyazomethine obtained in surfactant solution and in organic (ethanol) solution; *insert*: effect of water on washed nanoparticles

model reaction a linear polycondensation, involving a siloxane dialdehyde and *p*-phenylenediamine. This reaction has previously been described [31] and the resulted polyazomethine had a T_g of 60 °C and showed thermotropic LC behavior between 140 °C and 195 °C. In the original method, the polymer precipitates from ethanol within a few minutes, so in the nanoprecipitation process, we injected the organic solution just after reagents mixing, in order to avoid premature polymer separation and to ensure that the reaction occurs in the particles.

The reaction product has been analyzed by IR spectroscopy, in comparison with the starting dialdehyde and the similar polymer prepared in solution. As can be observed in Fig. 5, the azomethine bond (absorption band at 1,623 cm^{-1}) was present in the spectrum of the formed nanoparticles, while the aldehyde band at 1,690 cm^{-1} disappeared completely. Here too, water plays a role in the reaction, since it is the by-product in the polycondensation. Interestingly, in the "solution" version, the aldehyde band was still present, although diminished, which means

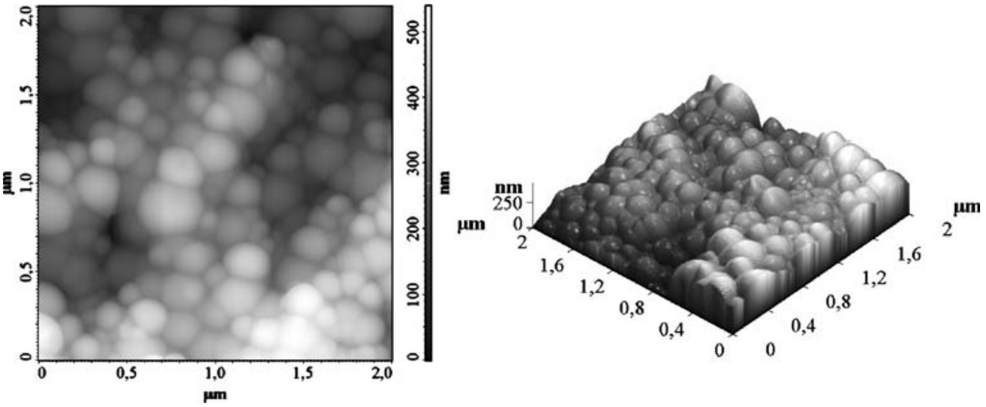


Fig. 6 AFM images of the polyazomethine nanoparticles

that the reaction equilibrium was established to a lower conversion, due to the involvement of the resulted water, while in the presence of the surfactant, the reaction advanced to a higher conversion.

In a subsequent experiment, both the nanoparticles and the polymer obtained by solution polycondensation were washed and incubated into water for 24 h, then the IR spectra were registered again. Partial cleavage of the azomethine bond was observed in both cases, since aldehyde band at 1,690 cm^{-1} reappeared (insert in Fig. 5) or increased, respectively (not shown). This confirms that the azomethine bond is sensitive to water and that in the stabilized nanoparticles, the polymer was protected from water. The AFM image (Fig. 6) shows well-individualized nanoparticles, with perfect spherical shape and no additional crystalline material outside them, thus proving again that the reaction occurred only in the stabilized particles.

The DLS data for particles size (Z_{ave}—average diameter, by intensity) and size distribution are summarized in Table 1. As can be observed, the best results, i.e., the smallest particles size and polydispersity, were obtained for the linear polycondensation, although in the other cases, the particles core is crosslinked; this is probably a consequence of the thermomechanical properties of the core material. Submicronic particles were obtained in all cases when a siloxane surfactant was used. The polydispersity index was rather high, which could be partly explained by that undiluted samples were analyzed and the integration was done in multimodal analysis. As mentioned before, a tendency of agglomeration was observed by microscopy techniques, which explains the large average diameter and polydispersity values. On the other hand, the smallest particles were larger than the surfactants micelle size. A similar result has been reported in the case of crosslinked polysiloxane particles obtained by polymerization of silane monomers in surfactants liquid crystalline phase [41]. Although the shape of the particles reported in this paper reflected the mesophase order, their size was three orders of magnitude higher than the characteristic size of the surfactant mesophase.

It is known that the particles size depends on many factors [23] and probably smaller particles and better size distributions could be obtained in our case, too, by modifying different parameters like, for example, concentration or solvent/water ratio. This remains to be investigated in the near future.

Conclusions

Three reactions have been tested in the presence of siloxane-containing surfactants, in order to obtain silicone elastomers or polyazomethine nanoparticles. These examples show that polymer nanoparticles can be obtained directly from the reagents mixture, by one step, very easy processes. Siloxane-containing surfactants proved to be useful for such procedure, since they provide good stabilization of the particles, allowing the reactions to occur without the involvement of environmental water.

Based on the IR investigations and on microscopy results, we may assume for all the studied reactions that, even if they start in the organic phase, they continue in the formed particles. In fact, the processes are going on in bulk but reduced at submicronic scale; in other words, they occur in micro-/nanoreactors.

Acknowledgments The financial support provided by the Romanian Ministry of Education and Research under grants: Idei_233 no. 5/2007 and Bilateral Franco-Romanian Program Brancusi (14760TM) is gratefully acknowledged. We also thank Dr. Aurelia Ioanid and Dr. Loredana Nita for the electron microscopy observations and DLS measurements.

References

1. Kabanov AV, Batrakova EV, Alakhov VYu (2002) Pluronic® block copolymers as novel polymer therapeutics for drug and gene delivery. J Control Release 82:189–212
2. Pfeifer BA, Burdick JA, Langer R (2005) Formulation and surface modification of poly(ester-anhydride) micro- and nanospheres. Biomaterials 26:117–124
3. Sanchez A, Tobio M, Gonzales L, Fabra A, Alonso MJ (2003) Biodegradable micro- and nanoparticles as long-term delivery vehicles for interferon-alpha. Eur J Pharm Sci 18:221–229
4. Harada A, Kataoka K (2006) Supramolecular assemblies of block copolymers in aqueous media as nanocontainers relevant to biological applications. Prog Polym Sci 31:949–982
5. Henselwood F, Liu G (1997) Water-soluble nanospheres of poly(2-cinnamoylethyl methacrylate)-block-poly(acrylic acid). Macromolecules 30:488–493
6. Guo A, Liu G, Tao J (1996) Star polymers and nanospheres from crosslinkable diblock copolymers. Macromolecules 29:2487–2493
7. Iijima M, Nagasaki Y, Okada T, Kato M, Kataoka K (1999) Core-polymerized reactive micelles from heterotelechelic amphiphilic block copolymers. Macromolecules 32:1140–1146
8. Nardin C, Thoeni S, Widmer J, Winterhalter M, Meier W (2000) Nanoreactors based on polymerized ABA triblock copolymer vesicles. Chem Commun 15:1433–1434
9. Nardin C, Widmer J, Winterhalter M, Meier W (2001) Amphiphilic block copolymer nanocontainers as bioreactors. Eur Phys J E 4:403–410
10. European Center for Ecotoxicology and Toxicology of Chemicals (1994) Joint assessment of commodity chemicals no. 26. European Center for Ecotoxicology and Toxicology of Chemicals, Brussels
11. Krikeldorf HR (1996) Silicon in polymer synthesis. Springer, New York

12. Angelova N, Hunkeler D (1999) Rationalizing the design of polymeric biomaterials. Trends Biotech 17:409–421
13. Zhou CJ, Guan RF, Feng SYu (2004) The preparation of a new polysiloxane copolymer with glucosylthioureylene groups on the side chains. Eur Polym J 40:165–170
14. Racles C, Hamaide T, Ioanid A (2006) Siloxane surfactants in polymer nanoparticles formulation. Appl Organomet Chem 20:235–345
15. Charleux B, Ganachaud F (2007) Precise synthesis, materials properties and applications. In: Matyjaszewski K, Gnanou Y, Leibler L (eds) Macromolecular engineering, chapter 14. Wiley, Weinheim, Germany, pp 1307–1339
16. Longuet C, Joly-Duhamel C, Ganachaud F (2007) Copolycondensation of regular functional silane and siloxane in aqueous emulsion using B(C_6F_5)3 as a catalyst. Macromol Chem Phys 208:1883–1892
17. Jungmann N, Schmidt M, Maskos M, Weis J, Ebenhoch J (2002) Synthesis of amphiphilic poly(organosiloxane) nanospheres with different core–shell architectures. Macromolecules 35:6851–6857
18. Kepczynski M, Lewandowska J, Romek M, Zapotoczny S, Ganachaud F, Nowakowska M (2007) Silicone nanocapsules templated inside the membranes of catanionic vesicles. Langmuir 23:7314–7320
19. Miller CR, Vogel R, Surawski PPT, Jack KS, Corrie SR, Trau M (2005) Functionalized organosilica microspheres via a novel emulsion-based route. Langmuir 21:9733–9740
20. Fessi H, Puisieux F, Devissaguet JPh, Ammoury N, Benita S (1989) Nanocapsule formation by interfacial polymer deposition following solvent displacement. Int J Pharm 55:R1–R4
21. Stainmesse S, Orecchioni AM, Nakache E, Puisieux F, Fessi H (1995) Formation and stabilization of a biodegradable polymeric colloidal suspension of nanoparticles. Colloid Polym Sci 273:505–511
22. Quintanar-Guerrero D, Allemann E, Fessi H, Doelker E (1998) Preparation techniques and mechanisms of formation of biodegradable nanoparticles from preformed polymers. Drug Dev Ind Pharm 24:1113–1128
23. Horn D, Rieger J (2001) Organic nanoparticles in the aqueous phase—theory, experiment, and use. Angew Chem Int Ed 40:4330–4361
24. Racles C, Hamaide T (2005) Synthesis and characterization of water soluble saccharide functionalized polysiloxanes and their use as polymer surfactants for the stabilization of polycaprolactone nanoparticles. Macromol Chem Phys 206:1757–1768
25. Nardin C, Meier W (2002) Hybrid materials from amphiphilic block copolymers and membrane proteins. Rev Mol Biotechnol 90:17–26
26. Chambon P, Cloutet E, Cramail H, Tassaing T, Besnard M (2005) Synthesis of core–shell polyurethane–polydimethylsiloxane particles in cyclohexane and in supercritical carbon dioxide used as dispersant media: a comparative investigation. Polymer 46:1057–1066
27. Nardin C, Hirt T, Leakel J, Meier W (2000) Polymerized ABA triblock copolymer vesicles. Langmuir 16:1035–1041
28. Nardin C, Meier W (2001) Polymerizable amphiphilic block copolymers: from nanostructured hydrogels to nanoreactors and ultrathin films. Chimia 55:142–146
29. Wang A, Jiang L, Mao G, Liu Y (2001) Direct force measurement of comb silicone surfactants in alcoholic media by atomic force microscopy. J Colloid Interface Sci 242:337–345
30. Hill RM (ed) (1999) Silicone surfactants. Surfactant Science Series 86. Dekker, New York
31. Racles C, Cozan V, Sajo I (2007) Influence of chemical structure on processing and thermotropic properties of poly(siloxane-azomethine)s. High Perform Polym 19:541–552
32. Eerikäinen H, Peltonen L, Raula J, Hirvonen J, Kauppinen EI (2004) Nanoparticles containing ketoprofen and acrylic polymers prepared by an aerosol flow reactor method. AAPS PharmSciTech 5(4):e68 http://www.aapspharmscitech.org
33. Alexandru M, Cristea M, Cazacu M, Ioanid A, Simionescu BC (2008) Composite materials based on polydimethylsiloxane and in situ generated silica by using the sol–gel technique. Polym Compos. doi:10.1002/pc.20608
34. Sun CC, Mark JE (1989) Comparisons among the reinforcing effects provided by various silica-based fillers in a siloxane elastomer. Polymer 30:104–106
35. Mark JE, Pan SJ (1982) Reinforcement of polydimethylsiloxane networks by in-situ precipitation of silica: a new method for preparation of filled elastomers. Macromol Rapid Commun 3:681–685
36. Huang HH, Orler B, Wilkes GL (1987) Structure–property behavior of new hybrid materials incorporating oligomeric species into sol–gel glasses. 3. Effect of acid content, tetraethoxysilane content, and molecular weight of poly(dimethylsi1oxane). Macromolecules 20:1322–1330
37. Pretsch E, Clerc T, Seibl J, Simon W (eds) (1989) Tables of spectral data for structure determination of organic compounds, 2nd edn. Springer, New York
38. Tamaki R, Chujo Y (1998) Synthesis of IPN polymer hybrids of polystyrene gel and silica gel by an in-situ radical polymerization method. J Mater Chem Mater Chem Comm 8:1113–1115
39. Brinker CJ, Keefer KD, Schaefer DW, Ashley CS (1982) Sol–gel transition in simple silicates. J Noncrystal Solids 48:47–64
40. Smith AL (1974) Analysis of silicone. Chemical analysis 41. Wiley, New York
41. Wadekar MN, Pasricha R, Gaikwad AB, Kumaraswamy G (2005) Polymerization in surfactant liquid crystalline phases. Chem Mater 17:2460–2465