Composite Particles of Silica/Poly(dimethylsiloxane)

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A simple procedure for the preparation of submicrometer composite particles of silica and poly(dimethylsiloxane) (PDMS) is described. There are two novel aspects to this preparation: first it is based on the direct entrapment of the polymer within the sol−gel forming silicate matrix, and second, it is the first description of silica/PDMS composite particles where the PDMS is of high molecular weight (36 000−115 000 g/mol). The particles are formed in an emulsion where the hydrophobic phase is the PDMS dissolved in the sol−gel precursor (tetraethoxysilane) with or without tetrahydrofuran, and the polar phase is alkaline ethanol. Identification of the suitable surfactant, DOW-190, was a key step in developing this procedure. Some properties of the new particles are described.

1. Introduction

We present a one-pot procedure for the preparation of poly(dimethylsiloxane)−silica (PDMS@SiO$_2$) composite particles, where the PDMS component is of high molecular weight (MW; 36 000, 90 000, and 115 000 g/mol). The approach we used is to *entrap* the desired polymer within the sol−gel matrix (rather than the common approach of synthesizing it from its monomer in the presence of the inorganic matrix, see below). In two recent papers published in this journal[1] we have demonstrated the feasibility of the polymer-entrapment approach for composite particles of polystyrene@SiO$_2$ (PS@SiO$_2$) particles. The general idea has been to dissolve the hydrophobic polymer in tetraethoxysilane (TEOS) and then to emulsify it with a carefully selected surfactant in a basic ethanolic solution.[1] Motivated by the simplicity of that procedure we have set to explore the possibility of extending it to a polymer of a completely different nature, namely, to PDMS. The transition from one type of polymer to the other (PS, solid at room temperature, vs PDMS, which is a viscous liquid) has not been straightforward, as it requires a search for suitable reaction conditions and especially for the suitable surfactant that can stabilize the specific emulsion and allow the sol−gel polycondensation reaction to proceed inside the droplet. Once the suitable surfactant was identified—DOW-190 (a silicone−ethylene oxide (EO)/propylene oxide (PO) copolymer, see structure below)—we were able to obtain good high-MW PDMS@SiO$_2$ particles of submicronic monodispersed radii.

Silica/PDMS composites have found many applications such as thermal insulations,[2] bioactive supports,[3] host matrixes for biocatalysts,[4] separating membranes,[5] matrixes for controlled drug release,[6] and piezoelectric materials.[7] It may, therefore, come as a surprise that two important aspects of these composites received limited attention: First, to the best of our knowledge, only low-MW PDMSs have been used in SiO$_2$/PDMS composites (the highest we could find is 18 000[8] and in most other studies it is much lower;[9] high-MW PDMSs are found in the context of reinforcement of the polymer by blending it with silica particles).[10] Second, the research toward preparation of small particles of these composites has been quite scarce, with examples including the procedure of Obey and Vincent[11] in which droplets of dimethyldiethoxysilane (DMDES) oligomers (MW of ∼500 g/mol) were synthesized and copolymerized with methyltriethoxysilane (MTES);[12] a later study, where the addition of TEOS to DMDES/MTES led to PDMS core−silica shell particles;[13] and the study of Schmidt et al.[14] who fabricated

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Table 1. Preparation, Composition, and Some Properties of the Particles

sample	polymer MW (g/mol)	polymer amount (g)	amount and type of solvent (mL)	average size (nm) by TEM	composition (wt % PDMS)	ζ potential (mV)
1	36 000	0.5	TEOS (2)	177.0 ± 25.0	47	−54
2	90 000	0.5	TEOS (2)	250.0 ± 29.5	54	−60
2a	90 000	0.2	TEOS (2)	193.5 ± 16.5		
3	115 000	0.3	TEOS (2) + THF (2)	165.0 ± 17.0	31	−14
3a	115 000	0.15	TEOS (2) + THF (2)	162.0 ± 21.0		

nanometric poly(organosiloxane) spheres with various core−shell architectures by the reaction of DMDES with substituted trialkoxysilanes and TEOS, where the MW of the PDMS produced inside the hydrophobic core was between 1000 and 3000 g/mol.[15]

As mentioned above, here we present a one-pot procedure for the preparation of PDMS@SiO$_2$ composite particles, where the PDMS component is of high MW. We report the detailed synthesis of these particles along with some of their properties and the extraction of the PDMS phase to obtain porous silica particles. A proposition as to what makes that surfactant so suitable for the formation of the composite particles is offered.

2. Experimental Details

Chemicals. The 98% TEOS was purchased from Aldrich and PDMS of MW 36 000 that was dihydroxy terminated (PDMS-36 000; viscosity, 2 000 centi-stokes (cs)), PDMS of MW 90 000 that was dihydroxy-terminated (PDMS-90 000; viscosity, 18 000 cs), and PDMS of MW 115 000 that was trimethyl-terminated (PDMS-115 000; viscosity, 60 000 cs) were purchased from Scientific Polymer Products, Inc. The surfactant DOW-190 (silicone−EO/PO copolymer, viscosity of 1555 cs) was kindly donated by Dow-Corning, Inc.

Particles Preparation. In a typical procedure (first entry in Table 1), 0.5 g of PDMS-36 000 was dissolved in 2.0 mL of TEOS using sonication for 10 min. This solution was poured into a solution of 75 mL of ethanol, 10 mL of ammonium hydroxide (∼25% NH$_3$ by weight), and 0.4 g of the surfactant (DOW-190). A white emulsion formed immediately without any evidence of floating silicone oil. The emulsion was then stirred for about 24 h at room temperature. The resulting particles were obtained by centrifuging for 15 min at 6000 rpm, after which the white precipitate was separated and then redispersed in either ethanol or water. Other formulations are collected in Table 1. For PDMS-115 000 it was necessary to use a cosolvent, 2.0 mL of tetrahydrofuran (THF), and the formation of a stable emulsion required warming to 35 °C for 10−20 min. These conditions represent the maximal possible loading of PDMS in the composites, and below we focus on these maximal loaded particles. However, particles with lower PDMS loading have also been prepared by similar procedures, and some typical results are shown below as well. In all cases, all of the PDMS was entrapped and the relevant column in Table 1 indicates the calculated composition (weight of PDMS divided by the weight of the final sample).

Removal of the PDMS Phase. This was performed on all samples in two ways: (i) Extraction with THF with a Soxhlet extractor for 24 h. (ii) Calcination, which was carried out by heating the sample at 750 °C for 5 h in air.

Exposure to THF. The precipitate (0.5−1 g) was exposed for time periods of 1−2 h to 5.0 mL of THF by stirring at room temperature. The THF was then removed by decantation, and the precipitate was redispersed in water.

Particle Characterization and Instrumentation. Transmission electron microscopy (TEM) observations were performed on a Philips CM 12 microscope operating at 120 or 100 kV. Samples for TEM observations were prepared by deposition of the ethanolic dispersions on Formvar/carbon 300 mesh copper grid. The dispersions were air-dried for 1 min, and the extra solution was blotted off. The diameters of at least 200 particles were determined for each sample using Analysis software, and statistical analysis was carried out with KaleidAgraph (from Synergy Software). Surface area and porosity measurements of the dried powders from which PDMS was removed were determined from nitrogen adsorption/desorption isotherms using a Micromeritics ASAP 2000 instrument, employing the BET equation for surface area computation and the BJH equation for pore size analysis. Thermogravimetric analysis (TGA) was preformed on a Mettler TG-50 system at 10 °C/min. IR measurements were carried out on a Bruker Vector 22 spectrometer.

3. Results and Discussion

TEM Observations. The successful formation of the composite particles is crucially dependent on the right choice of the stabilizing surfactant. We shall return shortly to the surfactant of choice, but first we present the resulting particles. Figures 1 and 2 show typical TEM observations of PDMS@SiO$_2$ of various MWs and compositions (Table 1). We focus on the particles with the maximal PDMS loadings (Figure 1a, MW 115 000 g/mol, sample 3; Figure 1b, MW 90 000 g/mol, sample 2; Figure 1c, MW 36 000 g/mol, sample 1), but it is also shown in Figure 2 that the developed procedure is applicable for lower PDMS loadings as well (samples 2a and 3a, Table 1). The composite smoothed-surface particles are obtained in monomodal distributions (Figure 1, Table 1), and the average particle sizes are all in the range of 160−250 nm. The majority of the particles are spherical (note the hexagonal packing, for instance, in Figure 2a); few particles are seen that are not spherical (Figure 1a), probably because of coalescence of two particles, and thin threads, apparently of PDMS, were sometimes seen for sample 2 [Figure 1b, which was prepared with excess PDMS to achieve maximal loading; indeed, these threads diminish for the particles with a lower loading of PDMS (Figure 2a, sample 2a, Table 1)]. It is perhaps surprising at first glance to see that the highest MW (115 000 g/mol) provides the smallest particles. We attribute it to the different procedure employed here, namely, to the use of a solvent (THF) for the polymer; solvent escape from the

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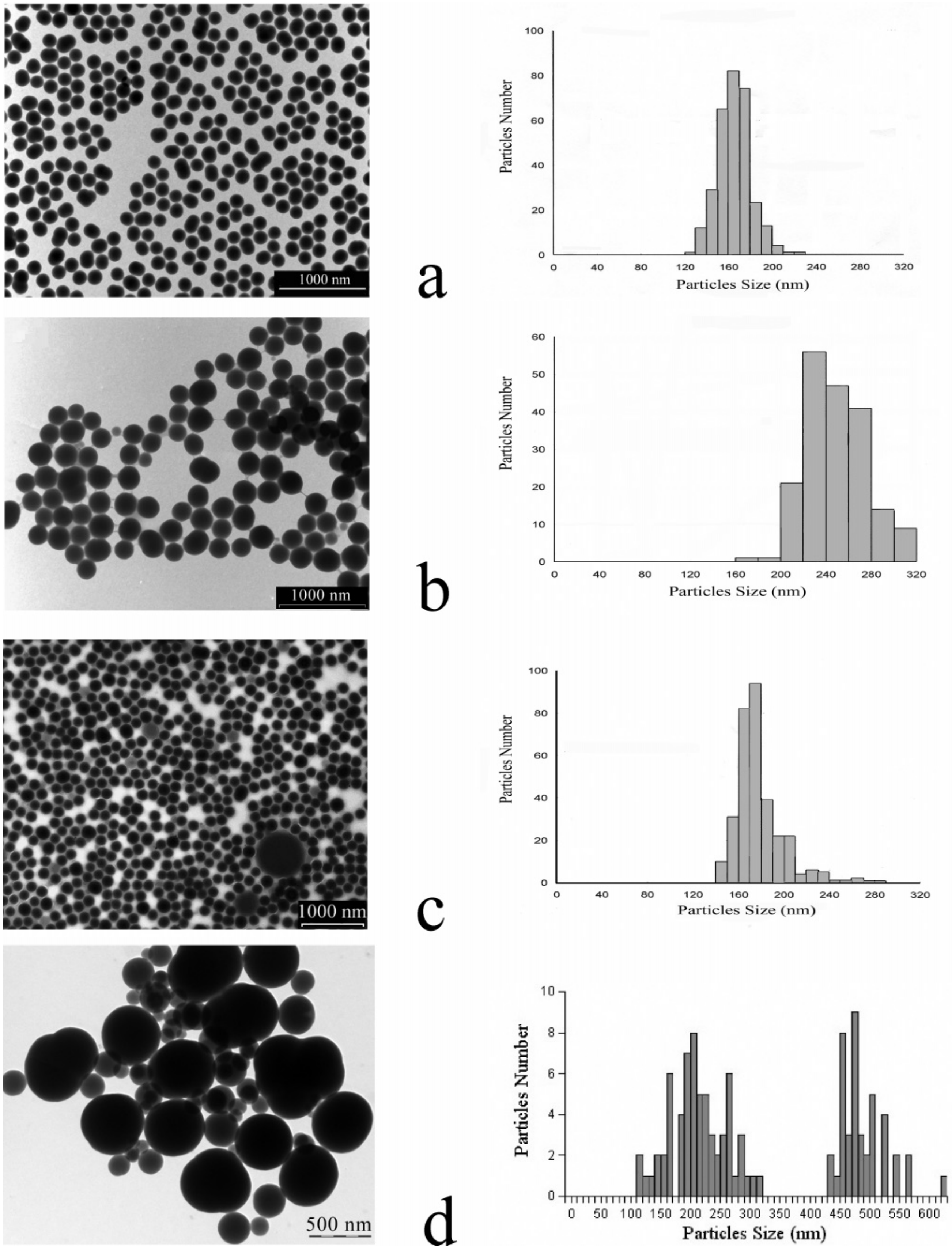


Figure 1. Typical TEM observations (left) of PDMS@SiO_2 of various MWs at maximal PDMS loading (Table 1) and the particle size distributions (right). (a) MW 115 000 g/mol, sample 3. (b) MW 90 000 g/mol, sample 2. (c) MW 36 000 g/mol, sample 1. (A rare droplet of un-entrapped PDMS is seen on bottom left.) (d) Sample 1 after exposure to THF (referred to later in the paper).

emulsion droplets then causes their shrinkage before solidification.

Identification of the Suitable Surfactant. The main difficulty to overcome toward the successful preparation of

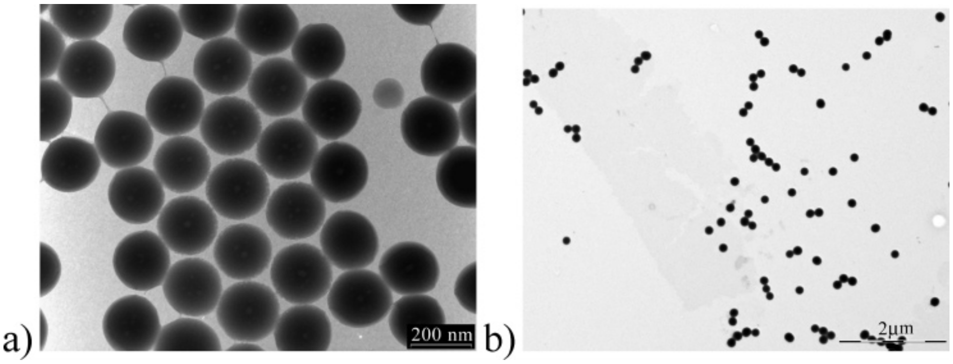
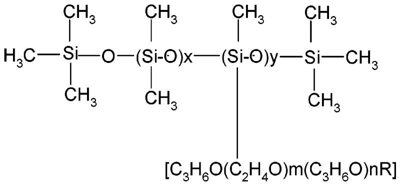


Figure 2. Typical TEM observations of PDMS@SiO$_2$ particles at the lower PDMS loading (Table 1). (a) Sample 2a. (b) Sample 3a.

the particles had been the dispersion of the viscous PDMS oils in the alkaline aqueous ethanolic phase. Another problem to solve was the selection of a suitable surfactant tailored to the interfacial tension between the hydrophobic phase (PDMS in TEOS) and the dispersing hydrophilic phase. To overcome these difficulties one needs a surfactant that is compatible with the specific characteristics of both phases and in particular with the long PDMS chains. Indeed, the nonionic surfactant Triton X-100, the cationic surfactant cetyltrimethylammonium bromide (CTAB), and the anionic surfactant sodium dodecyl sulfate (SDS) failed to stabilized an emulsion of droplets. Both the anionic SDS and the cationic CTAB did form a stable emulsion, but instead of particles, a continuous framework formed. In fact, the ionic surfactants failed because they do not form stable micelles in ethanolic solutions. The success of DOW-190 to disperse in a homogeneous way the hydrophobic phase, resulting eventually in monodispersed composite particles, can be understood from its structure:



$$\mathrm{H_3C{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}(\underset{CH_3}{\overset{CH_3}{Si}}{-}O)x{-}(\underset{[C_3H_6O(C_2H_4O)m(C_3H_6O)nR]}{\overset{CH_3}{Si}}{-}O)y{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}CH_3}$$

DOW-190

It is seen that the surfactant is composed of two types of chains: an oligomeric PDMS chain to which an oligomeric EO/PO copolymer is grafted. Thus, while the polysiloxane branch dissolves well the high-MW PDMS phase, the polyether side chain dissolves well in the water/alcohol phase, resulting in the desired emulsification. The failure of the nonionic surfactant Triton X-100 to form a stable emulsion points to the importance of the principle of "like dissolves like" in the selection of the surfactant.

IR Spectroscopy. An easy and convenient way to gain immediate proof of composite nature is IR spectroscopy. Indeed that nature was confirmed by typical IR bands, as follows: the vibrational bands of PDMS[16] that are seen in the spectrum (Figure 3) include the C−H stretching at 2967 cm^{-1}, the bending of the CH$_3$ group as a sharp peak at 1263 cm^{-1}, and the rocking of the CH$_3$ at 803 cm^{-1}. These are superimposed on the typical silica bands, most notably the silanol stretchings at 3430 and 940 cm^{-1}. Common to both phases is the broad asymmetric Si−O−Si stretching vibration at 1000−1200 cm^{-1}, and in fact, after calcinations (at 750 °C for 5 h), all carbon-associated peaks disappear and that broad band remains as the main feature of the IR spectrum (not shown).

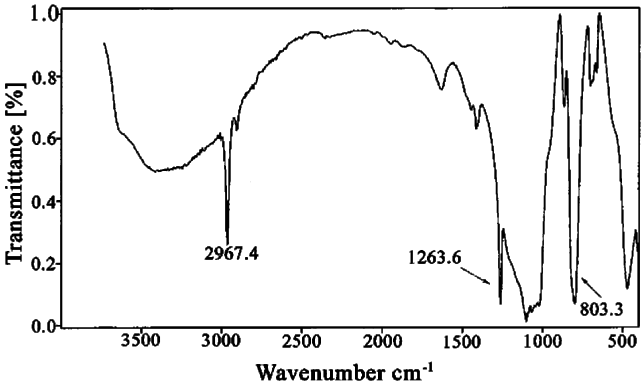


Figure 3. IR spectrum of sample 1. Indicated are the peaks of the PDMS; the other peaks (see text for assignment) are due to the silica component of this composite.

Interface: Zeta Potential Measurements. While IR provides information on the bulk, information on the interface can be obtained from ζ potential measurements. The ease of redispersion of the particles of *all compositions* in hydrophilic solvents (water and ethanol) already indicated that they are hydrophilic at their surface, namely, that the interface is rich in silica. Support to this hypothesis was provided by the ζ potential measurements (Table 1). Thus, sample 1 showed a negative ζ potential of −54.5 mV and sample 2 showed a negative ζ potential of −60 mV, both in the range of the ζ potential of pure silica. Sample 3 showed a sharp peak at a lower value of −14 mV to which we shall return shortly. The abundance of silanols at the surface of samples 1 and 2 is understood from the surfactant's structure: The EO/PO chains that point into the hydrophilic phase are at the same time also compatible with TEOS, an ether itself, and its partially hydrolyzed species are, thus, enriching the particle's interface. On the other hand, the lower ζ potential of sample 3 indicates that the composite nature of the particles is represented at its interface. The origin of this difference can be understood if one recalls that THF was used as a cosolvent of the hydrophobic phase only for the highest MW: PDMS-115 000 (sample 3). THF, a good solvent of PDMS, is capable of carrying to the interface more

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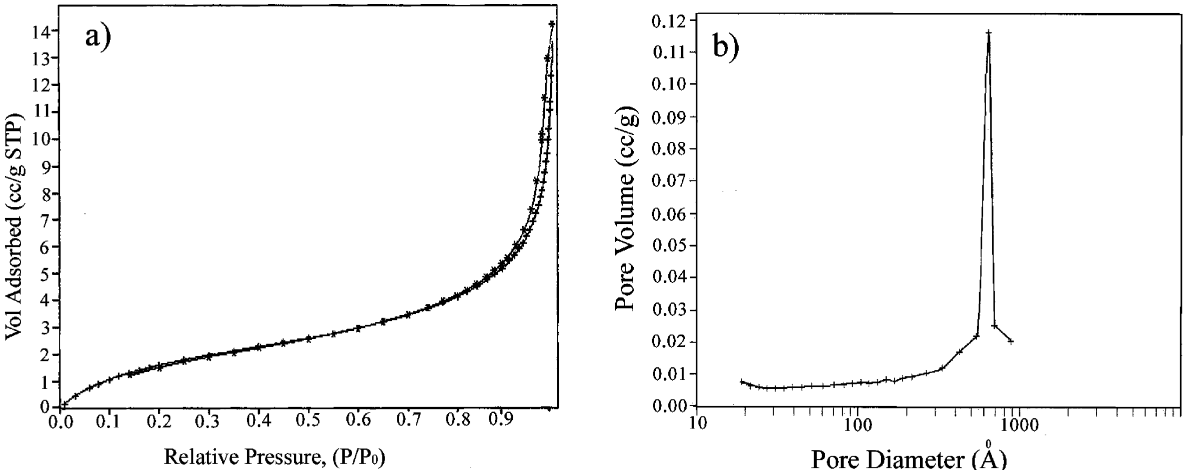

Figure 4. Adsorption−desorption hysteresis loop (a) and pore size distribution (b) of the porous silica obtained after PDMS extraction from sample 3 (PDMS-115 000@SiO$_2$).

Table 2. Weight Loss, Surface Area, and Porosity of the Composite Particles[a]

	property	sample 1	sample 2	sample 3
after extraction	weight loss (%)	39.6	26.4	7.6
	surface area (m^2/g)	7.4	7.8	9.1
	average pore size (nm)	8	10	13
TGA analysis	weight loss (%)	27.8	29.4	15.8
after calcination	weight loss (%)	28.3	25.5	11.0
	surface area (m^2/g)	0.8	*a*	*a*
	average pore size (nm)	13	*a*	*a*

[a] Very low (below instrument sensitivity).

of the PDMS chains. It should be added that in all these cases we do not have evidence for a core−shell architecture, and we can only assume that the rich-in-silanols surface indicates perhaps a membrane-thin layer. This is not surprising if one takes into account that, for core−shell architecture to evolve, phase separation must occur during the particle formation stage, and in our case this is unlikely because of the high viscosity of the high-MW PDMS we use.

Weight Loss by PDMS Removal. Weight loss determinations were carried out in two distinctly different ways—extraction with THF and calcination in air—leading indeed to different results. As seen in Table 2, extractions provided a higher weight loss compared to calcination. Starting with the latter, the low weight loss is due to the fact that while calcination removes the carbon moieties from PDMS, it does leave behind an added silica skeleton. Thus, the calcination-driven weight loss is partially compensated by the increase in the weight of the silica. A similar trend is seen also for oxidative TGA (Table 2). Although weight loss by extraction is higher, it is clear that the extraction is not full and that the extraction becomes less efficient as the MW increases, as a resut of the increase in viscosity and the size of the polymer. The partial extraction is an indication of the intimate, molecular-level entanglement of the two phases, as also confirmed by porosity analysis (next section).

Surface Area Measurements. Extraction leaves behind a meso- to macroporous silica, characterized by an adsorption/desorption isotherm hysteresis loop which is typical for such materials, namely, by a type II isotherm (Figure 4a), by low surface areas of 7−9 m^2/g (Table 2), and by pores of about 10 nm in size (Figure 4b, Table 2). This picture changes completely for calcination: At the high temperature of 750 °C, the silica collapses and coalesces, and the surface areas and porosities become very low (below 1 m^2/g). The pore sizes after extraction may perhaps provide a hint as to the PDMS size domain. It is seen (Table 2) that the size increases with MW from 8 to 10 and to 13 nm, all of which are of the order of a few PDMS molecules. The *non*-extractable polymer is apparently captured in narrower pores, and there is no reason not to believe that some of the PDMS molecules are entrapped on a single molecule level. Thus, the PDMS@SiO$_2$ seems to be a composite on a molecular or near the molecular level.

Exposure to THF. An interesting observation was made when the particles were exposed to THF (a good solvent for PDMS) for several hours under gentle stirring conditions (see Experimental Details). This treatment turned out to change the particle size distribution from monomodal to bimodal for samples 1 and 2 and to a wide distribution for sample 3, moving in all cases mainly to larger particles as well as to somewhat smaller particles (Figure 1d; the new average sizes for sample 1 are 228 and 484 nm; for sample 2, 172 and 399 nm; and for sample 3, in the 130−500 nm range). We assume that the particles grow up because of three processes: swelling of the particles by THF maintaining their spherical shape; coalescence of two or more particles resulting in the observed nonspherical shapes; and some PDMS migration from small to larger particles.

4. Conclusion

All of the above points to a particle formation mechanism which is comprised of the following steps: Formation of droplets which contain PDMS and TEOS (and THF, when used), stabilized by the special surfactant, so that the oligomeric PDMS chains are dissolved in their “like”, namely, the high-MW PDMS droplet, whereas the EO and PO chains point to the ethanolic dispersing phase. These chains allow penetration of the base from the dispersing phase to the outer surface of the droplet, where the sol−gel polymerization begins, forming an initial confining silica membrane. Once formed, the process continues inward, fast enough, on one hand, to avoid phase separation, and on the other hand to form a composite where silica and PDMS are intimately intermingled.

This report is our second example of the concept of preparing composite polymer@silica particles by a simple procedure of direct entrapment of the desired polymer in the sol–gel-forming matrix, in an emulsion. The first example was PS@silica,[15] and high-MW PDMS@silica is now the second. The procedures are simple and one-pot and provide an alternative to the opposite approach where the organic polymer is synthesized in the presence of the silica (or other oxide) particles from its monomers. While the concept is general, each family of polymers requires the tailoring of suitable conditions and, in particular, the identification of the proper emulsification conditions. Yet we believe our approach to be more generic, because it utilizes one inorganic polycondensation reaction, which may serve many presynthesized polymers; indeed, other composite particles will be described in subsequent papers.

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