Nanostructured Amorphous Silicas Hydrophobized by Various Pathways

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ABSTRACT: Various nanostructured amorphous silicas [fumed silicas such as crude (A-300), hydro-compacted (cA-300, TS 100), and precipitated silica Syloid 244] were modified by different polydimethylsiloxanes such as PDMS5, PDMS100, PDMS200, PDMS1000, and PDMS12500 (the label numbers show the viscosity (η) values) using dimethyl carbonate (DMC) as a siloxane-bond-breaking reagent. In addition, hexamethyldisilazane was used to modify fumed silica cA-300. The nanocomposites were characterized using microscopy, infrared spectroscopy, thermodesorption, nitrogen adsorption–desorption, solid-state NMR spectroscopy, small-angle X-ray scattering, and zeta-potential methods. It was found that the morphological, textural, and structural characteristics of silicas grafted with PDMS depend strongly not only on the type and content of the polymers used but also on the organization of nonporous nanoparticles (NPNP) in secondary structures (aggregates of NPNP and agglomerated aggregates, ANPNP), as well on the reaction temperature (T). Specifically, we determined that ANPNP with a macro/mesoporous character are favorable for the effective modification of the silicas studied with short polymers and no DMC addition but at higher temperatures or for a longer silicone polymer with the presence of DMC and at lower temperatures. In particular, the PDMS/DMC-modified silicas are of great interest from a practical point of view because they remain in a dispersed state with no strong compaction of the secondary structures after modification, and this corresponds to a better distribution of the modified nanoparticles in polymeric or other matrices.

1. INTRODUCTION

Nanostructured amorphous silicas (NAS) can be synthesized under different conditions affecting their morphological, structural, textural, and other characteristics. For example, fumed silicas are synthesized (using, e.g., SiCl₄ as a precursor) at high temperatures in an O₂/H₂/N₂ flame, precipitated silicas are synthesized (using, e.g., sodium silicate) in liquid media at relatively low temperatures, and thermosilica is synthesized using fumed silica hydrated and treated at high temperatures. These materials with similar values for their specific surface area (SₖBET) may have structural and textural characteristics that differ in some ways and are similar in others. We can assume that the results of the chemical modification of various NAS by the same modifiers, as well as the results of modification of the same NAS by different modifiers may therefore be different. This aspect is analyzed in the present work with respect to the hydrophobilization of a set of NAS by different polydimethylsiloxanes (PDMSs) alone or with the presence of dimethyl carbonate (DMC) as a reagent for Si–O bond cleavage.

Hydrophobilized NAS are of interest from a practical point of view because these materials are better fillers of nonpolar or weakly polar polymers as well as being more appropriate for other practical applications than hydrophilic NAS. Therefore, a deeper insight into the problem of hydrophobilization of various NAS by various modifiers is of importance. The morphological, textural, and structural features of various NAS can strongly affect the results of hydrophobilization: the degree of hydrophobilization (θ), possible length of hydrophobic functionalities, and changes in the porosity and SₖBET, and so forth. Clearly, these aspects are of importance because the hydrophobilization of NAS influences not only the structure of a solid surface but also other characteristics and properties of the materials. Different modifiers with low-molecular weight (MW) can be applied for the hydrophobilization of NAS, such as organosilanes [(CH₃O)ₓSiR₄₋ₓ], chlorosilanes (ClₓSiR₄₋ₓ where R = CH₃ or other organic functional groups), and hexamethyldisilazane (HMDS).
Table 1. Textural Characteristics of Synthesized Composites

| sample                  | label      | C_C (wt %) | C_H (wt %) | S_BET (m²/g) | r (nm) | V_p (cm³/g) | S_nano (m²/g) | S_meso (m²/g) | S_macro (m²/g) | V_nano (cm³/g) | V_meso (cm³/g) | V_macro (cm³/g) | R_V(nm) | R_S(nm) | ζ (mV)  |
|-------------------------|------------|------------|------------|--------------|--------|------------|--------------|--------------|---------------|----------------|---------------|----------------|---------|---------|--------|
| A-300                   | A          | 275        | 0.910      | 9.46         | 0.9    | 228        | 46           | 0            | 0.341         | 0.569         | 37.55         | 12.79             | −4.18   |
| A-300/PM5S              | AP1        | 167        | 0.520      | 9.69         | 0.88   | 245        | 31           | 0            | 0.246         | 0.274         | 32.87         | 15.64             | −0.94   |
| A-300/PM50/DMC          | AP2D       | 195        | 0.574      | 7.74         | 0.88   | 245        | 31           | 0            | 0.288         | 0.287         | 33.39         | 15.12             | −2.81   |
| A-300/PM100/DMC         | AP4D       | 276        | 0.695      | 5.21         | 0.88   | 245        | 31           | 0            | 0.360         | 0.335         | 31.39         | 11.11             | −6.23   |
| A-300/PM1250/DMC        | AP5D       | 244        | 0.691      | 5.95         | 0.97   | 241        | 64           | 0            | 0.328         | 0.364         | 33.81         | 12.69             | −1.69   |
| cA-300                  | cA         | 305        | 1.387      | 4.47         | 0.97   | 241        | 64           | 0            | 0.662         | 0.725         | 34.52         | 18.25             | −0.55   |
| cA-300/PM50/DMC         | cAP3D      | 171        | 1.089      | 8.83         | 1.59   | 116        | 55           | 0            | 0.464         | 0.624         | 42.01         | 29.15             | −3.24   |
| cA-300/PM50/DMC         | cAH        | 248        | 1.312      | 5.83         | 0.97   | 173        | 75           | 0            | 0.571         | 0.741         | 35.13         | 23.59             | −0.63   |
| A300                    | AE         | 242        | 0.798      | 5.63         | 1.59   | 197        | 41           | 0.001        | 0.266         | 0.531         | 39.05         | 12.26             | −3.60   |
| A300/PM50               | AEP1       | 187        | 0.574      | 8.49         | 2.03   | 154        | 33           | 0            | 0.269         | 0.304         | 32.49         | 14.78             | −2.67   |
| A300/PM50/DMC           | AEP2D      | 198        | 0.596      | 7.35         | 1.08   | 162        | 36           | 0            | 0.279         | 0.317         | 31.89         | 14.67             | −1.02   |
| A300/PM100/DMC          | AEP4D      | 211        | 0.611      | 6.84         | 0.98   | 182        | 30           | 0            | 0.296         | 0.315         | 33.96         | 13.20             | −2.96   |
| TS 100                  | T          | 269        | 0.773      | 5.07         | 0.98   | 236        | 33           | 0            | 0.389         | 0.383         | 33.26         | 12.07             | −0.73   |
| TS 100/PM20/DMC         | TP3D       | 171        | 0.620      | 8.75         | 1.50   | 132        | 40           | 0            | 0.267         | 0.353         | 36.87         | 19.41             | −1.28   |
| Syloid 244              | S          | 380        | 1.584      | 3.59         | 0.51   | 328        | 52           | 0            | 0.870         | 0.714         | 37.38         | 18.52             | −1.91   |
| Syloid 244/PM20/DMC     | SP3D       | 280        | 1.398      | 5.36         | 0.51   | 221        | 59           | 0            | 0.678         | 0.720         | 39.54         | 23.17             | −2.44   |

“DFT” method with a model of voids between nonporous spherical nanoparticles was applied to the nitrogen adsorption—desorption isotherms at 77.4 K. The values of $V_{nano}$ and $S_{nano}$, $V_{meso}$ and $S_{meso}$, and $V_{macro}$ and $S_{macro}$ were computed by integration of the $f_V(R)$ and $f_S(R)$ functions at $0.35\text{nm} < R < 1\text{nm}$, $1\text{nm} < R < 25\text{nm}$, and $25\text{nm} < R < 100\text{nm}$, respectively. The values of $(R_V)$ and $(R_S)$ as the average pore radii were calculated as a ratio of the first moment of $f_V(R)$ or $f_S(R)$ to the zero moment (integration over the $0.35–100\text{nm}$ range) $(R) = \int f(R) R\, dR / \int f(R)\, dR$. The values of the average nanoparticle radius $(r)$ were calculated as $r = 3/[S_{BET} \times (\rho_0,SO_2 \times C_{SO_2} + \rho_m \times C_m)]$, where $\rho_0,SO_2 = 2.2\, \text{g/cm}^3$, $\rho_m = 0.97\, \text{g/cm}^3$, $C_m$ is the relative content of a modifier. Zeta potential $(\zeta)$ values were determined in THF/water (1:1) solution.
To enlarge the hydrophobic functionalities attached to a surface, NAS hydrophobization may be carried out using organosiloxanes with the presence of DMC. This modification results in a greatly thicker functional layer\(^{1,3,28,34,35,39,41}\) than that obtained upon modification using short silanes, as mentioned above, that is of importance for fillers of polymers. However, the textural characteristics (porosity and pore size distribution (PSD)) can play a more important role than in the case of short molecules of modifiers. The characteristics of the modifiers and modified surfaces can strongly affect not only the interactions of modified NAS (used as fillers) with polymers but also the morphology and texture of modified surfaces (and even the solubility of silicas).\(^{8,9,27}\) Thus, the modification of fillers can strongly affect important physicochemical characteristics of the final materials. Notice that cyclic organosiloxanes can be applied for the SiO\(_2\) surface modification, but much higher reaction temperatures are required than with linear PDMS and the presence of DMC catalyzing the decomposition of PDMS into more reactive fragments.

The physicochemical properties and characteristics of modified NAS strongly depend on the surface distribution and structure of the attached functionalities, their amounts, the degree of substitution of surface OH groups by grafted functionalities [e.g., Si(OR)(CH\(_2\))\(_n\)Si(CH\(_3\))\(_3\)]\(^{3,8,11}\) the fragments of depolymerized PDMS, and so forth. Clearly, features of unmodified NAS (e.g., particulate morphology, porosity, PSD, etc.) can affect the modified material properties.\(^{3–12}\) For fumed NAS, the size distribution of the nonporous nanoparticles (NPNP), \(S_\text{BET}\) textural porosity of NPNP aggregates and agglomerates of aggregates (ANPNP), and chemistry (e.g., content of surface hydroxyls) are important factors for interactions with PDMS/DMC. The properties of unmodified and modified NAS depend on the organization of ANPNP.\(^{41–50}\) ANPNP features depend on the morphology and synthesis route of NAS and the determining NPNP bonding in the secondary structures, as well on the constitution of a functional layer at the surface of unmodified and partially or completely modified SiO\(_2\) nanoparticles. The distribution of the surface hydroxyls (initial and residual after surface modification) and grafted functionalities on modified SiO\(_2\) surfaces can change the properties of NAS-filled polymers.\(^{13–15,51–61}\) Thus, it is of interest (and this is the aim of our study) to elucidate the influence of the characteristics of unmodified NAS of various origins [fumed initial (A-300), hydro-compact ed at low (CA-300) and high (TS 100) temperatures, and precipitated (Syloid 244) silicas] on the results of hydrophobization by PDMS alone (short PMSS) or DMC-depolymerized longer PDMS (PMS100, PMS200, PMS100, and PMS12500), depending on the MW of PDMS, as well to compare NAS modified by HMDS [at different reaction temperatures of \(T = 80 \, ^\circ\text{C}\) (HMDS), 200, 220 °C (PDMS/DMC)], or 250 °C (PMS), selected depending on the reactivity of the modifiers. Note that different aspects of the interactions of PDMS-hydrophobized silicas with water, as well as other adsorbates, have been analyzed elsewhere.\(^{41,50,62–65}\) Typically, uniform hydrophobic surfaces, for example, modified by PDMS fragments, are characterized by a contact angle for settled water drops not greater than \(\theta_c = 120^\circ\). Nano/microstructured hydrophobic particles (structures) can provide much larger \(\theta_c\) up to \(170^\circ\) due to a surface geometry factor.\(^{66–67}\) Thus, hydrophobic nanostructured systems may be considered as a part of more complex systems with a complex geometrical, particulate morphological hierarchy.\(^{66–68}\) However, the effects of different organization of various nano-/microstructured silicas composed of NPNP upon hydrophobization by various PDMS alone or with the presence of DMC have not been previously studied.

2. MATERIALS AND METHODS

2.1. Materials. Five silicas were employed as follows: (i) fumed silica A-300 (Pilot Plant of Chukto Institute of Surface Chemistry, Kalush, Ukraine) preheated at 450 °C for 2 h (label A in samples) to remove water and other compounds adsorbed from air; (ii) preheated A-300 hydro-compact ed with addition of distilled water (1:2 w/w), stirred for 10 min, and then heated at 105 °C for 8 h (label ca); (iii) fumed silica A300 (Evonik) preheated at 450 °C for 2 h (label AE); (iv) silica TS 100 (Evonik Ind.) based on fumed silica strongly agglomerated due to treatment at high temperature (label T); and (v) Syloid 244 (precipitated silica, Grace Davidson, label S). These were subjected to hydrophobization by PDMS. Five PDMS were used: PMS5 (WACKER AK 5 silicone fluid, viscosity \(\eta \approx 5 \, \text{mm}^2/\text{s} \) (label P1)), PMS100 (WACKER AK 100 silicone fluid, \(\eta \approx 100 \, \text{mm}^2/\text{s}\) (label P2)), PMS200 (Kremniypolymer’, Zaporozh’ye, Ukraine, \(\eta \approx 200 \, \text{mm}^2/\text{s}\) (label P3)), PMS1000 (WACKER AK 1000 silicone fluid, \(\eta \approx 1000 \, \text{mm}^2/\text{s}\) (label P4)), and PMS12500 (WACKER AK 12500 silicone fluid, purity > 99%, \(\eta \approx 12500 \, \text{mm}^2/\text{s}\) at 25 °C, density of ca. 0.97 g/cm\(^3\)) (label P5). Note that the PDMS viscosity (see the Supporting Information) depends strongly on the MW, and this could be affected by the coil-like shape of the polymer chain.\(^{51,69}\) The MW values are ca. 815, 6004, 9670, 28 000, and 67 700 g/mol for PMSS, PMS100, PMS200, PMS1000, and PMS12500, respectively. Clearly, the structural features of PDMS can affect the chemical modification of various silicas (having different textural characteristics) by PDMS of different lengths due to several factors (vide infra).

Several silicas were functionalized using the same amounts of reagents of PDMS + DMC (2 g PDMS and 2 g DMC per 10 g SiO\(_2\)) at a temperature range of 100–250 °C in gaseous dispersion media (see Tables 1 and S1 in the Supporting Information). The samples demonstrating better results (in terms of the degree of hydrophobization) versus \(T\) were selected for subsequent detailed investigations.

The content of the grafted organic (\(C_\text{C}\) and \(C_\text{H}\) in Table 1) groups in the modified NAS was measured twice by a Vario MACRO cube analyzer (Elementar, Germany) in order to estimate average values for carbon and hydrogen content and relative deviations.

2.2. Scanning and Transmission Electron Microscopy. A scanning electron microscopy (SEM) study (Figures S3–S6) of the obtained materials was performed using a FE-SEM (Hitachi S-4700, Japan) equipped with a standard secondary electron (SE) detector at an operating voltage of 15 kV at the magnification range of ×5000 to ×100 000.

A transmission electron microscopy (TEM) (Figures 1, 2, S1, and S2) analysis was performed using a TECNAI G2 F30 microscope (FEI-Philips, Holland) equipped with a high-angle annular dark field detector at an operating voltage of 300 kV. The powder samples were added to acetone (chromatographic grade) and sonicated. A drop of the suspension was then deposited on a copper grid with a thin carbon film. After acetone evaporation, sample particles remaining on the film were studied.

2.3. Small-Angle X-ray Scattering. Small-angle X-ray scattering (SAXS) analysis of initial A-300, hydro-compact ed silica caA-300, and modified cAP3D (Figure 3) was performed
using an Empyrean (PANalytical, Netherlands) diffractometer with Cu Kα radiation (with a parallel-beam X-ray mirror with a W/Si crystal) using a transmission mode with scans over the 0.115°–5° range at a step of 0.01° using a continuous-scan mode at 293 K. Prior to the analysis, the samples were placed on a 6 μm Mylar film, levelled and gently kneaded by hand. Beam weakness was measured after passing through the sample, then corrected taking into account the background observed calculating the absorption factor of each sample. SAXS patterns were studied using the PANalytical EasySAXS V. 2.0.0.405 program (with the purpose of particle-size distributions (PaSDs) calculation).

2.4. Textural Characteristics. To study the textural properties of synthesized samples all samples were degassed at 180 °C for 12 h (Table 1). Low-temperature (77.4 K) nitrogen adsorption–desorption isotherms (see Figure S7 in Supporting Information) were recorded using an ASAP 2460 adsorption analyser (Micromeritics Instrument Corp., USA). The specific surface area (Table 1, S_BET) was calculated according to the standard BET method.70 The total pore volume (Table 1, V_p), pore-size distributions (PSD), and differential PSD as dV/dR were calculated as it was described previously in refs71–73 and in Supporting Information, Figure S8.

2.5. 1H MAS and 29Si CP/MAS NMR Spectroscopy. Solid-state 29Si CP/MAS NMR (Figure 5 and S9b) study of the synthesized materials was performed using a Bruker AVANCE 400 III HD spectrometer (Bruker, USA, magnetic field strength of 9.3947 T) with cross-polarization (CP), magic-angle spinning (MAS), and high-power 1H decoupling. The powder samples were poured in a pencil-type zirconia rotor of 4.0 mm o.d. The spectra were recorded at a spinning speed of 8 kHz (4 μs 90° pulses), a 8 ms CP pulse, and a recycle delay of 4 s. The Si signal of tetramethylsilane (TMS), assuming for this a 0 ppm shift, was used as a reference for the 29Si chemical shift for the silicas studied. Solid-state 1H MAS NMR (Figures 6 and S9a) study of the synthesized materials was performed on a Bruker AVANCE 400 III HD spectrometer (Bruker, USA, magnetic field strength of 9.3947 T). The powder samples were poured in a pencil-type zirconia rotor of 4.0 mm o.d. The spectra were recorded at a spin...
speed of 10 kHz and a recycle delay of 1 s. The adamantane was used as a reference for the 1H chemical shift.

2.6. Infrared Spectroscopy. FTIR spectra were recorded using a Specord M-80 spectrophotometer (Carl Zeiss, Jena, Germany) in the 4000−300 cm−1 wavenumber range. The obtained materials were pressed into rectangular 28 × 8 mm plates of 25 mg weight. A FTIR Bruker spectrophotometer coupled with an attenuated total reflection (ATR) tool using a diamond crystal was also used. To record spectra in the range 4000−1200 cm−1, the composites obtained were pressed into thin pellets (15−20 mg) and the transmittance spectra were recorded with 4 cm−1 step. To record spectra in the range 2000−300 cm−1, the samples were mixed with KBr (Sigma-Aldrich, for spectroscopy) as 1:400, stirred and pressed into thin pellets.

2.7. Zeta Potential. A Zetasizer Nano ZS instrument utilizing a 632.8 nm HeNe laser was used to study average zeta potential (Table 1, ζ). Measurements were performed using a Malvern “dip” cell kit in a tetrahydrofuran (THF)/water mixture.
3. RESULTS AND DISCUSSION

Initial and pretreated fumed silicas are characterized by relatively similar values for the specific surface area (Table 1, $S_{\text{BET}} = 242–305 \text{ m}^2/\text{g}$) and the average radius of primary nanoparticles ($r \approx 4.5–5.5 \text{ nm}$). However, precipitated silica Syloid 244 is composed of smaller NPNP ($r \approx 3.6 \text{ nm}$) but stronger aggregated (see Figure S2). The organization of NPNP in the secondary structures, ANPNP significantly differs for the silicas studied (Figures 1, 2, and S1–S6), and this results in large differences in the volumes of mesopores (Table 1, $V_{\text{meso}}$) and macropores ($V_{\text{macro}}$), as well as in the average radius of pores with regard to the pore volume ($\langle R_0 \rangle$) and the pore size distributions (PSD) [Figure 4 (incremental PSD) and Figure S8 (differential PSD)]. This factor could be of importance in interactions with PDMS. However, the bulk density of modified A-300 changes insignificantly, for example, $\rho_b = 0.047, 0.056, 0.047,$ and $0.050 \text{ g/cm}^3$ for A-300, cAP3D, AP4D, and AP5D, respectively. This is matching with the TEM images (Figure 1) of A-300 and related modified fumed silicas with no strong compaction of the secondary structures (note that stronger compaction results in greater $\rho_b$ values). For other silicas, the modification does not result in great changes in the compaction of the secondary structures (Figures 2 and S2–S6 in the Supporting Information), despite a certain increase in the $r$ values (Table 1). These results are of importance for the application of these composites as fillers for various nonpolar media (e.g., polymers), since strong compaction of ANPNP can lead to a worsened and nonuniform distribution of filler particles in the polymer matrices. This can lead to impairment of the mechanical and other characteristics of the final materials. Note that the secondary structures of Syloid 244 (precipitated silica) look like more strongly compacted (see Figures S2 and S6 in Supporting Information) than for other silicas such as CA-300 or TS 100 undergoing compaction treatments at low and high temperatures. However, Syloid 244 has a maximal $S_{\text{BET}}$ value and a minimal $r$ value (Table 1) among the silicas studied. Therefore, the contents of attached hydrophobic functionalities (Table 1, $C_C + C_H$) for samples SP3D and cAP3D are similar. It is worth mentioning that nanoparticles (voids between adjacent NPNP in ANPNP at $r < 1 \text{ nm}$ in pore radius) are practically absent (Table 1, $V_{\text{nano}}$ S nanost, Figures 4 and S8, PSD) in the unmodified and modified silicas. This is of importance for effective silica modification as nanoparticles are poorly accessible for relatively large PDMS molecules or their fragments.

The values of $\langle R_0 \rangle > 25 \text{ nm}$ and $V_{\text{macro}} > V_{\text{meso}}$ (Table 1), as well the PSD (Figure 4, PSD maxima at $R > 25 \text{ nm}$) suggest that the organization of ANPNP corresponds to meso/macroporous materials rather than to mesoporous ones. This could be of importance for SiO$_2$ surface modification by the polymer fragments (formed as a result of interactions with DMC), as the surfaces of NPNP are better accessible in broad mesopores and macropores than in narrow mesopores or nanoparticles (voids between NPNP in ANPNP), whereas for TS 100 and Syloid 244, $V_{\text{macro}} < V_{\text{meso}}$ but $\langle R_0 \rangle > 25 \text{ nm}$. Thus, both these compacted silicas are characterized by significant macroporosity.

The modification of NAS by short PDMS (PMSS at an average degree of polymerization of ca. 11), long PDMS (but with DMC addition used to cleave the Si−O bonds in PDMS), or HMDS typically leads to reduction of the values of $V_r$ and $S_{\text{BET}}$ (Table 1) and an increase in the average radius ($r$) of nanoparticles. However, changes in the textural characteristics of mesopores and macropores are different for modified A-300 (A and AE series) and other silicas (cA, T, and S series) due to the differences in the PSD of the unmodified silicas (Figure S8e,f), reflecting the organization of ANPNP. However, changes in the NPNP per se after additional treatment of nanosilicas (e.g., hydro-compaction A-300 $\rightarrow$ cA-300 and A-300 (AE) $\rightarrow$ TS 100) are not significant. For example, SAXS analysis of the PaSDs for A-300 and cA-300 shows similar curves with the same position for the PaSD maximum (Figure 3), which shifts toward larger values due to cA-300 functionalization (cAP3D). This is in agreement with the changes in the $r$ values (Table 1) computed from the nitrogen adsorption isotherms. It should be noted that hydro-compaction (cA-300) or PDMS/DMC modification (cAP3D) of A-300 results in a diminishing ANPNP contribution (Figure 3, $r > 10 \text{ nm}$), in comparison to unmodified A-300. In other words, both processes cause a certain amount of decomposition of ANPNP (see e.g., Figure 2a,b).

The difference in the organization of secondary structures, ANPNP causes certain changes in the adsorption of water from air (Figures 7 and S10–S14, a broad IR band at 3500–3250 cm$^{-1}$). Adsorbed water partially remains after preheating (see the IR spectra of preheated samples in the Supporting Information). This effect depends also on the structure of the silica surface hydroxyl layer. This appears in variations in intensity of $^1$H MAS and $^{29}$Si CP/MAS (Q$_2$—SiOH, Q$_2$—Si(OH)$_2$) NMR spectra of unmodified silicas (Figures 5, 6, and 9) and also in the values of zeta potential (Table 1, $\zeta$), which becomes less negative due to surface hydrophobization upon substitution of silanols, which is responsible for the surface charging versus pH, for example, pH at negative charging $> pH$ at point of zero charge, by nonpolar functionalities. For example, samples A-300 (hydrophilic) and A-300/PMSS (hydrophobic) are characterized by the $\zeta$ potential of $-4.2$ and $-0.9 \text{ mV}$, respectively. However, there is no linear dependence of $\zeta$ potential on the $C_C$ value as a certain measure of the hydrophobicity of modified surfaces (see Table 1) due to the structural features of a modifier layer depending on a type of PDMS and reaction conditions, as well as structural features of the silicas studied.

![Figure 7](https://example.com/figure7.png)

The IR spectra (in the 3800–1350 cm$^{-1}$ range) of CA-300 unmodified (preheated at 105 and 450 °C) and modified by P3D (cAP3D) and HMDS (cAH).
Thus, features in the organization of NPNP in ANPNP (Figures 1–3 and S1–S6) and changes in the porosity and specific surface area in the ranges of mesopores and macropores (Table 1, Figures 4, and S8), as well as changes in the concentrations of surface silanols (single $\equiv$SiOH and twin $\equiv$ Si(OH)$_2$) can affect the hydrophobilization of NAS by various silicones. This appears first in the different content of the attached hydrophobic functionalities (Table 1, C$_s$ and C$_q$).

Second, the length of PDMS plays a very important role in the degree of hydrophobilization (Table 1, Figures S11–S15). As a whole, the effects of PDMS length on the degree of hydrophobilization can be explained by several factors, such as: (i) longer molecules are characterized by lower molecular mobility due to stronger molecule–molecule or molecule–nanoparticle interactions (the $\eta$ value increases for a polymer alone); (ii) penetration of longer molecules into narrower pores is strongly restricted because longer linear molecules tend to form clews; (iii) longer molecules generate greater steric barriers for interaction of DMC with a silica surface and neighboring PDMS; and (iv) surface-attached longer PDMS fragments produce greater negative effects (umbrella screening) on the possibility of other fragments becoming attached to neighboring active surface sites.

The barriers generated by longer PDMS molecules or their fragments are well seen in the incomplete substitution of surface silanols (the $\theta$ values decreased by 14–50% in comparison to the reaction of silica with short PMS or HMDS, Figures S11–S14). In addition, these factors result in a diminution of intensity of the $D_1$ ($\equiv$Si(CH$_3$)$_2$) line in the $^{29}$Si CP/MAS NMR spectra and also the incomplete disappearance of the $Q_2$ (Si(OH)$_2$) line at $-91$ ppm (Figure 5) or $^1$H MAS NMR at $\delta_{1H} = 4–5$ ppm (related to silanols and bound water) (Figure 6). For AP1 and AEPI, the intensity of the $D_1$ line is maximal and the $Q_2$ line at $-91$ ppm is not observed (Figure 5), as well as the line of silanols/water at $\delta_{1H} = 4–5$ ppm (Figure 6). The IR and NMR spectral features correspond to complete substitution of surface silanols by hydrophobic functionalities generated by PMSS reacted with a silica surface with no DMC (but it is optimal at slightly higher temperatures). These results are close to the ones obtained upon modification of cA-300 by HMDS (Figures 5 and 6) at lower temperature. However, the total weight of the attached cation both by short organosiloxane (e.g., PMSS giving $C_C = 8.2$ wt % (A300) or 9.1 wt % (A-300) at 250 °C) alone or for longer polymers with the presence of DMC. Silicas TS 100 and Syloid 244 modified by PMS200/DMC demonstrate similar $C_C$ values ($\sim$5 wt %) but smaller than that (5.4 wt %) for hydrocompacted cA-300 modified by PMS200/DMC.

Overall, the PDMS/DMC-modified nanostructured silicas could be of interest from a practical point of view, as they remain in a dispersed state with no strong compaction of the secondary structures after the functionalization that is appropriate for better distribution of the modified nanoparticles in various polymer matrices or other nonporal media.

## ASSOCIATED CONTENT

* Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01508.

Information of studied samples; TEM and SEM images of studied samples; nitrogen adsorption–desorption isotherms (77–350 K) data; differential pore size distribution data for synthesized samples; incremental and differential PSD data of unmodified NAS with pore models as voids between silica NPNP and cylindrical pores in silica; $^1$H MAS and $^{29}$Si CP/MAS NMR spectra of unmodified silicas; IR spectra (in the 1380–1350 cm$^{-1}$ range) of synthesized samples; ATR FTIR spectra (in the 1300–750 cm$^{-1}$ range) of various samples; IR spectra (in the 4000–250 cm$^{-1}$ range) of neat PDMS samples; and weight loss due to desorption of water in air from hydrocompacted cA-300 versus time (PDF)

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### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

I.P. is grateful to the China Postdoctoral Science Foundation (grant no. Z741020001) and Z.L. is grateful for financial support to Special Funding from the “Belt and Road” International
Cooperation of Zhejiang Province (grant no. 2015C04005). The authors are grateful to the Center for Integrated Nanotechnologies, an Office of the Science User Facility operated for the U.S. Department of Energy (DOE), Office of Science by Los Alamos National Laboratory (contract DE-AC52-06NA25396), and Sandia National Laboratories (contract DE-NA-0003525) for providing some experimental data.

**ABBREVIATIONS**

NAS, nanostructured amorphous silicas; SiO\(_2\), silica; NPNP, nonporous nanoparticles; A-NPNP, aggregates of NPNP and agglomerated aggregates; \( T_r \), reaction temperature; PDMS, poly(dimethylsiloxane); HMDS, hexamethydisilazane; DMC, dimethyl carbonate; \( \gamma_{\text{BET}} \), surface area; \( \% C_o \), carbon weight percentage; \( \gamma \), chemical shift; CP/MAS NMR, cross polarization magic-angle spinning nuclear magnetic resonance; SAXS, small-angle X-ray scattering; SEM, scanning electron microscopy; TEM, transmission electron microscopy; PSD, pore-size distributions; \( \zeta \), zeta potential; ATR, attenuated total reflection; IR, infrared spectroscopy; \( r \), pore radius; \( V_\text{pore} \), pore volume; \( V_{\text{meso}} \), volume of nanopores (\( R < 1 \, \text{nm} \)); \( V_{\text{meso}} \), volume of mesopores (\( 1 \, \text{nm} < R < 25 \, \text{nm} \)); \( V_{\text{macropore}} \), volume of macropores (\( 25 \, \text{nm} < R < 100 \, \text{nm} \)); \( S_{\text{meso}} \), specific surface area of mesopores (\( R < 1 \, \text{nm} \)); \( S_{\text{macropore}} \), specific surface area of macropores (\( 25 \, \text{nm} < R < 100 \, \text{nm} \)); NLDFT, nonlocal density functional theory; \( R_v \) and \( R_{sp} \), the average pore radii with respect to the pore volume and specific surface area, respectively

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