**Monolithic Hierarchical Fractal Assemblies of Silica Nanoparticles**

Crosslinked with Polynorbornene via ROMP:

A Structure-Property Correlation from Molecular to Bulk through Nano

Dhairyashil P. Mohite[1], Zachary J. Larimore[1], H. Lu[*,2], Joseph T. Mang[*,3],

Chariklia Sotiriou-Leventis[*,1] and Nicholas Leventis[*,1]

1. Department of Chemistry, Missouri University of Science and Technology, Rolla, MO 65409, U.S.A. leventis@mst.edu, cslevent@mst.edu

2. Department of Mechanical Engineering, The University of Texas at Dallas, Richardson, TX 75080, U.S.A. hongbing.lu@utdallas.edu

3. Los Alamos National Laboratory, Los Alamos, NM 87545, U.S.A. jtmang@lanl.gov

Supporting Information

Figure S.1   Rheology during the base-catalyzed (NH$_4$OH, 40 μL) gelation of TMOS at 20 ^{o}C, according to the procedure described in the Experimental section

Figure S.2   Representative IR data (in KCl) of selected aerogel samples

Figure S.3   Overlaid SAXS and SANS data for **n-SiNAD**

Figure S.4   TEM data for the three **X-SiNAD(xx)** samples in comparison to **n-SiNAD** as the latter is shown in Figure 7 of the main article

Table S.1   GPC analysis of **X-SiNAD** samples as well as their crosslinking baths

Appendix I.   Calculation of the fraction of empty space in secondary particles from SAXS data (radii of the primary and secondary particles and the mass fractal dimension)

Appendix II.   Calculation of the polymer content in the **X-SiNAD(xx)** samples

Appendix III.   Calculation of the thickness of a polymer shell from experimental skeletal density data
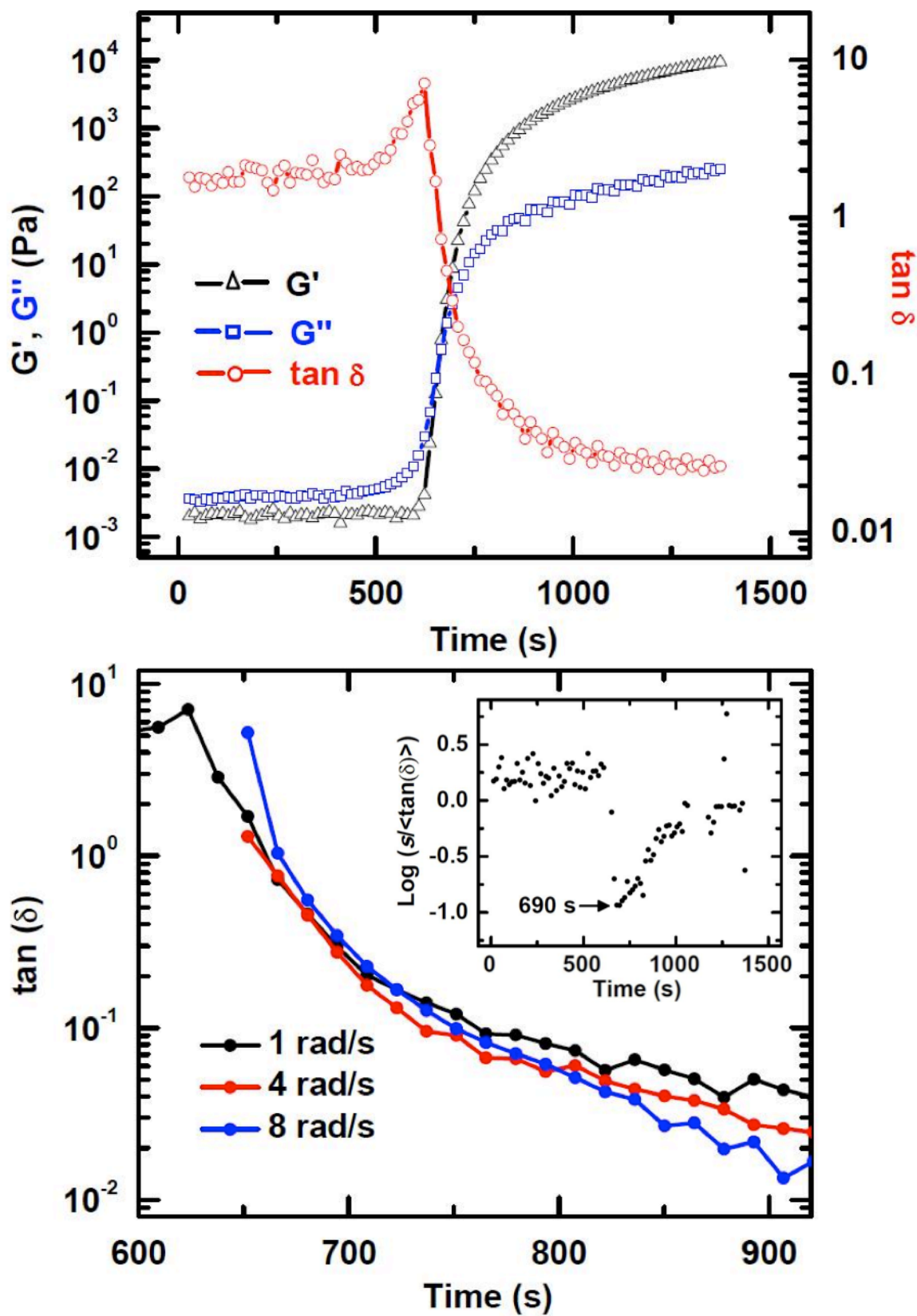
Figure S.1 Rheology during the base-catalyzed (NH$_4$OH, 40 µL) gelation of TMOS at 20 ^{o}C, according to the procedure described in the Experimental section.
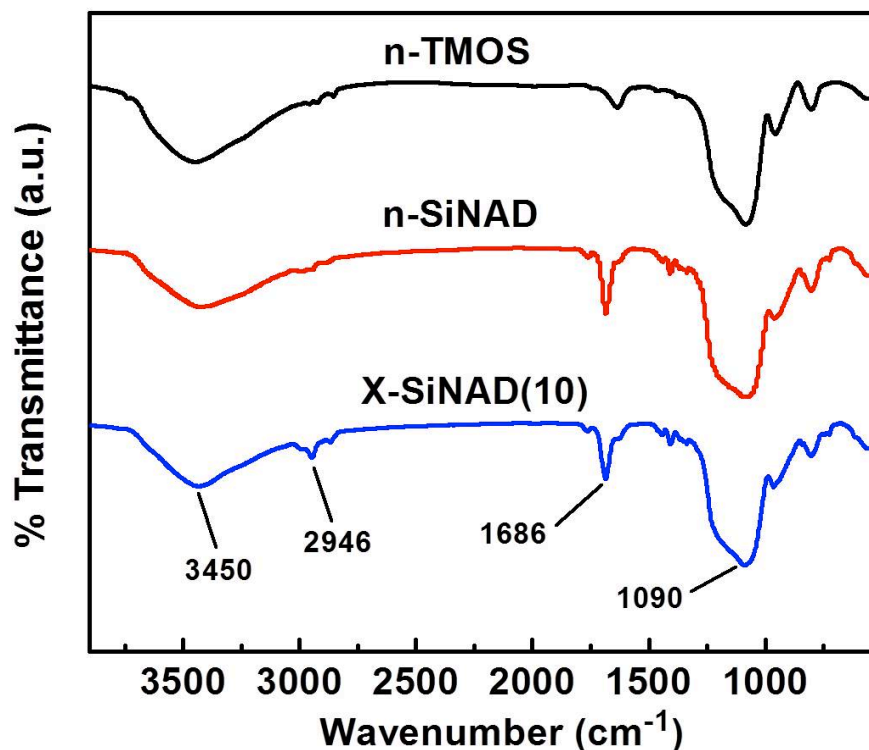
Figure S.2 Representative IR data (in KCl) of selected aerogel samples. All IR spectra are dominated by the characteristic Si-O stretch of silica at 1090 cm^{-1} and the broad absorption of remaining unreacted surface –OH groups in the 3500 cm^{-1} region. The absorption at 1686 cm^{-1} is assigned to the imide C=O stretch of **Si-NAD**, while the absorption bands in the 2870-2960 cm^{-1} range are due to C-H stretches from both **Si-NAD** and polyborbornene.
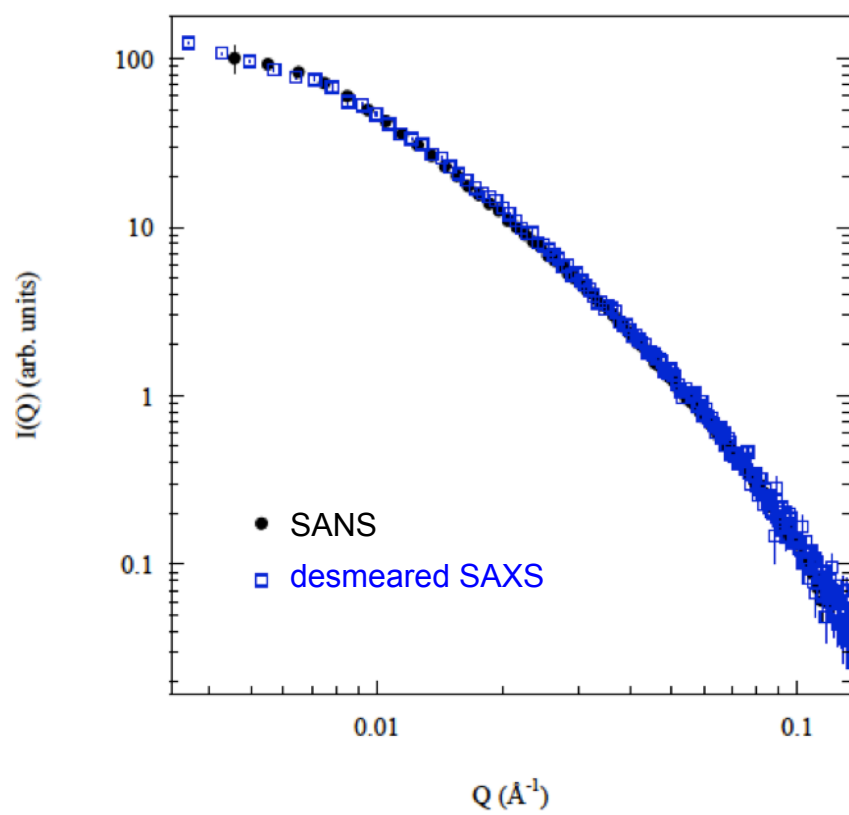
Figure S.3 Overlaid SAXS and SANS data for **n-SiNAD**.
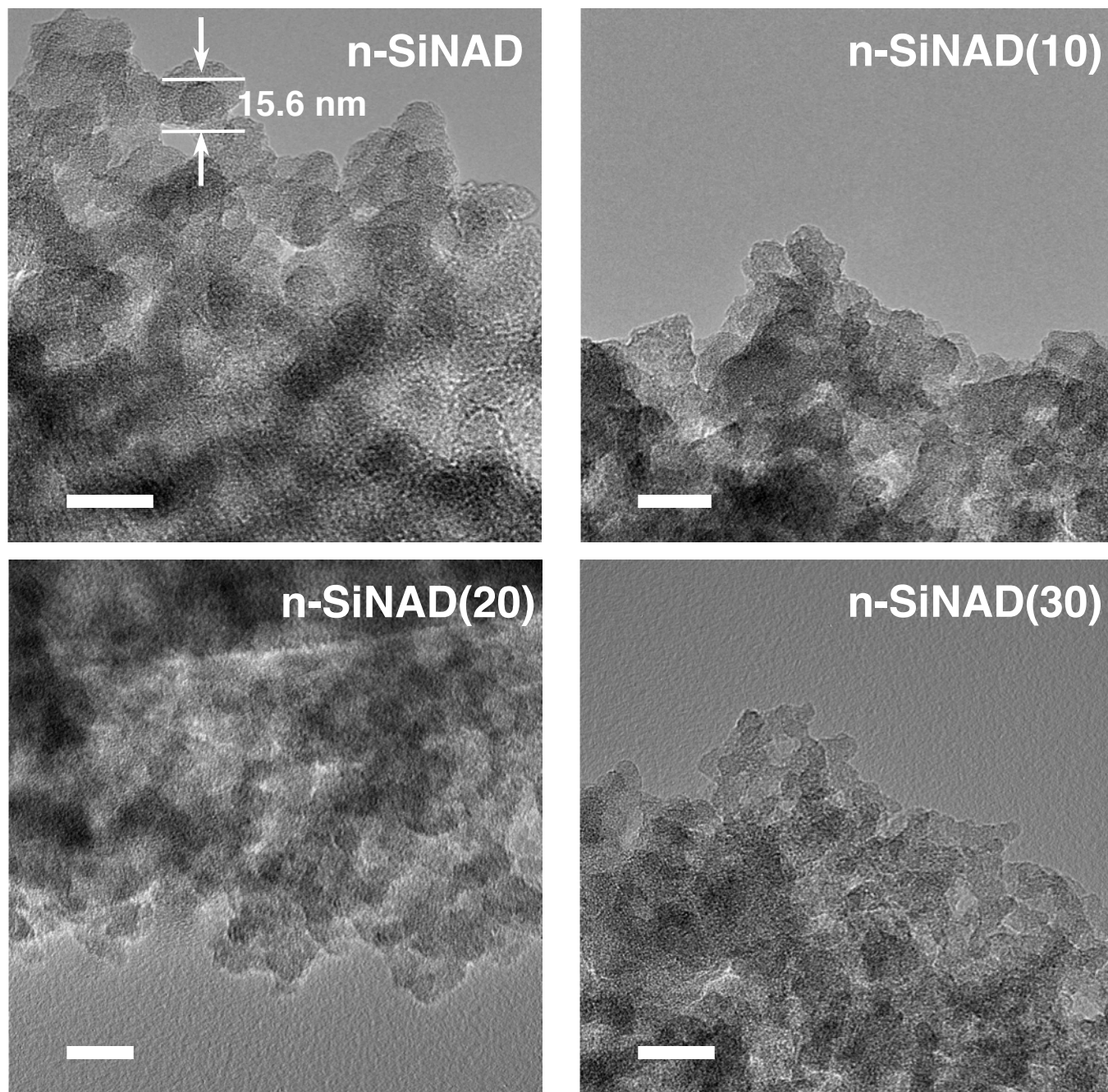
Figure S.4 Transmission electron microscopy (TEM) data for the three **X-SiNAD(xx)** samples in comparison to **n-SiNAD**, as the latter is shown in Figure 7 of the main article. Images of the **X-SiNAD(xx)** samples are blurred due to the small Z-attenuation difference between silica and polymer, and are not conclusive in terms of particles and sizes. All scale bars at 20 nm.

Table S.1   GPC analysis of **X-SiNAD** samples as well as their crosslinking baths [a]

	R_{time} [b] (min)	area[c] %	M_n	M_w	M_w/M_n [d]	N [e]	R_{g_S} [f] (nm)	R_{g_theta} [g] (nm)
X-SiNAD(10)	6.40	32.0	25209	47467	1.88	505	8.29	4.45
	9.65	68.0	457	1033	2.26	11	0.83	0.66
X-SiNAD(20)	6.70	41.2	16583	35661	2.15	379	6.98	3.85
	9.80	58.8	438	763	1.74	8	0.70	0.56
X-SiNAD(30)	6.60	50.2	18064	41244	2.28	439	7.62	4.15
	9.75	49.8	380	961	2.53	10	0.79	0.63
X-link_bath(10)	5.80	23.9	61258	73989	1.20	784	10.80	5.54
	8.4	49.5	1024	10492	10.25	112	3.36	2.10
	10.5	26.6	229	293	1.28	3	0.38	0.34
X-link_bath(30)	6.10	28.3	43780	55839	1.28	594	9.14	4.83
	8.35	52.6	1230	8985	7.30	96	3.06	1.94
	10.7	19.1	176	226	1.28	2.4	0.33	0.31

a. Using a Shodex GPC KH-803L column connected to a Schimadzu liquid chromatograph (LC-10AD) equipped with a UV-Vis detector (SPD-10AV). HPLC grade THF was used as eluent at 1 mL min^{-1}. Linear polystyrene standards from Varian (Polystyrene Low EasiVials; Part No. PL2010-0400 and PL2010-0403) were used for calibration.

b. Retention time

c. Area under groups of peaks as shown in Figure 10 of the main article

d. Polydispersity

e. Number of monomer units = $M_w/M_{w,monomer}$ ($M_{W,monomer}$=94)

f. R_{g_S}: radius of gyration in good swelling solvents (via eq. 6 of the main article)

g. R_{g_theta}: radius of gyration in theta solvents (via eq. 7 of the main article)

Appendix I.   Calculation of the fraction of empty space in secondary particles from SAXS data (radii of the primary and secondary particles and the mass fractal dimension)

The number of spherical primary particles, $n(r)$, of radius r_o in a larger sphere (e.g., a secondary particle) of radius r is given by:

$$n(r) = \xi \left[\frac{r}{r_o} \right]^{D_f}, \text{ where}$$

ξ: packing factor, indicating how primary particles are packed. For Euclidian space and cubic or hexagonal close-packing, $\xi = \pi/3\sqrt{2} = 0.7405$ [S.1].

Also,

volume of secondary particle $= \dfrac{4}{3}\pi r^3$

volume of primary particles $= \dfrac{4}{3}\pi r_o^3$

therefore,

volume of empty space in secondary particles =

$$= \frac{4}{3}\pi r^3 - n(r)\frac{4}{3}\pi r_o^3 = \frac{4}{3}\pi \left[r^3 - \xi\left(\frac{r}{r_o}\right)^{D_f} r_o^3 \right] = \frac{4}{3}\pi r_o^3 \left[\left(\frac{r}{r_o}\right)^3 - \xi\left(\frac{r}{r_o}\right)^{D_f} \right] = \frac{4}{3}\pi r^3 \left[1 - \xi\left(\frac{r}{r_o}\right)^{D_f-3} \right]$$

or,

$$\text{volume of empty space in secondary particles} = \frac{4}{3}\pi r^3 \left[1 - \xi\left(\frac{r}{r_o}\right)^{D_f-3} \right]$$

For D_f=3, this formula reproduces the volume fraction of empty space in close-packed spheres, that is $(1-\xi) \approx 0.26$

For native **n-SiNAD** from SAXS (Table 2 in the main article):
r_o = 7.71 nm (primary particles)
r = 28.7 nm (secondary particles)
D_f=2.07
Therefore,
volume of empty space in secondary particles = 78 %

[S.1]   Lee, D. G.; Bonner, J. S.; Garton, L. S.; Ernest, A. N. S.; Autenrieth, R. L. *Wat. Res.* **2000**, *34*, 1987-2000.

Appendix II. Calculation of the polymer content in the X-SiNAD(xx) samples

Table S.2 TGA data for the native and crosslinked aerogel samples

Sample	% wt loss from TGA in air	% residue from TGA in air	% polymer
n-SiNAD	24	76	N/A
X-SiNAD(10)	36	64	16
X-SiNAD(20)	44	56	26
X-SiNAD(30)	53	47	38

Consider 1 g of any **X-SiNAD(xx)** sample. It has two components, silica and organic. Therefore:

1 g of **X-SiNAD** = Mass (Silica) + Mass(Organic Component)

In turn, the Organic Component has also two contributing components: (a) from the native skeletal framework (due to the **Si-NAD** moieties); and, (b) from the accumulated polymer (polynorbornene). Therefore:

1 g of **X-SiNAD** = Mass(Silica) + Mass(Organic from native network) + Mass(Polymer)

Always,

Mass(Silica) = TGA residue

Also,

Mass(Organic from native network)/Mass(Silica) = 0.24/0.76 (from the TGA analysis of the native **n-SiNAD**)

Or,

Mass(Organic from native network) = (0.24/0.76) × (TGA residue)

Therefore,

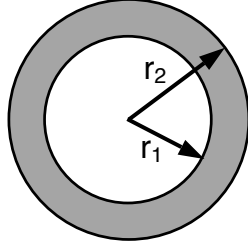1 g of **X-SiNAD** = (TGA residue) + (0.24/0.76) × (TGA residue) + Mass(Polymer)

For **X-SiNAD(10)** for example:
From TGA in air, TGA residue = 0.64 g, therefore Mass(Polymer) = 0.16 g

Similarly for **X-SiNAD(20)** and **X-SiNAD(30)**.

Appendix III. Calculation of the thickness of a polymer shell from experimental skeletal density data

Volume of core $= \dfrac{4}{3}\pi r_1^3$

Volume of shell $= \dfrac{4}{3}\pi\left(r_2^3 - r_1^3\right)$

$Mass_{Total} = Mass_{core} + Mass_{shell} = \dfrac{4}{3}\pi r_1^3\rho_{core} + \dfrac{4}{3}\pi\left(r_2^3 - r_1^3\right)\rho_{shell}$

Density of the entire assembly =

$= \dfrac{Mass_{Total}}{Volume_{Total}} = \dfrac{\dfrac{4}{3}\pi\left[r_1^3\rho_{core} + (r_2^3 - r_1^3)\rho_{shell}\right]}{\dfrac{4}{3}\pi r_2^3} = \left(\dfrac{r_1}{r_2}\right)^3\rho_{core} + \left[1 - \left(\dfrac{r_1}{r_2}\right)^3\right]\rho_{shell}$

whereas here,

Density of the entire assembly $= \rho_s$ (experimental skeletal density for each **X-SiNAD**(xx))

$\rho_{core} = \rho_{silica}$ (skeletal density of the native **n-SiNAD** aerogels, measured at 1.811 g cm^{-3})

$\rho_{shell} = \rho_{polymer}$ (density of polynorbornene, measured by He pycnometry at 1.129 g cm^{-3})

Now, let $\dfrac{r_1}{r_2} = x$

Then, $\rho_s = \rho_{silica}x^3 + (1 - x^3)\rho_{polymer}$, hence $x = \dfrac{r_1}{r_2} = \sqrt[3]{\dfrac{\rho_s - \rho_{polymer}}{\rho_{silica} - \rho_{polymer}}}$

For **X-SiNAD(10)**

$\rho_s = 1.609$ g cm^{-3} (Table 4 in main article), therefore $\dfrac{r_1}{r_2} = 0.89 \Rightarrow r_2 = \dfrac{r_1}{0.89}$

Since the radius of the primary particle r_1=7.71 nm (by SAXS, Table 2 in main article), then $r_{core-shell\_particle}$=8.7 nm (found by SAXS 7.7±0.1 nm, with a surface density-gradient layer thickness of 0.6 nm)

For **X-SiNAD(20)**

ρ_s = 1.505 g cm^{-3} (Table 4 in main article), therefore $\dfrac{r_1}{r_2} = 0.82 \Rightarrow r_2 = \dfrac{r_1}{0.82}$

Since the radius of the primary particle r_1=7.71 nm (by SAXS, Table 2 in main article), then $r_{core-shell\_particle}$=9.4 nm (found by SAXS 8.2±0.3 nm, with a surface density-gradient layer thickness of 0.7 nm)

And, for **X-SiNAD(30)**

ρ_s = 1.391 g cm^{-3} (Table 4 in main article), therefore $\dfrac{r_1}{r_2} = 0.73 \Rightarrow r_2 = \dfrac{r_1}{0.73}$

Since the radius of the primary particle r_1=7.71 nm (by SAXS, Table 2 in main article), then $r_{core-shell\_particle}$=10.6 nm (found by SAXS 9.4±0.1 nm, with a surface density-gradient layer thickness of 0.63 nm)