SUPPORTING INFORMATION

On the origin of scattering of contrast-matched nanoparticle: A study of chain and filler structure in polymer nanocomposites

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This document gives additional information about the silica volume fraction in nanocomposites, glass-transition temperatures, determination of various scattering length densities, and fits of SANS curves for the various silica volume fractions using the model presented in the article.

1. Silica volume fractions in nanocomposites

The silica volume fraction Φ_{Si} in nanocomposites was measured by thermogravimetric analysis (TGA) using a procedure described previously [1].

Table S1. Silica volume fractions (%v) in nanocomposites measured by TGA.

Nominal Φ_{Si}	17k, 5nm	17k, 14nm	100k, 5nm	100k, 14nm
1	0.8	0.4	1.2	0.9
3	2.4	2.3	-	2.6
5	-	4.4	5.5	3.2
10	9.6	8.7	10.3	8.9

2. Glass-transition temperature of nanocomposites

The glass-transition temperature (T_g) of nanocomposites was measured using a Modulated Differential Scanning Calorimeter (MDSC**).** Two temperature ramps of 20 K/min from 253 K to 423 K were performed before a modulated ramp with a period of 60 s, amplitude of 0.5 K and ramp of 3 K/min. T_g was determined as the maximum of the reversible heat capacity derivative versus temperature.

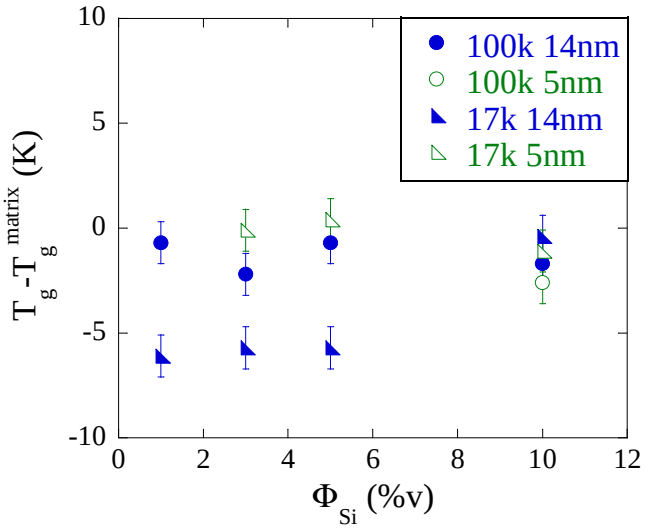

Figure S1. T_g shifts of nanocomposites with respect to the matrix as a function of silica volume fraction for both silica particle sizes and both polymer molecular weights.

Up to Φ_{si} = 10%v, there is no significant impact of silica on the polymer T_g in nanocomposites.

3. Contrast variations

To determine the scattering length densities of silica nanoparticles (NPs) and nanolatex particles we used the contrast-variation method [2]. Four dilutions of each colloidal solution were performed using different D_2O/H_2O mixtures. Figures S2 and S3 display the contrast-variation results. Table S2 summarizes concentration of solutions and measured scattering length densities.

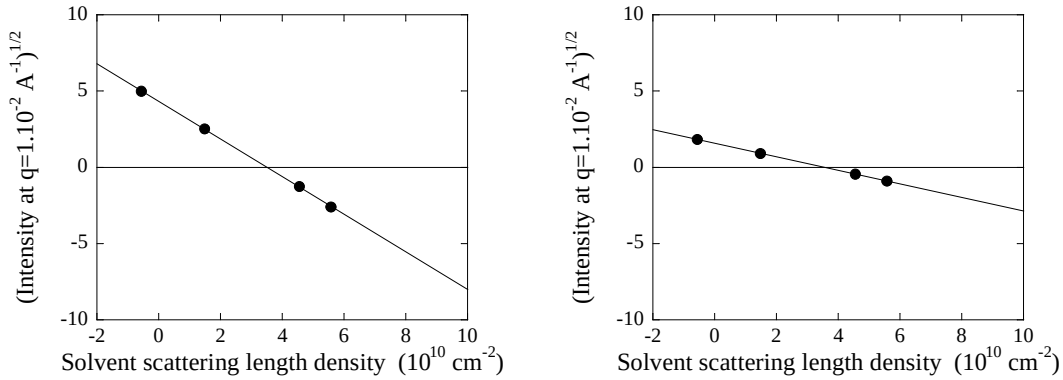

Figure S2. Contrast variation of silica nanoparticles **(a)** TM40-3.5, **(b)** SM30-3.5

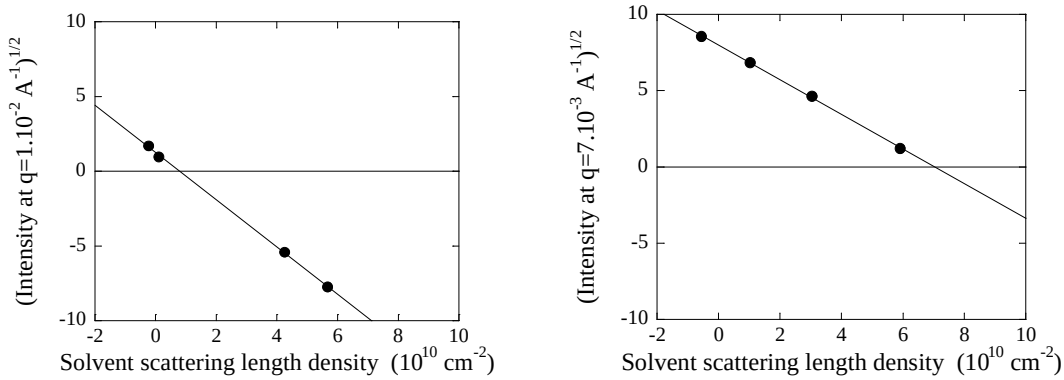

Figure S3. Contrast variation of lattices **(a)** Hydrogenated PEMA latex-0.8, **(b)** Deuterated PEMA latex-7.0.

Table S2. Summary of volume fractions used for contrast-variation experiments and scattering length densities measured.

Sample	**Φ (%v)**	**ρ (10^{10} cm^{-2})**
TM40	0.8	0.5 +/- 0.1
SM30	0.8	0.5 +/- 0.1
H-PEMA	0.5	0.8 +/- 0.1
D-PEMA	0.2	7.0 +/- 0.1

4. Fits of SANS curves

Figure 7b of the article displays the comparison of SANS curve of 10%v-nanocomposites made with small silica NPs with the shell model, which includes the partially dissolved latex bead contribution in the 100k case. In Figures S4 and S5, the same comparisons are performed for lower values of Φ_{Si}.

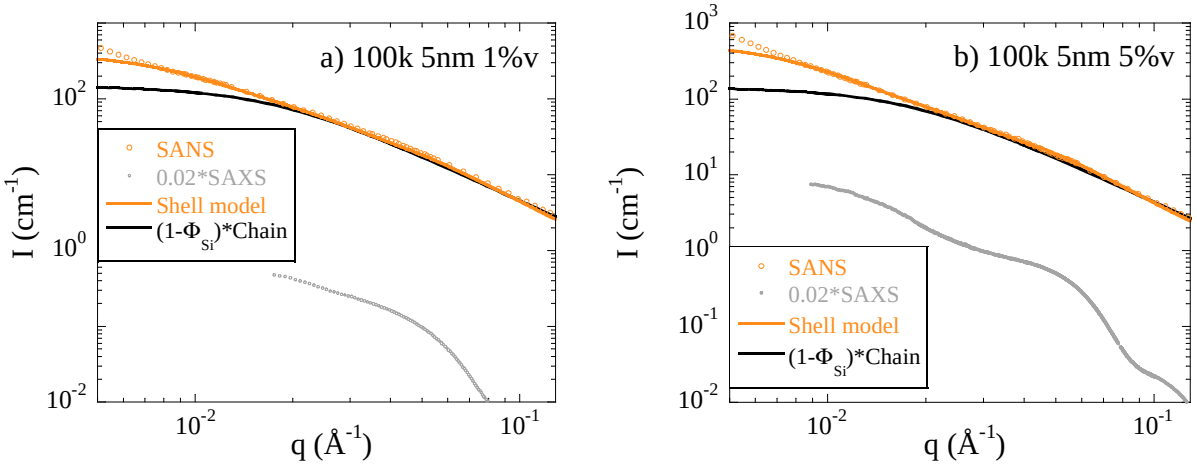

Figure S4. (a) 1%v, **(b)** 5%v. Comparison of the SANS intensity of the nanocomposites (long chains, small NPs) with partially dissolved latex beads. The shell model predicts a negligible contribution (included) of the corresponding silica signal as shown in the plot.

In long chains, small NPs nanocomposites, the latex beads dissolution parameter decreases continuously with increasing silica fraction from α = 86% in the pure matrix to 41% in the 10%v-nanocomposites. The dissolution levels for 1% and 5%-nacocomposites are 80% and 75%, respectively.

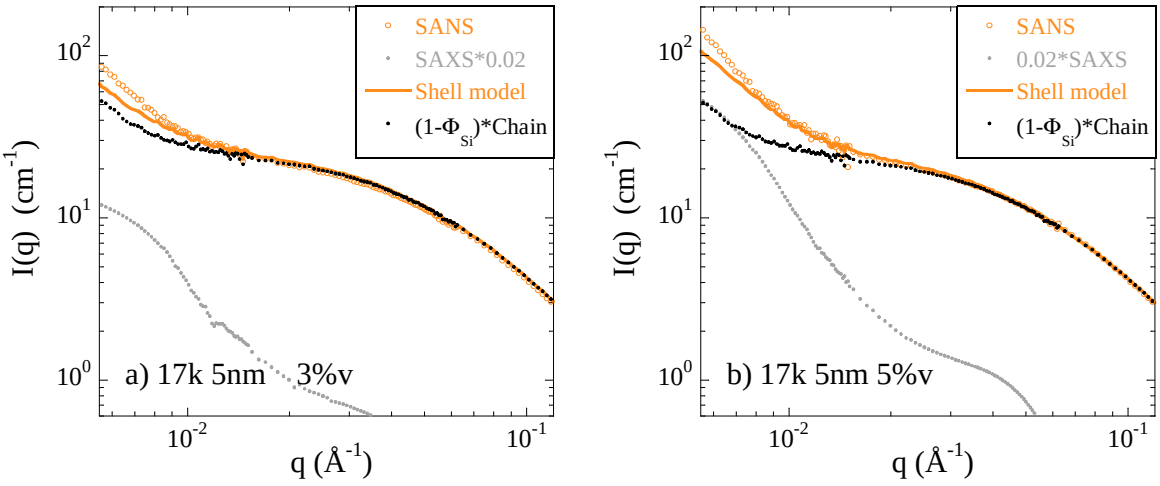

Figure S5. (a) 3%v, **(b)** 5%v. Comparison of the SANS intensity of the nanocomposites (short chains, small NPs) with a linear combination of the experimental chain signal and the silica contribution following the shell model explained in the article.

In short chains, small NPs nanocomposites, the low-q upturn is described by a shell contribution with a constant factor K = 0.02 corresponding to a 1.6 nm-thick shell.

References

(1) Banc, A.; Genix, A. C.; Chirat, M.; Dupas, C.; Caillol, S.; Sztucki, M.; Oberdisse, J. *Macromolecules* **2014,** *47* (9), 3219–3230.

(2) Lindner, P., *Neutrons, X-ray and Light Scattering*. North Holland, Elsevier: 2002.