

Supporting Information

Morphology of Blends with Cross-Linked PMMA Microgels and Linear PMMA Chains

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Estimation of Polydispersity of Deuterated Colloids by DLS in Water. Colloids were characterized by means of DLS in order to investigate the polydispersity, which is expressed in terms of var_z . Each colloid was characterized in the range of $30^\circ \leq \theta \leq 80^\circ$ and the resulting intensity-correlation functions were evaluated with a decay to 31 % and to 10 % of the amplitude by the second order cumulant method.¹

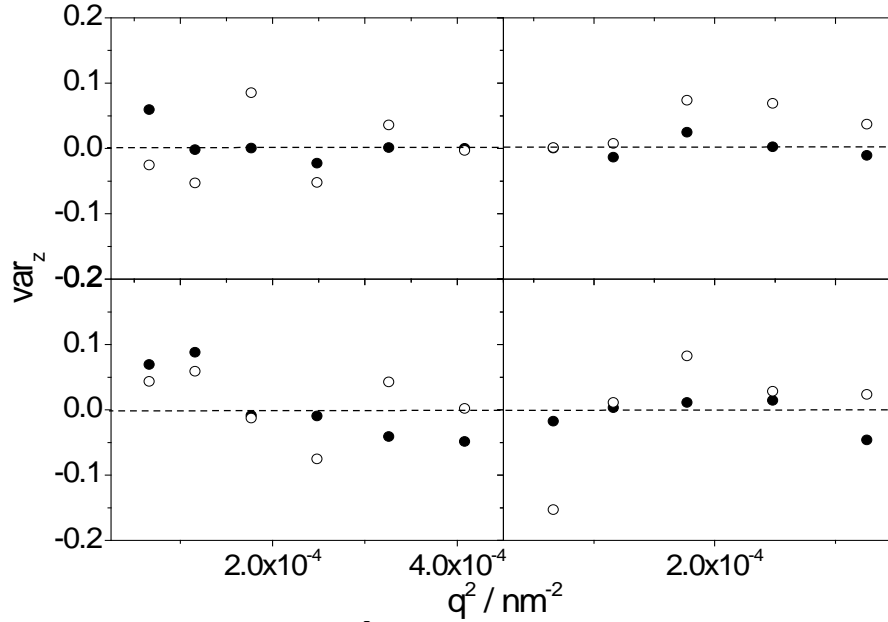


Figure S1: Plot of var_z -values versus q^2 , which were established by DLS in water for colloids D70-LC (A), D70-HC (B), D140-LC (C) and D140-HC (D). The field-time-autocorrelation-functions were evaluated with a decay to 31 % (●)¹ and to 10 % (○) of the initial value. The dashed line represents the mean value of the averaged var_z -values where a decay to 31 % was used.

Swelling Behavior of Deuterated Colloids and Hydrogenated Colloids. Hydrogenated colloids were synthesized according to the same protocol also used for the preparation of deuterated colloids (see Experimental Part). The amount of added cross-linker was successively increased from 1.5 mol-% up to 20 mol-% cross-linker leading to 6 samples of hydrogenated colloids all having a size in water, which is close to $R_g = 70$ nm. The resulting colloids were characterized by means of DLS in water and THF. Figure S2 depicts the swelling ratios of the hydrogenated colloids including an exponential regression in comparison with the swelling ratio

for the deuterated colloids D70-LC and D70-HC and the hydrogenated colloids H70-LC and H70-HC all used in the present work.

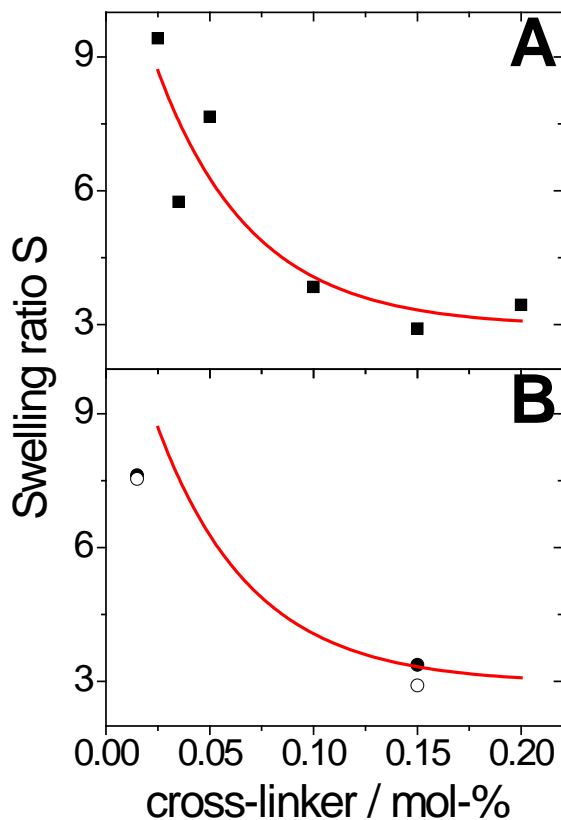


Figure S2: (A) Calculated swelling ratios S for a series of hydrogenated colloids (■) as a function of the added cross-linker including an exponential regression to these swelling ratios. (B) Swelling ratios of the deuterated colloids D70-LC and D70-HC (●) and the hydrogenated colloids H70-LC and H70-HC (○), which were used for the SANS-experiments on blends, in comparison with the exponential regression (—) of Figure S2(A).

Scanning Electron Microscopy (SEM) on Deuterated Colloids. The solutions of deuterated colloids in THF, which were used for SANS-experiments, were also applied for the SEM-experiments. A few drops of the solution with $c = 1$ g/l were placed on a glass substrate. The solvent was gently evaporated and the remaining solid was sputtered with a 3 nm gold layer to avoid charging effects (Bal-Tec SCD 500. U.K.). All SEM-images were taken with a NEON 40 focused ion beam scanning electron microscope (Zeiss. Germany). Figure S3 - S6 show

exemplary SEM-pictures of all four deuterated colloids at magnification levels indicated in the respective Figures.

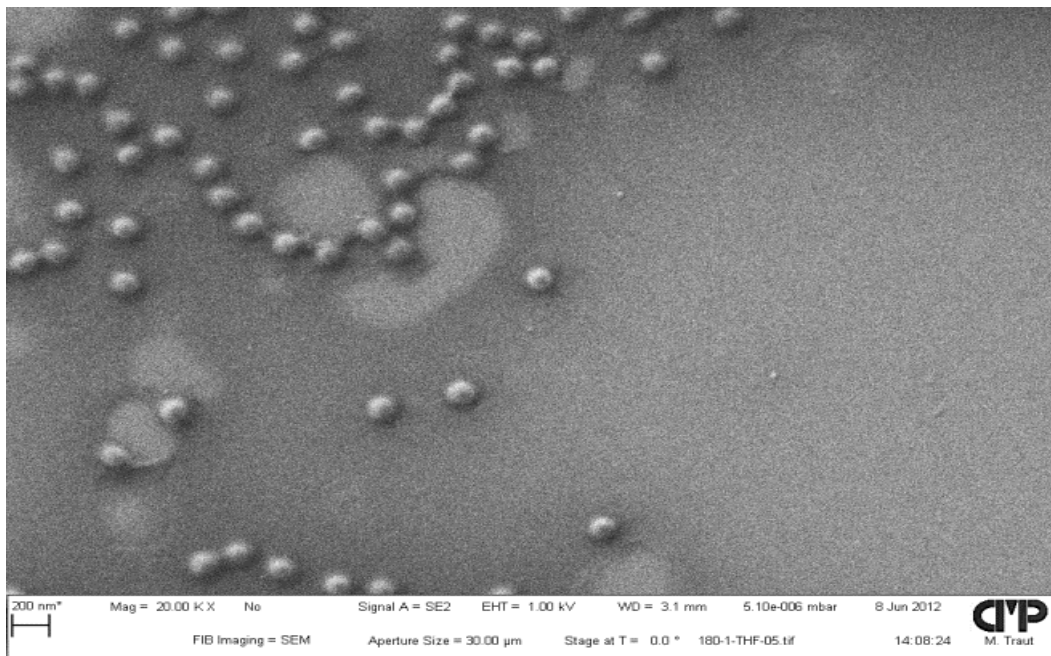


Figure S3: SEM-image of the deuterated colloid D70-LC.

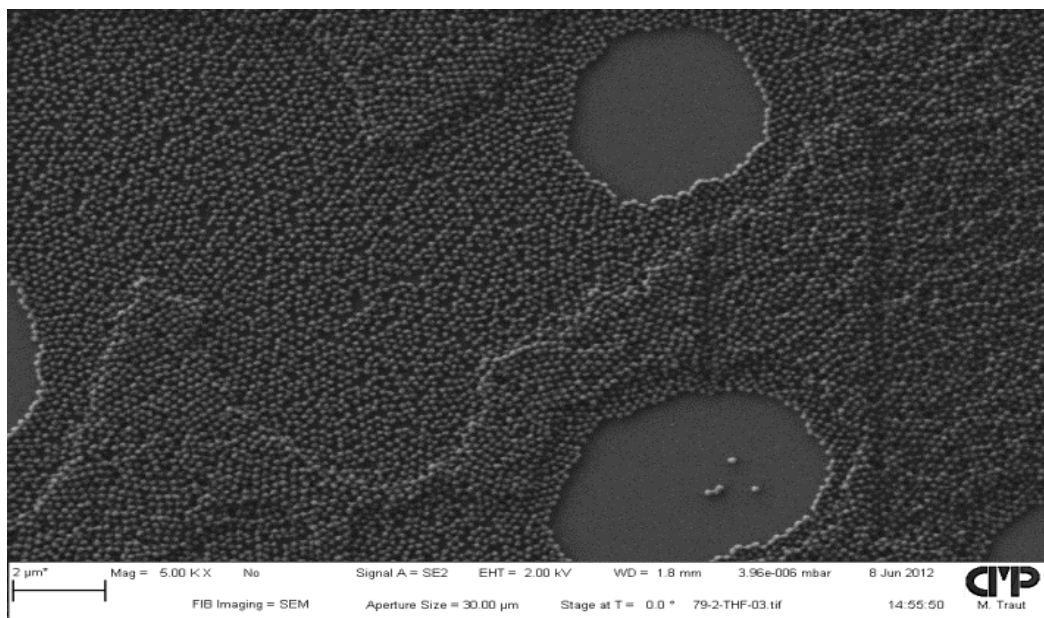


Figure S4: SEM-image of the deuterated colloid D70-HC.

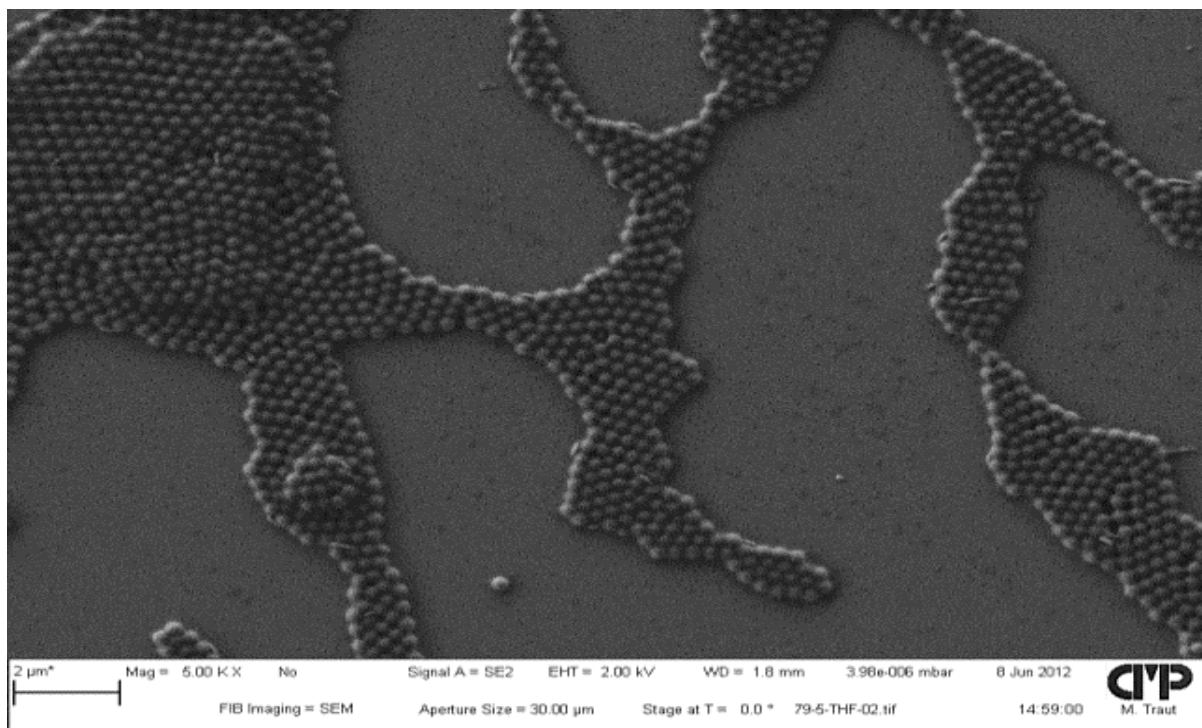


Figure S5: SEM-image of the deuterated colloid D140-LC.

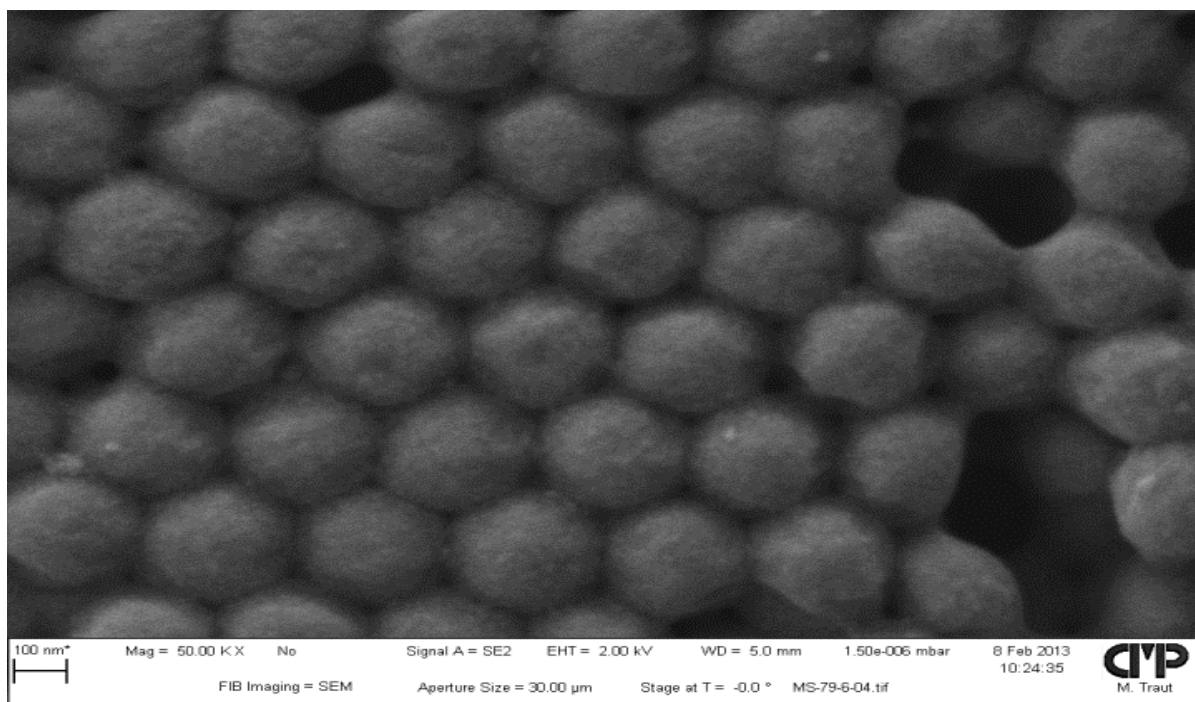


Figure S6: SEM-image of the deuterated colloid D140-HC.

SANS-Investigations of Blends with Deuterated and Hydrogenated Colloids. SANS-experiments were performed on blends with binary mixtures of the deuterated colloids D70-LC and D70-HC and the respective hydrogenated colloids H70-LC and H70-HC. The blends were composed of 95.0 % PMMA-6N, 0.5 wt-% deuterated colloid species D70-LC or D70-HC and 4.5 wt-% hydrogenated species H70-LC or H70-LC. For the background subtraction, we prepared two blends, which included 95 wt-% PMMA-6N and 5 wt-% of the hydrogenated colloid H70-LC or H70-HC respectively. The hydrogenated colloids H70-LC and H70-HC were prepared according to same protocol as applied for the deuterated colloids (see Paragraph Surfactant-Free Emulsion Polymerization (SFEP) of the Experimental section). The reaction volume for the synthesis of hydrogenated colloids was a scale-up from $V = 0.185$ l for the deuterated colloids to a reaction volume of $V = 0.4$ l, since larger amounts of the hydrogenated colloid were required for blend preparation. The resulting colloids were characterized by combined SLS and DLS-experiments in water and THF in order to prove, if the hydrogenated colloids have nearly the same particle size and swelling behavior as the respective deuterated colloids. The comparison of SLS and DLS-results are summarized in Table S1. The swelling ratio in function of the amount of added cross-linker, which is shown in Figure S2B, nicely illustrates that the hydrogenated colloids exhibit almost identical swelling ratios as the respective deuterated colloids. Nearly identical particle size values and swelling ratios of the hydrogenated and deuterated colloids enabled us to prepare blends with binary colloidal mixtures, where the two colloids only differ in their scattering contrast. These blends were prepared according to the FD method.

The results summarized in Figure S6 und S7 showed (in agreement with the data in Figure 6 of the manuscript) that the low cross-linked colloids are well dispersed in the polymer matrix and

the high cross-linked particles are aggregated. Unlike to the SANS experiments on blends with purely deuterated colloids at a high cross-linking density, the slope towards lower q -values significantly decreased (see Figure S7) and a second and third shoulder got observable. Strikingly the decay of the initial Guinier shoulder to the undulation is much smaller in case of the colloid with the high cross-linking density (where aggregates are formed) than with the colloid having a low cross-linking density.

Table S1: Characterization of the hydrogenated colloids H70-LC and H70-HC in water and THF by combined SLS and DLS.

Batch	c [MMA] / mol/l	cross-linker / mol-%	H ₂ O			THF			S
			R_g / nm	R_h / nm	ρ	R_g / nm	R_h / nm	ρ	
H70-LC	0.1	1.5	74.0	96.0	0.77	77.3	188.3	0.53	7.54
H70-HC	0.1	15.0	83.4	104.2	0.80	102.4	148.8	0.69	2.91

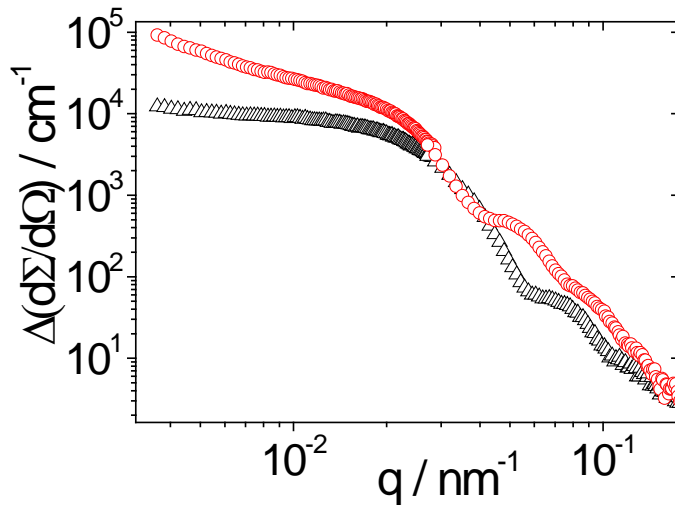


Figure S7: SANS data of blends with 95.0 wt-% PMMA-6N, 0.5 wt-% deuterated colloids D70-LC (Δ) or D70-HC (\circ) and 4.5 wt-% of the corresponding hydrogenated colloid, which is H70-LC or H70-HC respectively. Both blends were prepared by the FD method.

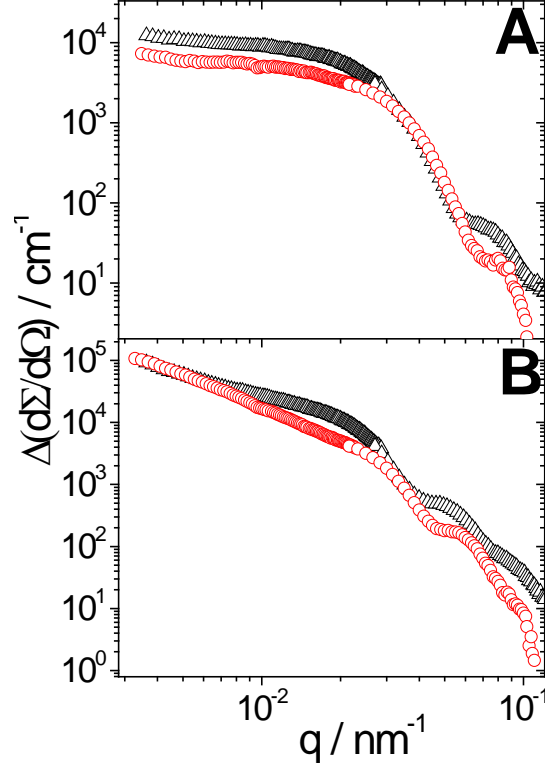


Figure S8: (A) Scattering curves of blends with 0.5 wt-% (Δ) of the pure deuterated colloid D70-LC and a binary mixture with 4.5 wt-% of the hydrogenated H70-LC and 0.5 wt-% of the deuterated colloid D70-LC (\circ). (B) Scattering curves of blends with 0.5 wt-% of the pure deuterated colloid D70-HC (Δ) and a binary mixture with 4.5-wt-% of the hydrogenated H70-HC and 0.5 wt-% of the deuterated colloid D70-HC (\circ).

Calculation of the Scattering Intensity of an Octahedron with Spherical Core. The scattering amplitude A_o of a homogeneous octahedron was given by Stokes and Wilson^{2,3} as a function of the octahedron radius R_o (= edge length / $2^{1/2}$) and of the spatial orientation defined by azimuth angle α and polar angle β .

$$A_o(q, R_o, \alpha, \beta) = \frac{6R_o^3(\rho_o - \rho_{\text{solv}})}{(x^2 - y^2)} \left(\frac{y \sin(y) - z \sin(z)}{y^2 - z^2} + \frac{z \sin(z) - x \sin(x)}{x^2 - z^2} \right) \quad (\text{S1})$$

where

$$x = qR_o \cos(\alpha) \sin(\beta) \quad (\text{S2})$$

$$y = qR_o \sin(\alpha) \sin(\beta) \quad (\text{S3})$$

$$z = qR_o \cos(\beta) \quad . \quad (S4)$$

Correspondingly, the scattering amplitude of a homogeneous sphere was given by Lord Rayleigh⁴ as a function of the sphere radius R .

$$A_s(q, R) = \frac{4\pi R^3(\rho_s - \rho_o)(\sin qR - qR \cos qR)}{(qR)^3} \quad (S5)$$

In eq(S1) and eq(S5), the scattering length densities of the octahedron, the sphere and the solvent are represented by ρ_o , ρ_s and ρ_{solv} . Since a sphere is invariant to spatial orientation, eq(S5) is independent of α and β . The sphere radius in eq(S5) in the present case corresponds to the radius of the spherical core and will be thus denoted as R_c .

In order to calculate the scattering intensity of octahedral particles with spherical cores, $I_{\text{so}}(q)$, the squared scattering amplitude has to be averaged over all possible spatial orientations according to

$$I_{\text{so}}(q, R_o, R_c, \rho_s, \rho_c, \rho_{\text{solv}}) = \frac{N}{4\pi V} \int_{\alpha=0}^{2\pi} \int_{\beta=0}^{\pi} (A_s + A_o)^2 \sin \beta \, d\beta \, d\alpha \quad (S6)$$

with N/V being the number concentration of particles. The smearing of the calculated octahedral core-shell form factor $P_{\text{SO}}(q)$ was taken into account by the instrumental resolution function $R(q, q')$ with $\Delta q/q = 0.13$ and the approximation $\sigma \approx \Delta q = 0.13$ is valid, which was defined in eq(16) of the manuscript. The smeared model intensity $I_{\text{smeared}}(q, \sigma)$ was calculated according to

$$I_{\text{smeared}}(q, \sigma) = \int_0^{\infty} R(q, q') I_{\text{SO}}(q') \, dq' \quad . \quad (S7)$$

Optical Transmission Measurements on Polymer-Colloid Solutions at Variable Shelf Life Time Compared to SANS-Experiments on Blends from these Precursor Solutions. Colloid-polymer solutions of all four deuterated colloids in chloroform were analyzed by transmission measurements at a fixed wavelength of $\lambda = 500$ nm. Mixed polymer-colloid solutions were referred to pure PMMA-6N solution at the same PMMA-6N concentrations as in the colloid-

polymer solutions, which served as reference. The results of time dependent transmission experiments are shown in Figure 11 of the manuscript. The transmission T of a colloid-polymer solution was calculated as follows

$$T = \frac{I(\text{polymer} + \text{colloid})}{I(\text{polymer})} \quad (\text{S8})$$

Parallel to the transmission-experiments, we took identically prepared solutions with D140-LC and D140-HC colloids corresponding to different ageing times and prepared blends by the SE method. The blends were characterized by means of SANS at a detector-to-sample distance of $L = 1.2$ m. The results for the blends are depicted in Figure S9.

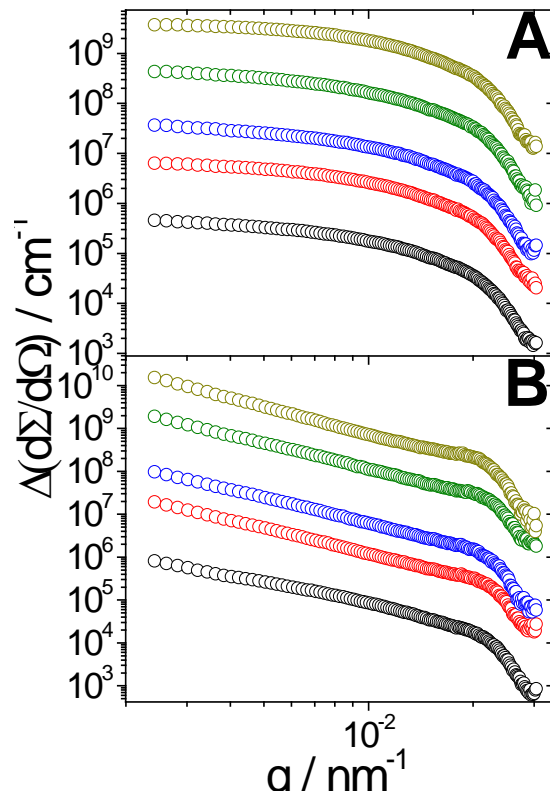


Figure S9: Scattering curves of blends with the colloid D140-LC with low cross-linking density (**A**) and the colloid D140-HC with high cross-linking density (**B**). Both blends were prepared by the SE method after 1 h (●), 1 day (●), 10 days (●), 14 days (●) and 20 days (●) of shelf life of the mixed colloid-polymer solution (precursor solution) in chloroform. The second, third, fourth and fifth scattering curve in (**A**) and (**B**) is shifted by a factor 10, 100, 1000 and 10000 respectively.

References

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