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On tuning microgel character and softness of cross-linked polystyrene particles - Electronic Supplementary Information (ESI)

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1 Additional tables and figures

Table 1 Weighed-in quantities in g and mmol of the syntheses of the particles discussed in section 3.1

0	1	1					
	Cross-link density	Styrene / g (mmol)	DIPB / g (mmol)	K ₂ S ₂ O ₈ / g (mmol)	SDS / g (mmol)	NaHCO ₃ / g (mmol)	Water / g
P150-10	1:10	13.2 (127)	1.01 (6.35)	0.100 (0.371)	0.126 (0.438)	0.0608 (0.724)	380
P150-50	1:50	18.0 (173)	0.280 (1.77)	0.201 (0.743)	0.445 (1.54)	0.121 (1.43)	380
P150-100	1:100	18.1 (174)	0.139 (0.876)	0.200 (0.741)	0.560 (1.94)	0.141 (1.67)	380
P180-10	1:10	13.2 (127)	1.00 (6.33)	0.100 (0.370)	0.100 (0.347)	0.0180 (0.214)	380
P180-25	1:25	14.0 (135)	0.425 (2.69)	0.100 (0.370)	0.100 (0.347)	0.0480 (0.571)	380
P180-50	1:50	18.0 (173)	0.270 (1.71)	0.129 (0.477)	0.243 (0.843)	0.0910 (1.08)	380
P180-75	1:75	18.0 (173)	0.183 (1.16)	0.130 (0.481)	0.240 (0.832)	0.0900 (1.07)	380
P180-100	1:100	14.0 (135)	0.101 (0.638)	0.150 (0.555)	0.346 (1.20)	0.0930 (1.11)	380
P250-10	1:10	24.0 (231)	1.82 (11.5)	0.130 (0.481)	0.0147 (0.0510)	0.470 (0.560)	380
P250-25	1:25	20.0 (192)	0.610 (3.86)	0.131 (0.485)	0.0499 (0.173)	0.0896 (1.07)	380
P250-50	1:50	18.1 (174)	0.270 (1.71)	0.130 (0.481)	0.0402 (0.139)	0.0151 (0.180)	380
P250-75	1:75	20.0 (192)	0.206 (1.30)	0.131 (0.485)	0.212 (0.734)	0.0899 (1.07)	380

Table 2 Results of particle characterization of the particles discussed in section 3.1. Radii R according to TEM and Mie-analysis of the SLS-data of the unswollen particles in water, as well as the hard sphere radius defined as $R_{HS} = R_{h,water}Q_{HS}^{1/3}$ in analogy to Ref. 1, the hydrodynamic radii R_h^* , the radii of the homogeneous sphere fit R_{SLS} and of the fuzzy sphere fit R_{fuzzy} in toluene and the effective hard sphere radii R_{eff} determined from the position of the structure factor in 2-EN are given. If the fuzzy sphere model was applied the fuzziess is given in brackets. Furthermore the polydispersities σ_R determined from TEM and SLS in water, as well as $\sigma_{R,SLS}$ of the form factor fits of the swollen particles are quoted. In general $\sigma_{R,SLS}$ is identical in case of the homogeneous sphere fits and the fuzzy sphere fits. The shown values are determined within the following accuracies: $R_{TEM} : \pm 4 nm$, $R_{Mie} : \pm 3 nm$, $R_{HS} : \pm 5 nm$, $R_h : \pm 5 nm$, $R_{SLS} : \pm 3 nm$, $R_{fuzzy} : \pm 10 nm$, $\sigma_{surf} : \pm 5 nm$, $\sigma_R : \pm 0.02$

	Cross-link								
	density	$R_{TEM}(R_{Mie}) / nm$	<i>R_{HS} /</i> nm	<i>R_h</i> */ nm	R _{eff} / nm	R _{SLS} / nm	R_{fuzzy} (a	σ_{surf})/nm $\sigma_{R,TEM}$	$\sigma_{R,SLS}$
P150-10	1:10	104 (102)	146	143	142	132	-	0. 03 (0.06)	0.07
P150-50	1:50	88 (77)	156	143	147	128	-	0.04 (-#)	0.06
P150-100	1:100	70 (63)	145	136	136	94	128(17)	0.09 (-#)	0.10
P180-10	1:10	122 (126)	184	172	168	166	-	0.05 (0.06)	0.05
P180-25	1:25	112 (108)	175	165	160	156	-	0.05 (0.07)	0.05
P180-50	1:50	99 (95)	178	168	165	151	165(7)	0.03 (0.07)	0.06
P180-75	1:75	95 (94)	190	156	169	130	171(20)	0.06 (0.07)	0.07
P180-100	1:100	71 (77)	169	152	149	116	146(15)	0.09 (0.06)	0.08
P270-10	1:10	170 (162)	258	243	243	230	-	0.05 (0.05)	0.07
P270-25	1:25	153 (148)	258	247	252	223	-	0.04 (0.05)	0.07
P270-50	1:50	143 (141)	270	248	265	237	265(14)	0.04 (0.05)	0.04
P270-75	1:75	104 (104)	277	240	241	≈228	252(40)	0.05 (0.08)	0.16

* R_h is the average hydrodynamic radius of measurements in the range of 1.5 < qR_{eff} < 3.5 with steps of 5°.

[#] Since the form factor minimum was not located within the experimental q-range $\sigma_{R,SLS}$ was fixed to $\sigma_{R,TEM}$ for the SLS-fits.

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Table 3 Additional details of the characterization of the particles discussed in section 3.1. The experimental freezing and melting point is given in units of the unswollen volume fraction. Additionally the swelling ratio $Q_{HS} = 0.494 / \Phi_{f,u}$, the melting point $\Phi_m = Q_{HS} \Phi_{m,u}$ and the interaction parameter n are shown. The volume fractions were determined within an accuracy of 0:001, the experimental errors of the interaction parameter n are given in the table

	Cross- link					
	density	$\Phi_{f,u}$	$\Phi_{m,u}$	Q_{HS}	Φ_m	n
P150-10	1:10	0.217	0.234	2.28	0.534	99 ± 15
P150-50	1:50	0.085	0.091	5.8	0.53	39 ± 3
P150-100	1:100	0.066	0.069	7.6	0.52	27 ± 3
P180-10	1:10	0.209	0.215	2.36	0.507	93 ±6
P180-25	1:25	0.152	0.161	3.25	0.523	66 ±1
P180-50	1:50	0.105	0.110	4.70	0.517	49 ± 4
P180-75	1:75	0.085	0.092	5.8	0.53	34 ± 2
P180-100	1:100	0.064	0.068	7.6	0.52	28 ± 5
P270-10	1:10	0.162	0.180	3.05	0.549	63 ± 3
P270-25	1:25	0.118	0.124	4.17	0.517	48 ±6
P270-50	1:50	0.090	0.100	5.5	0.55	39 ±6
P270-75	1:75	0.038	0.042	13	0.55	27 ± 3



Figure 1: Representative TEM pictures of the particle series 270-xx. a) P270-10; b) P270-25; c) 270-50; d) P270-75.

1:xx indicates the crosslink density. It should be noted that there is no indication of fuzziness or a density gradient visible in the TEM viewgraphs, even not in case of P270-75 which shows a very peculiar internal structure in the swollen state as indicated by its P(q) shown in Fig.3d.



Figure 2: Comparison of the position of the structure factor maximum as function of volume fraction Φ of P270-50 with the position calculated for hard spheres of polydispersity σ_R . The lines correspond to spheres of radius R = 267 nm (monodisperse), R = 267 nm ($\sigma_R = 0.03$) and R = 266 nm ($\sigma_R = 0.07$).



Figure 3: Experimental form factors and model fits of swollen particles in toluene. Symbols: experimental P(q), solid lines: homogeneous spheres model, dashed lines: fuzzy sphere model (in (a) – (c) fuzzy sphere fits were calculated fixing $R_{fuzzy} = R_{eff}$). The fit parameters are quoted in Table 2. For easier comparison P(q) was multiplied by the factors quoted on the right side of the figure. (a) 1:10-cross-linked particles. (b) 1:25-cross-linked particles. (c) 1:50-cross-linked particles. (d) 1:75-cross-linked particles.

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Figure 4: Storage and loss moduli, G'(ω) and G''(ω), for the particles of series P270-x (a-d) with a crosslink density of 1:x as well as the plateau moduli G_P derived from these data (e). G_P was determined by the condition $tan(\delta)$ = min which turned out to be coincident with the minimum of $G''(\omega)$ within experimental accuracy. For clarity the G_P data of P270-25 have been multiplied by a factor of 2. Dashed lines in (e) are power law fits according to $G_P \propto \Phi^m$ with the exponents m as indicated in the figure. Symbols in brackets indicate data which have been excluded from the fits due to systematic deviations from power law behavior. Data at high Φ were most likely affected by aging or by insufficient sample equilibration which required exceedingly long times. Data of P270-75 at the lower volume fractions of the monitored Φ-range showed liquid-like behavior (cf. Fig.4d). Obviously, for this particle species the glass transition volume fraction was shifted to a much higher volume fraction ($0.61 < \Phi_g < 0.62$) which may well be a result of the differing peculiar ("open") internal structure as indicated by the unusual form factor P(q) (cf. Fig.3d). For P270-50 data from an independent measurement are shown in addition (open circles; original G'(ω) and G''(ω) data not included in Fig.4c) in Fig.4e. While the two data sets coincide within experimental error in the lower Φ-range clear deviations are seen at the highest volume fractions.

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2 Determination of effective hard sphere radii

Another important parameter needed for mapping any colloidal model system onto hard spheres is the effective hard sphere radius.² Knowledge of this quantity is necessary whenever data obtained on a particular model system are to be compared with data from other model systems - either from experiment or from computer simulation - on absolute scale. Here, data are typically reported in rescaled, radii dependent units, e.g. rescaled shear moduli $G'R/k_BT$ and $G''R/k_BT$ or rescaled short-time and long-time self-diffusion coefficients $(D_s^S / D_0 \text{ and } D_s^L / D_0, \text{ respectively, with } D_0 =$ $k_BT/(6\pi\eta R)$). A major problem here is that different experimental approaches deliver different types of radii varying on an absolute scale.³ Typically the hydrodynamic radius R_h measured by DLS is larger than the radius measured by static scattering methods and the latter is often larger than the radius obtained by TEM. In addition, "static radii" obtained from different techniques like static light scattering (SLS), small angle X-ray scattering (SAXS) and small angle neutron scattering (SANS) again differ from each other. This problem is significantly aggravated in case of microgel particles as scattering contrast influences the contribution of different areas of the particles to the obtained form factor. For example in case of fuzzy spheres the outer area of the fuzzy corona contributes only weakly to the scattering pattern in SANSexperiments and is, thus, difficult to resolve. Therefore, it is often only indirectly observed by its interactions with the dispersion medium in DLS.4 To give an overview of the different particle size measures the corresponding values for the systems reported in this work are listed in Table 2 of this ESI. In addition to the radii in the unswollen state obtained by TEM and and by SLS in water, R_{TEM} and R_{Mie} respectively, we give the hydrodynamic radii R_h in the good solvents toluene, the effective hard sphere radii R_{eff} obtained from static structure factor (S(q)) measurements in 2-EN as well as "static radii" in toluene - either from homogeneous sphere or from fuzzy sphere fits, R_{SLS} and R_{fuzzy} , respectively. Besides these directly measurable radii we report as well two alternative measures of the effective hard sphere radii: R_{HS} used previously for sake of convenience and obtained by multiplying the easily accessible hydrodynamic radius in aqueous dispersion, $R_{h,water}$, by the swelling ratio $Q_{HS}^{1/3}$ and another candidate for R_{eff} , obtained by multiplying the averaged values $R_u = (R_{TEM} + R_{Mie})/2$ again with $Q_{HS}^{1/3}$. The averaging was suggested by the observation that $R_{\rm TEM}$ and $R_{\rm Mie}$ are identical within experimental accuracy. When comparing the values in the swollen state one notices that the "static radii" R_{SLS} and R_{fuzzy} are systematically smaller than the R_{eff} obtained from S(q) measurements, especially when there is a measurable fuzziness. But, as already discussed in the main text of this work, the differences between the "static radii" and R_{eff} are within the accuracy of the model description and indicate that the fuzzy corona is not fully resolved by the fits. In contrast the R_{HS} - previously used as hard sphere radii - are systematically larger than the R_{eff} . Recently, we found first

indications that that these R_{eff} are consistent with R_{eff} values obtained from the main Bragg reflex of crystalline sample or of crystals in the fluid-crystal coexistence region.⁵ Therefore, these R_{eff} appear to be a more reasonable measure of hard sphere radii for PS microgel particles. Interestingly, as shown in Fig. 3a the alternative definition of R_{eff} via the averaged R_u multiplied by $Q_{HS}^{1/3}$ yields values which are within some scatter identical with the R_{eff} from S(q) measurements.

This demonstrates that R_{eff} is a suitable measure of the radius determining the thermodynamic behaviour of the particles, as it can be derived from the direct interactions of the particles, defining their structure in the fluid an crystalline phase (i.e. the position of the S(q)-maximum), as well as from the swelling behaviour defining the first order freezing point.

However, both methods require the beforehand knowledge of the swelling ratio Q_{HS} as this is required for setting the correct volume fraction scale for the S(q) measurements and enters directly into the calculation of R_{eff} in the other case. This again raises the problem of the delay incurred by the lengthy Q_{HS} determination via the analysis of the phase diagram. It would be of considerable help if there were a measure of R_{eff} that is at the same time fast and sufficiently reliable to obtain. In this context it is of interest to notice that the hydrodynamic radii R_h , measured very accurately in toluene, appear to be rather close to the R_{eff} obtained from S(q) measurements in 2-EN. For easier comparison of the data Fig. 5b shows a plot of R_h against R_{eff} .



Figure 5: Comparison of the radii of swollen particles determined by different techniques. The dashed line corresponds to $R_x = R_{eff}$. (a) radii calculated from the radii $R_u = (R_{TEM} + R_{Mie})/2$ of the unswollen particles in water and the one dimensional swelling ratio $Q_{HS}^{1/3}$; (b) hydrodynamic radii R_h in toluene. The colour represents the approximate particle size, while the symbols represent the cross-link density. Representative error-bars are given in the figure.

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As Fig. 3b demonstrates both radii are nearly identical within some experimental scatter with some tendency of a slight deviation for larger particle size. This result implies, that from the measured R_h in toluene a good first approximation for the effective hard sphere radii can be obtained which can then be later refined. Thus, the success of a synthesis with a particular target radius can be evaluated rather quickly by DLS measurements without the need to wait for the lengthy determination of the swelling ratio Q_{HS} . This finding is in contrast to the observation of Eckert et al. who demonstrated that for their PNiPAM-microgels $R_{eff} < R_h$.⁶ They argued that this difference is caused by the compressibility of the outer areas of the fuzzy corona and therefore caused by the softness of the particles. Since our PS-microgels are less soft, R_h is in better agreement with R_{eff} than in case of PNiPAM-microgels.

3 References

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