This file includes:
Supplementary Data for the article "Electrostatics Reshape the Internal Architecture of Ionic Microgels" by Mohanty et al.
Supplementary Text
Tables S1 to S2
Figures S1 to S5.

Supplementary Tables

Table S1: Amounts of the reagents used in the microgels synthesis.

microgel type	$M_{\mathbf{NIPAM}}$ **(g)**	$M_{\mathbf{BIS}}$ **(g)**	$M_{\mathbf{AA}}$ **(g)**	$M_{\mathbf{water}}$ **(g)**
neutral	1.43	0.11	0.00	100
ionic	1.43	0.11	0.08	100

Table S2: Microgel structural parameters as a function of temperature under various pH conditions, as determined by SLS and DLS scattering analyses.

T (°C)	R_c (nm)	σ (nm)	$R_c + 2\sigma$ (nm)	R_{H} (nm)	PDI
ionic, pH 7					
15	555.7 ± 0.9	100.2 ± 2.9	756.1 ± 5.9	1015.9	0.050
20	545.1 ± 2.2	96.5 ± 2.5	738.1 ± 5.5	961.9	0.055
25	536.7 ± 5.3	96.3 ± 4.6	729.3 ±10.6	940.7	0.058
30	521.9 ± 4.2	86.6 ± 0.8	695.1 ± 4.5	992.5	0.073
35	482.4 ± 4.0	76.3 ± 2.8	635.0 ± 6.9	947.2	0.052
40	330.7 ± 0.9	–	330.7 ± 0.9	833.9	0.050
ionic, pH 3.5					
15	529.4 ± 1.3	100.2 ± 1.2	729.8 ± 2.7	650.3	0.058
20	518.7 ± 1.0	92.0 ± 0.9	702.7 ± 2.1	611.9	0.065
25	488.2 ± 3.5	82.5 ± 2.5	653.2 ± 6.1	577.8	0.073
30	438.0 ± 1.1	68.0 ± 1.1	574.0 ± 2.5	518.5	0.050
35	343.6 ± 0.2	–	343.6 ± 0.2	347.2	0.050
40	340.4 ± 0.2	–	340.4 ± 0.2	330.9	0.050
neutral					
15	407.2 ± 1.1	63.5 ± 0.8	534.2 ± 1.9	472.6	0.095
20	392.0 ± 0.4	57.5 ± 0.4	507.0 ± 0.9	468.9	0.091
25	372.6 ± 0.6	45.8 ± 0.4	464.2 ± 1.0	446.9	0.085
30	340.0 ± 0.3	31.3 ± 0.2	402.6 ± 0.5	394.7	0.079
35	297.5 ± 0.3	–	297.5 ± 0.3	303.6	0.088
40	287.0 ± 0.1	–	287.0 ± 0.1	285.8	0.088

Supplementary Figures

Figure S1 reports DLS measurements performed on two different batches of the studied ionic microgels, synthesized in two different labs at different times. Despite we do not impose a constant pH, data are fully reproducible and ensure that the protocol used to synthesize ionic microgels is robust.

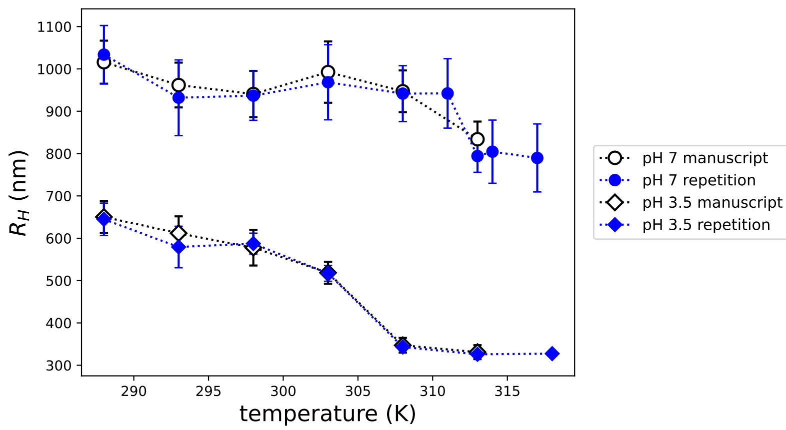

Figure S1: Swelling curves, R_{H} Vs temperature, at two pH values, measured by DLS on two different batches of microgels synthesized using the same protocol reported in the manuscript.

Figure S2 shows the temperature dependence of the experimental hydrodynamic radius R_{H} of ionic microgels at pH 7, for different concentrations between 0.001 wt% and 0.01 wt%. In particular, a concentration-induced deswelling is observed at the highest concentration, where electrostatic interactions between microgels are maximized due to high deprotonation of AA monomers. This effect is instead not observed at the lower concentrations, probably due to counterion release from the microgel. Since ionic microgel at pH 3.5 and neutral ones experience weaker electrostatic interactions, we expect that concentration-induced deswlling occurs at higher concentrations than for ionic microgel at pH 7. Based on these considerations, we selected the concentration of 0.001 wt% for all SLS and DLS experiments reported in the main text, to minimize interparticle interactions and ensure single particle behavior.

Fig. S3 shows a comparison of the experimental data with alternative models that fail to reproduce the observed behavior, see also Fig. 4 of the main text. In Fig. S3(a)-(b) ionic microgel form factors measured experimentally are compared to those of heterogeneous microgels with added charges, as also discussed when describing the snapshots reported in Fig. 3 of the main text. In Fig. S3 (c), the form factors of neutral microgels are compared to simulations of homogeneous microgels. Neither of

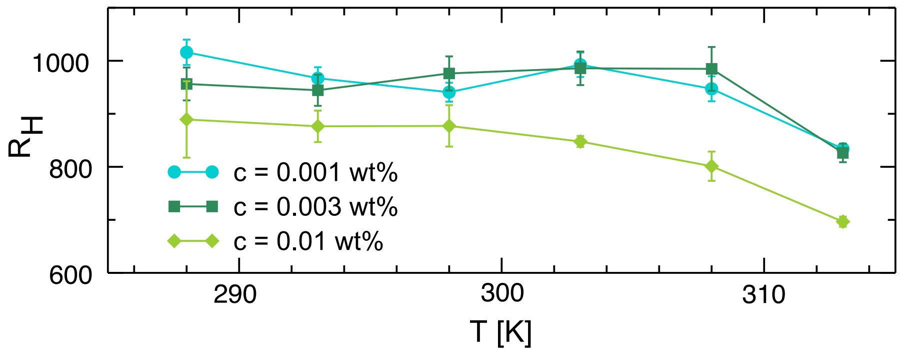

Figure S2: Evolution of R_{H}, measured by DLS, as a funtion of temperature, for ionic microgels at pH 7 and different concentrations. Above $c = 0.003$ wt%, the trends highlight a concentration-dependent deswelling of the microgels. Under the conditions used in this study ($c = 0.001$ wt%), we are in the asymptotic low-concentration regime, sufficiently dilute such that the concentration dependence of the swelling properties can be neglected.

these models adequately describes the experimental data. This justifies the modeling choices made in the main text: using homogeneous microgels with added charges to describe the ionic systems—the main new result of this manuscript—and using heterogeneous microgels to describe neutral ones, in agreement with previous findings reported in Refs. [**?**] and [**?**], and here confirmed for a different batch of microgels synthesized in an independent laboratory.

Fig. S4 shows that the two assembly protocols cannot be reconciled. The heterogeneous microgel without charges—which performs well for neutral microgels synthesized with initiators only—does not exhibit a swelling behavior comparable to that of the homogeneous microgel containing a small amount of charges from initiators. This suggests that when only initiators are present during synthesis, their concentration is too low to influence the tendency of crosslinkers to localize preferentially in the microgel core. By contrast, when a significant amount of ionic AA groups is introduced (e.g., $f = 7.5\%$ molar concentration), these charges strongly affect the resulting network architecture. Of course, if ionic microgels are prepared with a much lower charge content—on the order of the initiator concentration ($1\% \lesssim f \lesssim 3\%$), as in Ref. [**?**]—the resulting structure is not known. This regime would require an *ad hoc* comparison of experimental form factors with simulations, where an intermediate behavior (e.g., reduced heterogeneity or modified crosslinker distribution) could emerge.

Finally, to gain insights into the internal modifications induced by the addition of charges to neutral microgels—synthesized either in the presence (heterogeneous)

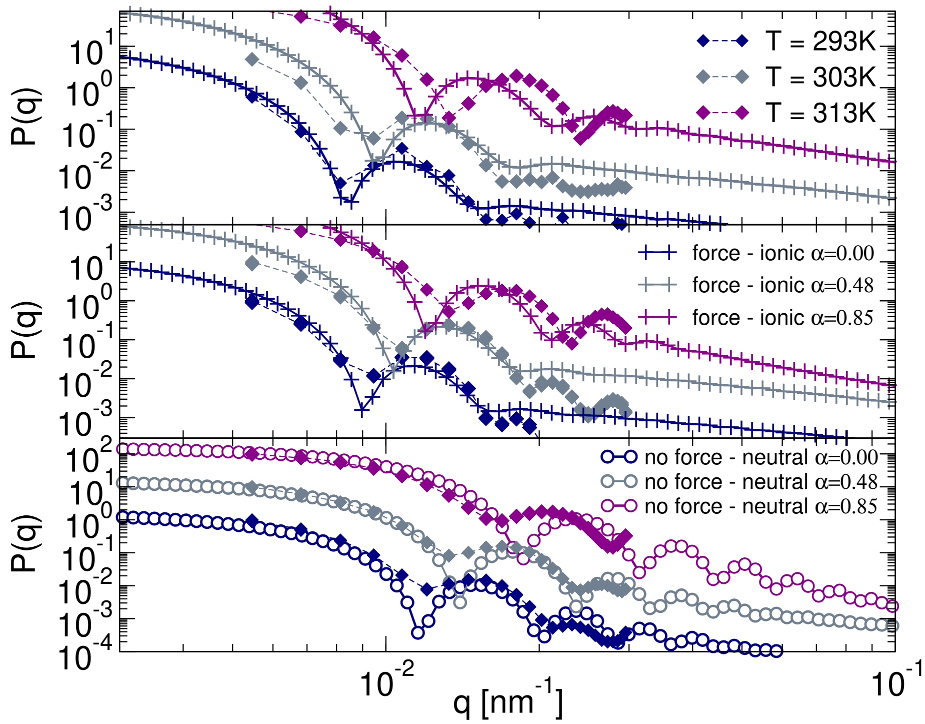

Figure S3: Modeling of form factors for ionic microgels with $c = 5\%$ at (a) pH 7 and (b) pH 3.5, as well as for neutral microgels in (c). The legends in (a) and (b) apply to both panels. This figure presents a comparison to scattering results, as in Fig. 4 of the main text, but using different simulation models. Scattering data are shown in the top to bottom graphs for $T = 293$, 303, and 313 K, respectively, and are compared in each case to numerical simulations at various α values. These α values are consistent with those previously established for neutral microgels in Ref. [**?**]. The numerical model includes an internal force acting on the crosslinkers for the charged microgels, but not for the neutral ones. In both cases, the comparison with experiments is unsatisfactory, reinforcing the choice of the model made in the main text (without force for ionic microgels and with force for neutral ones).

or absence (homogeneous) of a force acting on the crosslinkers— in Fig. S5 we report the form factors of the microgels at low temperature ($\alpha = 0.0$). All microgels are assembled with the same number of monomers ($N = 112{,}000$) and confined within the same spherical volume, thereby keeping their initial number density fixed. However, we observe that the position of the first minimum in $P(q)$ is altered upon the introduction of charges. Two network scenarios can be distinguished: for heterogeneous microgels, the first minimum decreases in amplitude and shifts to higher q values;

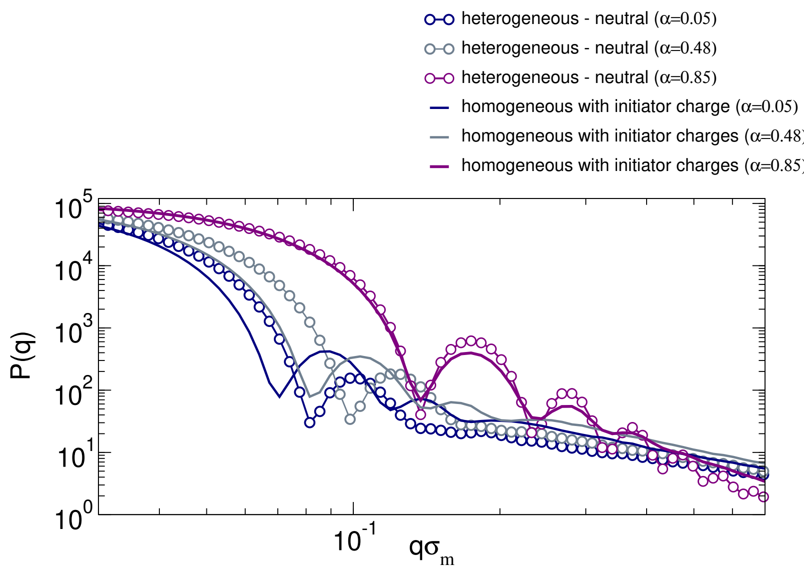

Figure S4: Form factors of numerical microgels assembled heterogeneously without charges (neutral) and homogeneously with few added initiator charges to show that the two models cannot be reconciled. Note that σ_m is the monomer diameter, as defined in the main text.

in contrast, when charges are added to homogeneous microgels, the opposite trend is observed. These different behaviors can be understood by looking at the corresponding density profiles, also reported in the figure, showing that the non-trivial alterations of the structure are simply not visible just by looking at the form factors. In particular, the homogeneous microgel has a much flatter and more extended core, which gives rise to the many peaks seen in $P(q)$ and its extension increases with increasing charges. The same is actually true for the heterogeneous one, but this is most visible in the tail of the density profile, with the inner part staying roughly constant. This means that the heterogeneous microgel is less affected in the core-corona region by the presence of charges, which instead act to extend considerably the most outer chains.

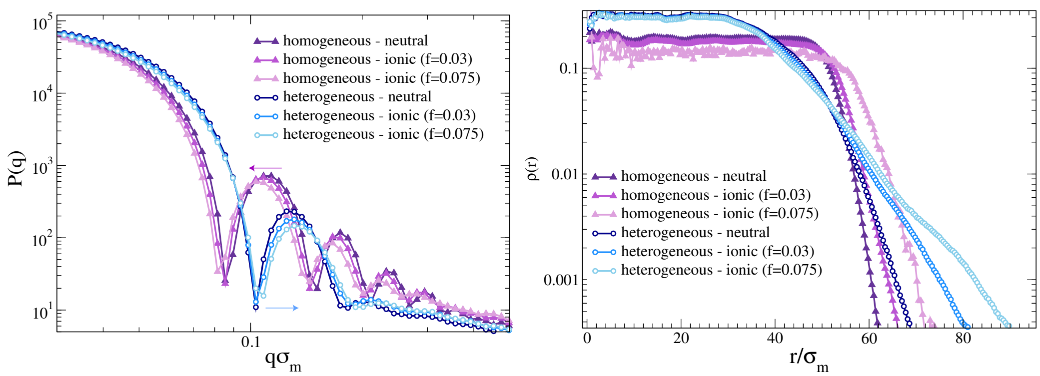

Figure S5: Left: numerical form factors of neutral and ionic microgels at low temperatures ($\alpha = 0.0$). Right: corresponding radial density profiles. Data refer to heterogeneous (filled triangles) and homogeneous (empty circles) microgels with different charge content, from neutral ($f = 0$) to pH 7 conditions studied in this manuscript ($f = 0.075$).