

Supplementary Information - Ionisation and swelling behaviour of weak polyampholyte core-shell networks - a Monte Carlo study

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Algorithm

Metropolis Monte Carlo simulations with the software MOLSIM were used for the microgel simulations. Our algorithm, which enables us to run our simulation on a GPU, is based on a work by Liang *et al.* with extensions for simulating network systems and using Ewald Summation. One simulation consists of 2.5 million Monte Carlo steps. In one Monte Carlo step, each particle is moved once. One Monte Carlo step can be summarized as follows:

1. For each particle a move type is chosen. In our simulations, there are two types of moves, and the type, which is used most, is the single-particle move, in which one particle is moved. The second move type is the charge-change move, in which a particle and its counterion can change their charge states.
2. New positions and charge states are calculated.
3. The energy difference of the part of the reciprocal part of the Ewald sum, which is independent on other particles, is calculated for each particle. Difference in surface

and self term of the Ewald sum is calculated, too.

4. The energy difference of the Coulomb energy in real space and bond and crosslink energies are calculated for each particle (bonds and crosslinks are distinguished in MOLSIM). Due to the sequential scheme of the Metropolis algorithm the positions of the other particles which are unknown. Therefore, the order of choosing particles in step 5 is handled by the index of the particles. With this scheme the differences of pair energies between particles, which have a higher index than the particle itself, with the current particle can be calculated. The validity of the sequential instead of random choice of particles was shown by Manousiouthakis *et al.* ²⁷
5. Loop from particle 1 to particle n with n as the number of particles
 - (a) The energy difference of the reciprocal part of the Ewald summation is calculated
 - (b) The different energies are summed up to ΔU
 - (c) Decision on whether the new state is accepted or rejected. A distinction is made between three different cases. For the case $\Delta U < 0$ the new state is accepted. In case $\Delta U > 0$ a random number r in the range of 0 and 1 is generated. For $r < e^{\frac{-\Delta U}{k_B T}}$ the new state is also accepted. Otherwise, the new state is discarded and the old one is retained. For the charge-change move the criterion is $r < \log(10)(\text{pH} - \text{pK})e^{\frac{-\Delta U}{k_B T}}$
 - (d) The state after the decision is included in the statistics for the calculation of statistical averages. The averages are calculated after every tenth Monte Carlo step
 - (e) The energy difference of Coulomb energy in real space, bond and crosslink energies with the current particle is calculated for each particle which has a higher index than the current particle
6. Transfer of positions, charge states and energies from GPU to CPU.

Comparison of sequential vs. random choice of particle

Since our algorithm with sequential choice of the particle violates the detailed balance condition, we compared the results obtained from simulations of alternating polyampholyte networks with a former publication.⁴² The network consisted of 71 crosslink beads, 920 acidic and 920 basic beads. For both, the pK_0 was set to 7.0. The results are in agreement within their statistical errors.

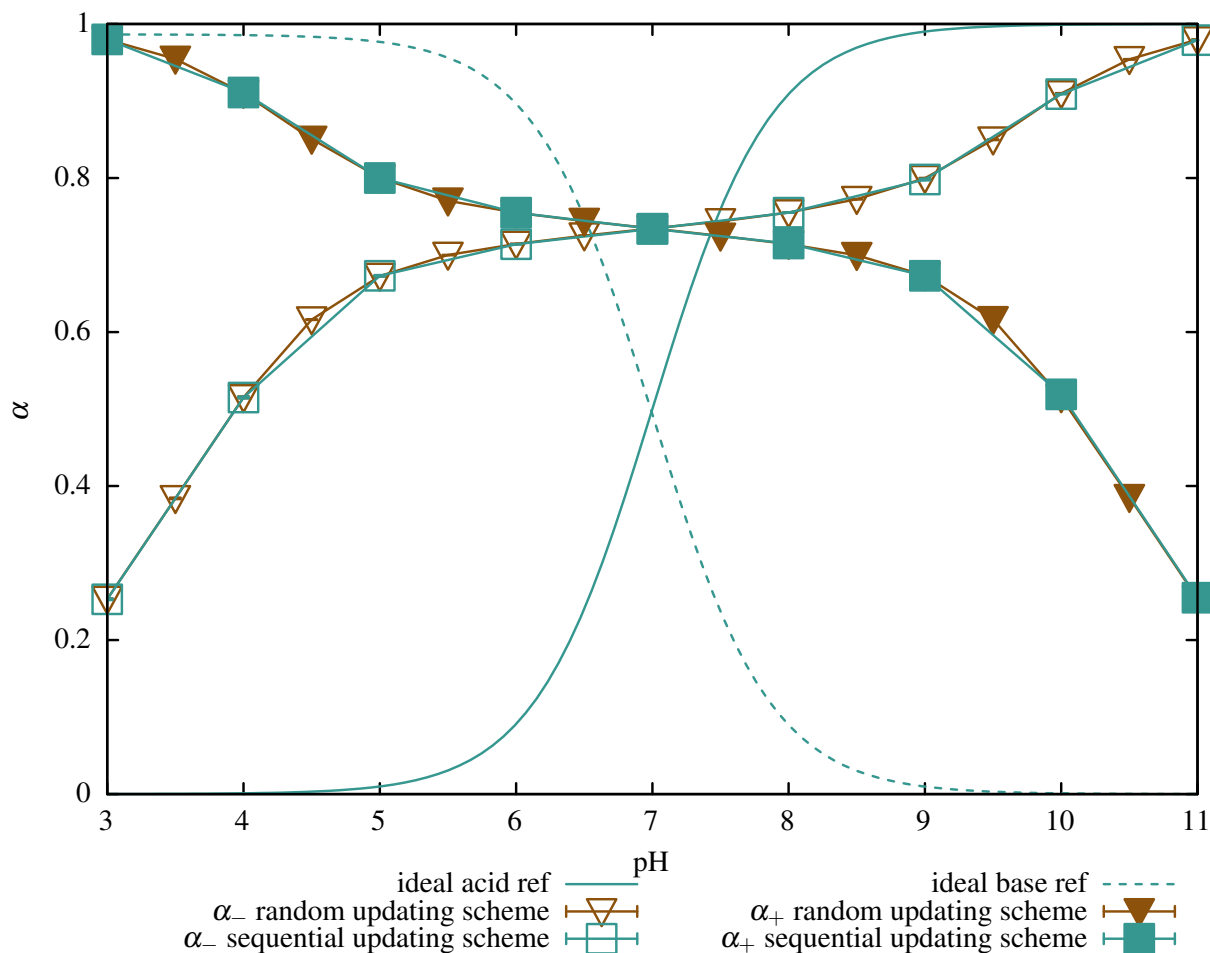


Figure S1: Degree of ionisation as a function of pH for the network with $\Delta pK=0$ without salt, at a salt concentration of 5 mM and with explicit charged particles mimicking the pH. Lines between data points serve as guidelines.

Screening effect of H⁺-ions

To demonstrate the influence of the screening effect of H⁺-ions at different pH, we added explicit charged particles at the concentration of the adjusted pH. The resulting degrees of ionisation show a smaller pH regime where both acid and bases are ionised. The presence of only one charged species leads to higher swelling in the pH regime of 10 to 11 for the system with explicit ions. At pH 3, the additional ions lead to the polyelectrolyte effect which causes slight deswelling of the network.

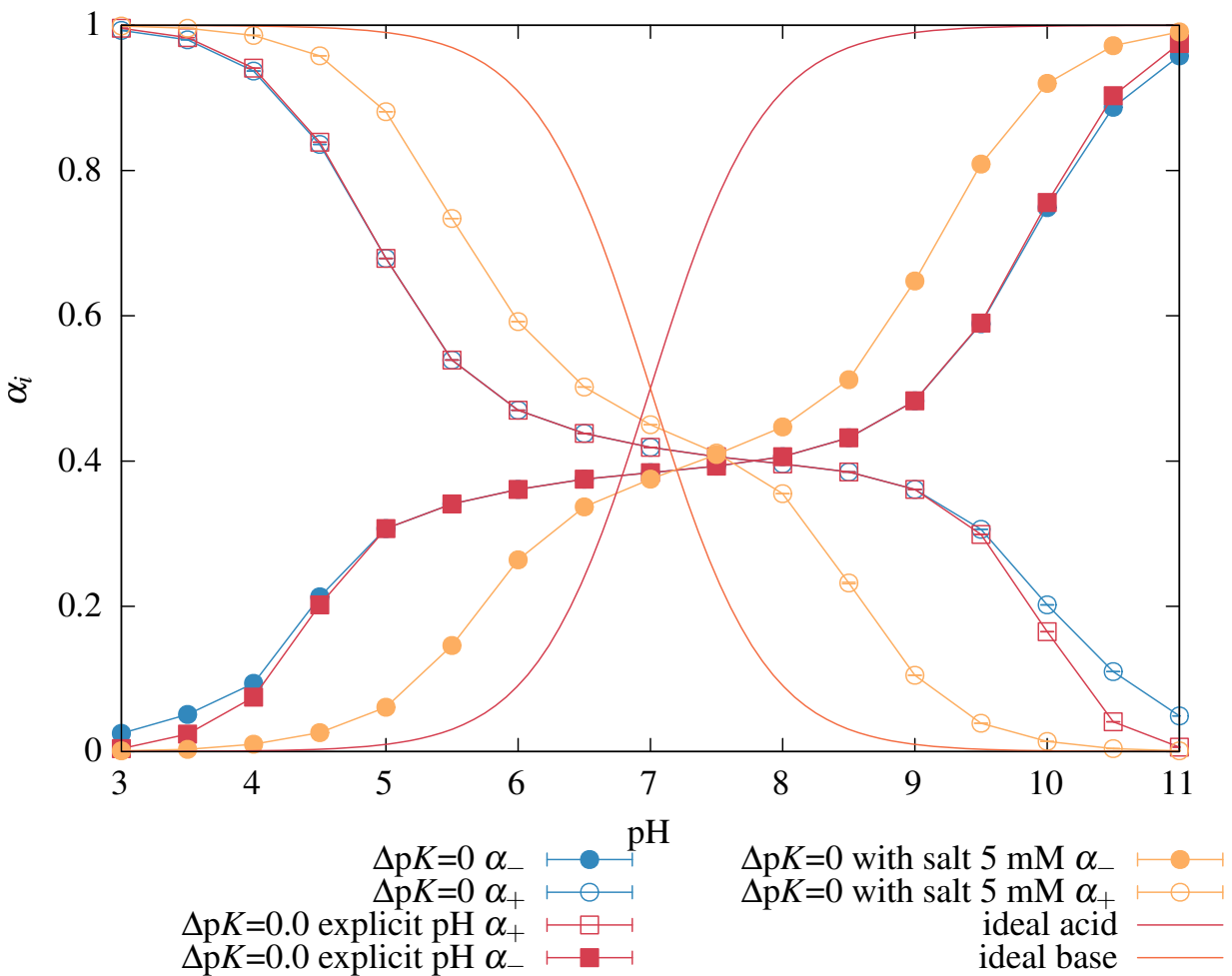


Figure S2: Degree of ionisation as a function of pH for the network with $\Delta pK=0$ without salt, at a salt concentration of 5 mM and with explicit charged particles mimicking the pH. Lines between data points serve as guidelines.

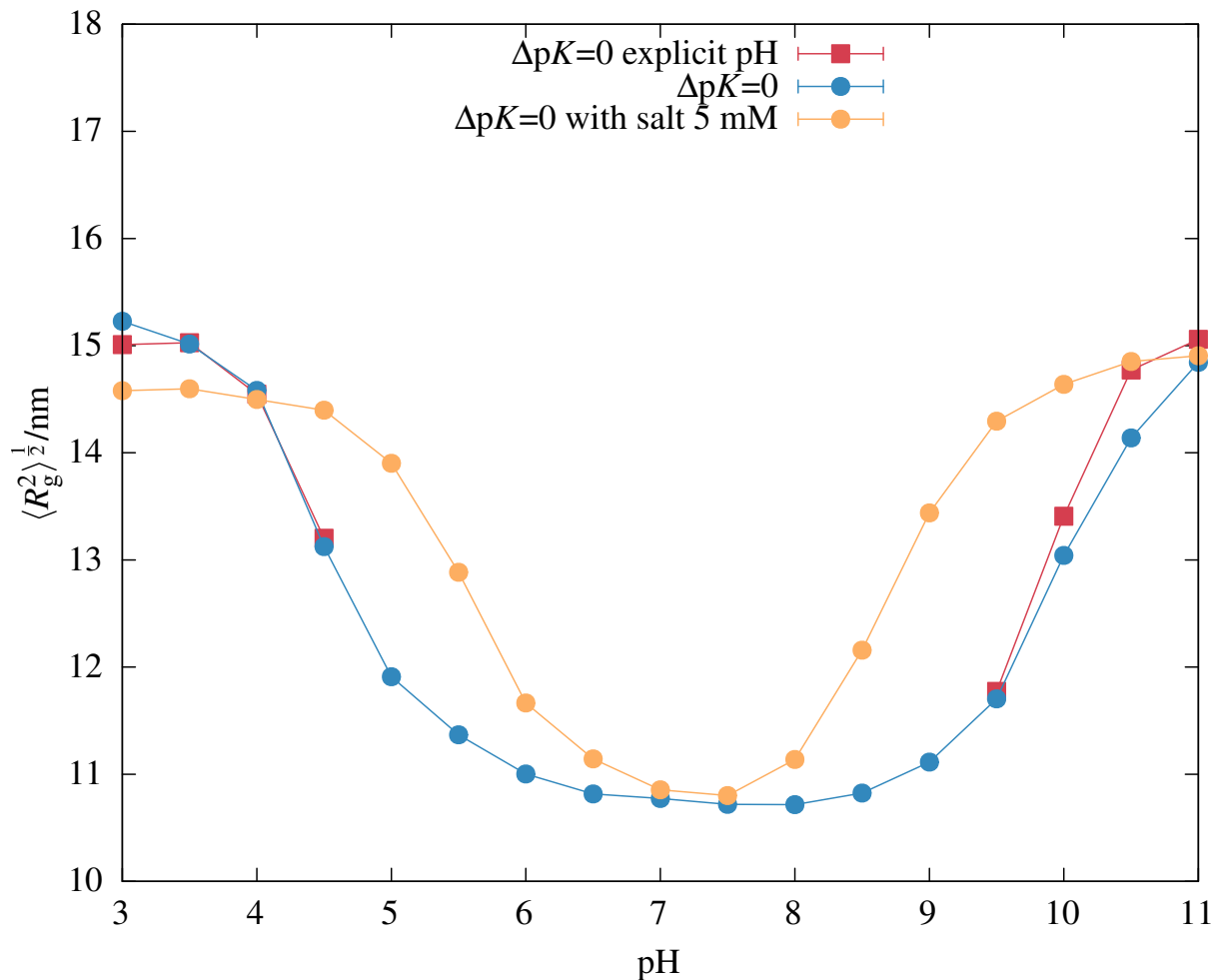


Figure S3: Degree of swelling as function of pH for the network with $\Delta pK=0$ without salt, at a salt concentration of 5 mM and with explicit charged particles mimicking the pH. Lines between data points serve as guidelines.

Influence of morphology

The distribution of ionisable monomers have a crucial influence on the ionisation behaviour of polyampholyte microgels (Figure S4). While attractive interactions between acids and bases dominate in an alternating network at the isoelectric point, repulsive interactions in the core-shell network lead to a decrease of the degree of ionisation compared to an isolated system at the isoelectric point. Due to the spatial separation of acids and bases, the degree of ionisation is lower for the core-shell network compared to the alternating network over the whole pH regime from 3 to 11. The ionisation behaviour of the random networks lies between those of

the alternating network and the core-shell network. The results for the network generated by the cubic diamond lattice approach and the *in silico* synthesis network indicate that the crosslinker distribution and network defects do not significantly influence the ionisation behaviour.

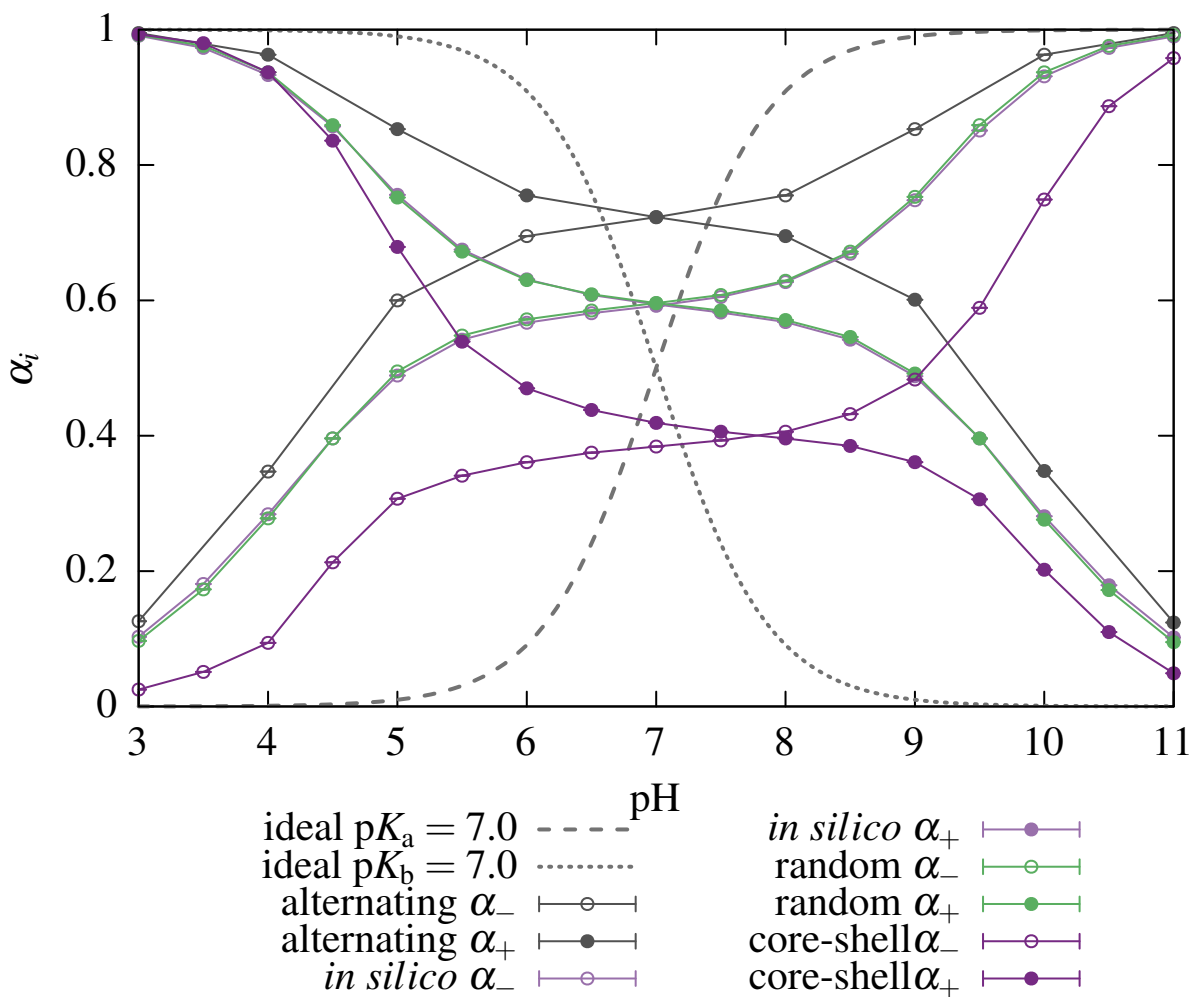


Figure S4: Degree of ionisation as function of pH for the network with $\Delta pK=0$ for networks with alternating, random and core-shell distribution generated with a cubic diamond lattice. For comparison of the cubic diamond lattice approach, the degree of ionisation for a network generated by del Monte with an *in silico* synthesis approach, which has a random distribution of ionisable monomers, is plotted. Lines between data points serve as guidelines.

Degree of ionisation as a function of total network charge

The degree of swelling increases approximately linearly with the total network charge. The influence of the microgel concentration is rather low, especially for the swelling of the core. This low dependence can be explained by similar degree of ionisation at the same total network charge, shown in Figure S5. In contrast, adding salt leads to lower degree of ionisation of both acid and base at the same degree of ionisation.

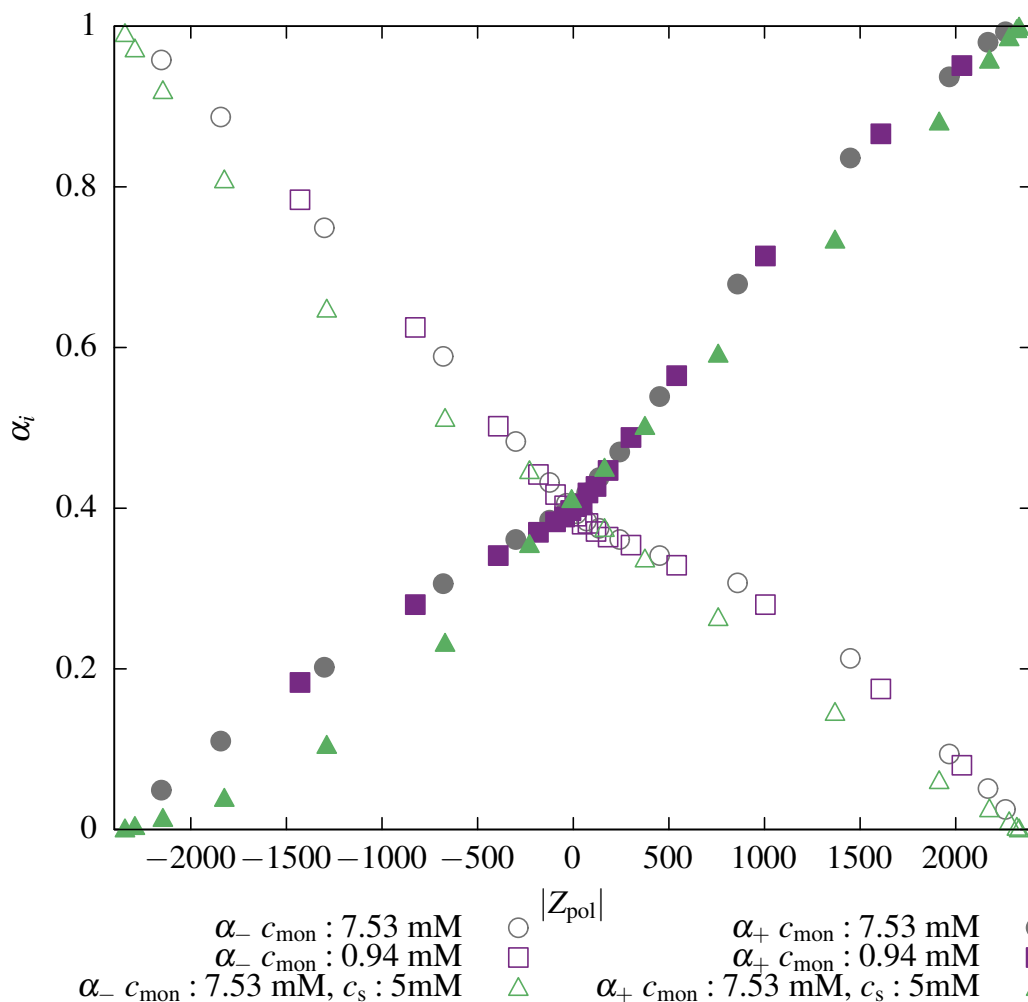


Figure S5: Degree of ionisation as a function of the total network charge for networks with $\Delta pK=0$ without salt, at a salt concentration of 5 mM and with lower microgel concentration.

Titration curves of polyelectrolyte networks

In addition to the swelling behavior, also the degrees of ionisation of the two polyelectrolytes in the core and shell were determined separately. Figure S6 shows the ionisation behavior separately for the polyelectrolyte core, for the polyelectrolyte hollow shell, and for the polyampholyte core-shell network.

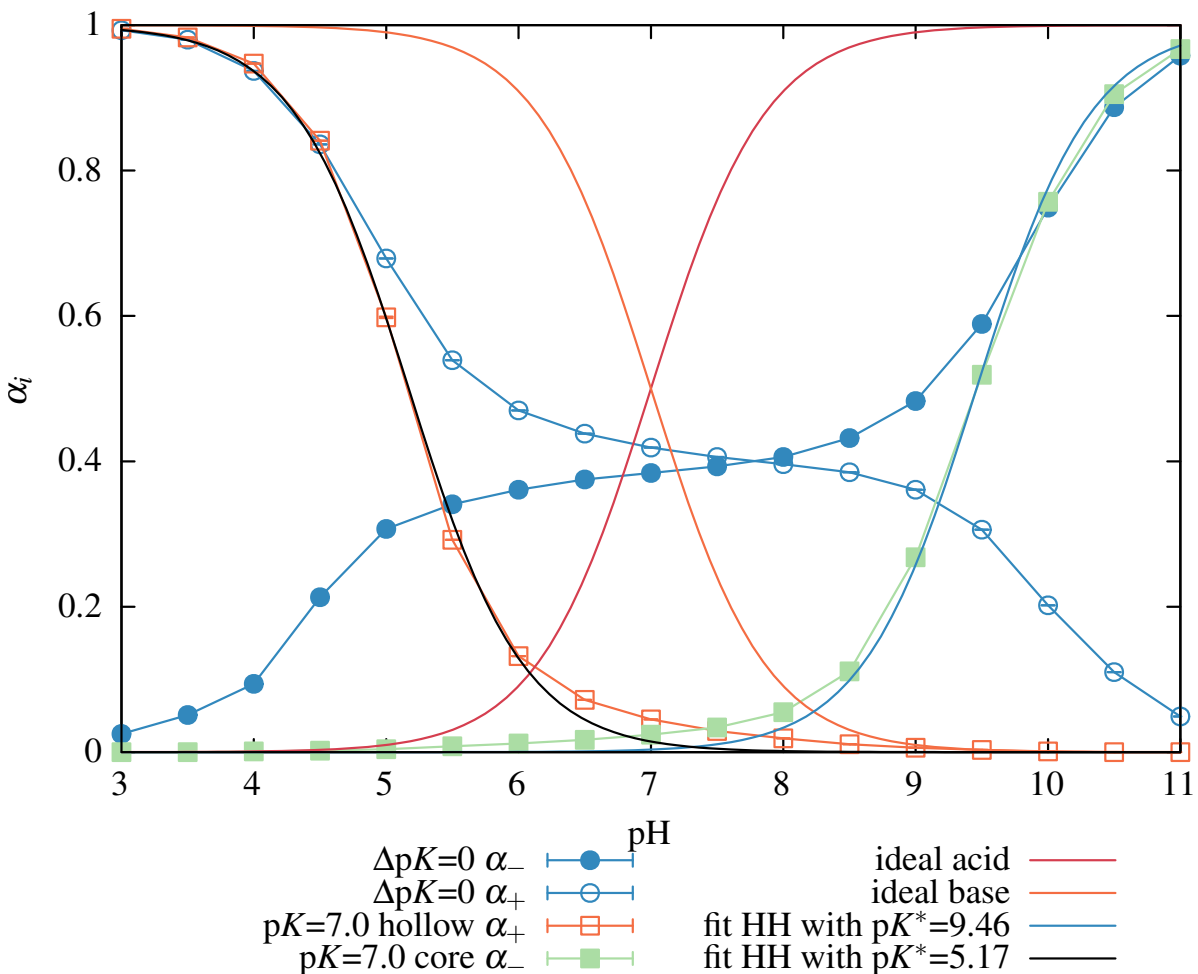


Figure S6: Degree of ionisation α as function of pH for the network with $\Delta pK=0$, a homogeneous polyelectrolyte in the size of the core and a hollow polyelectrolyte in the size of the shell. Lines between data points serve as guidelines.

At high degree of ionisation, the polyelectrolytes behave similar to the core-shell network. Due to the presence of equally charged particles. As it is typical for polyelectrolytes, the ionisation is suppressed compared to the isolated monomers. The ionisation behavior of the

polyelectrolytes can be described with the Henderson-Hasselbalch equation and an apparent pK value. The deviations from the fit at low degree of ionisation can be explained by an easier ionisation of the particles situated in the dangling chains.

Effective pK values

From the radius of gyration as a function of pH and from equation 15, effective pK values can be obtained. In Figure S7, we fitted the values for the reference system with $\Delta pK = 0$.

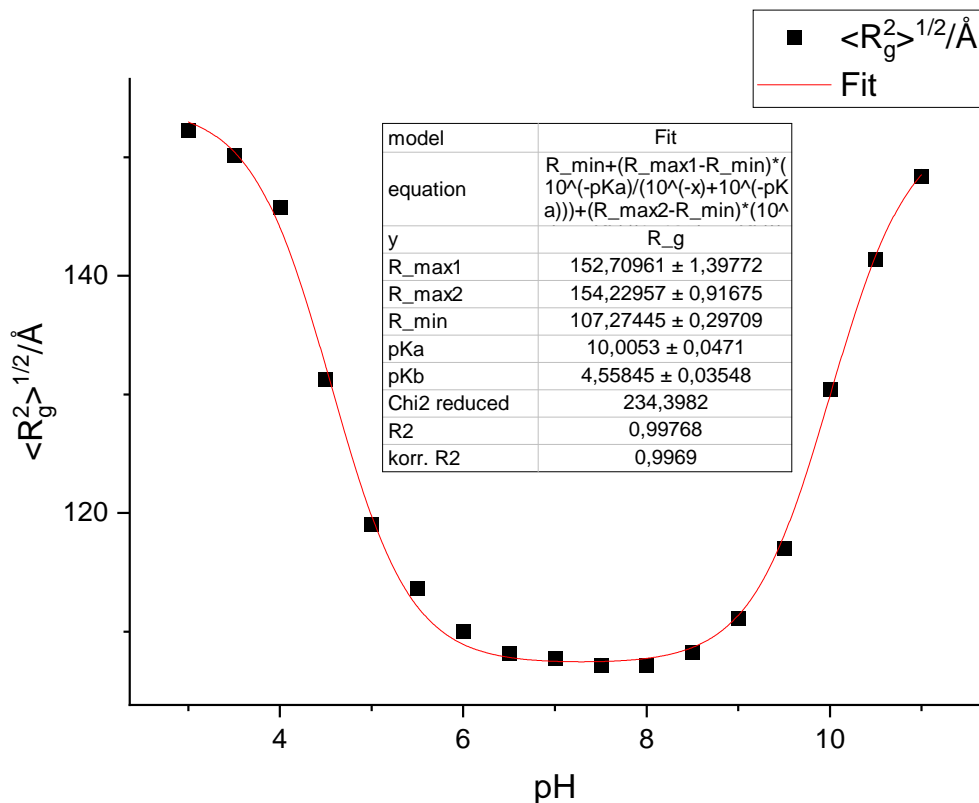


Figure S7: Radius of gyration as function of pH for the network with $\Delta pK = 0$. The points were fitted according to equation 15.

Acknowledgements

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