Electronic Supplementary Material (ESI) for Soft Matter.

SUPPORTING INFORMATION

Anions make the different: insights from the interaction of big cations and anions with poly(N-isopropylacrylamide) chains and microgels

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1. Methodology of ABF-MD Simulations

In the main paper, we describe in full detail the methodology of the performed simulations, except in the case of the ABF-MD simulations (simulations S5 and S6 in Table 1), which are only briefly described. Here we provide more details on the parameters employed and other technicalities of interest for the reproducibility of our results.

The adaptive biasing force (ABF) methodology (see ref. 31) is implemented in the standard version 2.9 of NAMD for the calculation of free energies along collective coordinates (the potential of mean force) in MD simulations. The biased simulations S5 and S6 employing the ABF-MD simulations were performed in order to obtain the potential of mean force (PMF) corresponding to the ion-PNIPAM interaction. As explained in the main text, the initial configuration for the calculation was obtained as follows. We started from the results of simulations S3 and S4 in Table 2 and removed all ions except one adsorbed ion and one counter-ion. We added more water, and performed further NPT runs (of about 30 ns). The final configuration of the NPT run was employed as the initial configuration for the ABF-MD calculation. The initial configuration is illustrated in Figure SI-1.

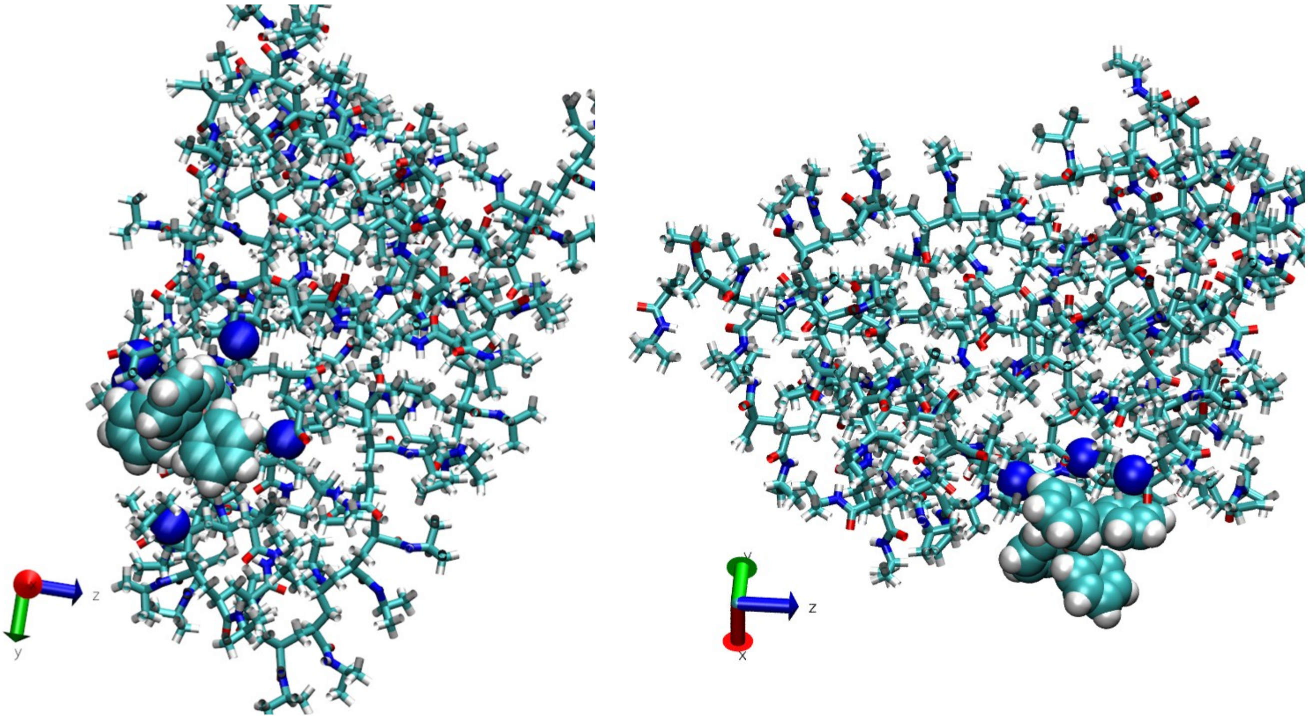

Figure SI-1: Snapshots of the initial configurations for the ABF-MD simulations. Left: Simulation S5 in Table 1 (adsorbed Ph_4B^- ion). Right: Simulation S6 in Table 1 (adsorbed Ph_4As^+ ion). The Ph_4B^- and Ph_4As^+ ions are shown in van der Waals representation. PNIPAM atoms are shown in bonds representation, except the reference atoms for the distance calculation which are shown with their van der Waals radius. Water molecules and the counterion of each adsorbed ion (Na^+ or Cl^-) are not shown for clarity. Figure made with VMD (Ref. 29)

The first choice to be made in the ABF calculation is the selection of the collective variable or “reaction coordinate”. We use the separation between the PNIPAM chains and the adsorbed ion. The separation between PNIPAM and the ion is computed using the central atom of the ion (B or As depending on the tetraphenyl ion) and a few reference atoms of the PNIPAM molecule which are located near the initial position of the ion. These atoms are indicated in Figure SI-1. Concerning the parameters of the technique, we tried different values for the force constant employed in the calculation and selected those which produced the better (less noisy) PMF curves. Our final choice was 5.0 kcal/mol/Å^2 in simulation S5 (adsorbed Ph_4B^- ion) and 3.0 kcal/mol/Å^2 in simulation S6 (adsorbed Ph_4As^+ ion). During the calculation, we avoid the displacement of the PNIPAM particle by applying an harmonic constraint with k=5.0 kcal/mol/Å^2 to the positions of the heavy atoms (C,N,O) of PNIPAM (as equilibrium positions we select their initial positions) . The potential of mean force of each ion was obtained with a 0.1 Å resolution in a simulation run with 2.5×10^6 steps. In each bin, the average of the PMF was calculated discarding the first 400 configurations. The results of these calculations are reported in Figure 4 in the main text.

2. Additional results for MD Simulations in presence of NaCl (S1 and S2)

In the main text, the results of the simulations in presence of NaCl (S1 and S2) are only briefly discussed in a subsection of the main paper, since our focus in the article is in the behaviour of the Ph_4B^- and Ph_4As^+ ions. Here we provide more details on these results mentioned in the main paper.

In our simulations S1 and S2 we have computed the number of water molecules in first hydration shell as identified form the radial distribution functions of the different PNIPAM atoms and water oxygen or water hydrogen atoms. In Figure SI-2, we show the total number of hydration molecules obtained for the PNIPAM particle at 25ºC and 45ºC.

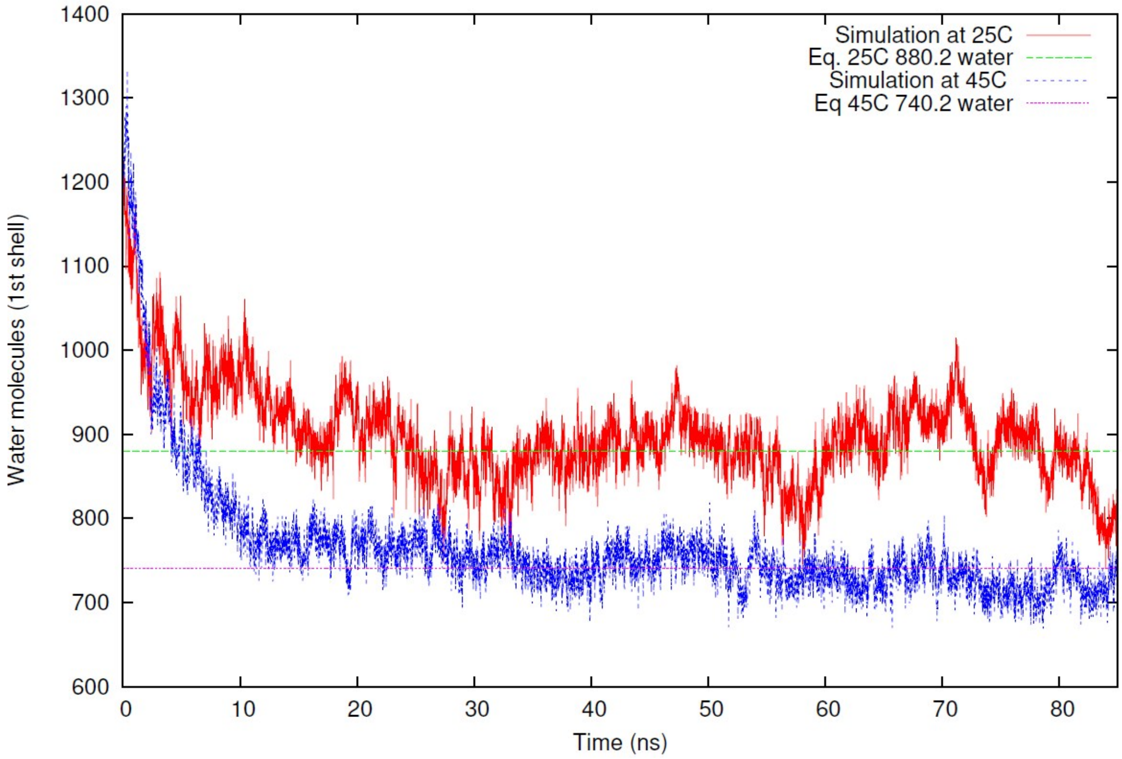

Figure SI-2: Time evolution of the number of water molecules in the first coordination shell of PNIPAM in simulations S1 (T=25ºC) and S2 (T=45ºC) in presence of NaCl. The equilibrium values, computed discarding the first 30 ns of simulation, are shown as lines.

Table SI-T1: Number of water molecules in the first coordination shell of PNIPAM. “Monomer” corresponds to the hydration per monomer (excluding the capping of the chains), and Methylene, Amide and Isoporpyl correspond to the hydration of the different functional groups indicated in Figure 2a in the main text. Note that hydration water is shared between functional groups, so the sum of columns 3, 4 and 5 is greater than the value reported in column 2.

System	Monomer	Methylene	Amide	Isopropyl
S1 (25C)	8.38	1.25	1.31	8.32
S2 (45C)	7.05	1.02	1.23	7.02

We can also obtain the hydration of the different groups of the PNIPAM monomer at 25ºC and 45ºC. The results are summarized in table SI-T1. According to our results, the hydration of the PNIPAM chains at 25ºC is larger than at 45ºC, consistent with the experimentally observed transition of PNIPAM from a swollen state to a collapsed state with temperature (see Figure 5 in the main paper). The largest change in hydration occurs in the isopropyl group, as has been discussed previously both in the experimental and simulation literature cited in the main paper.

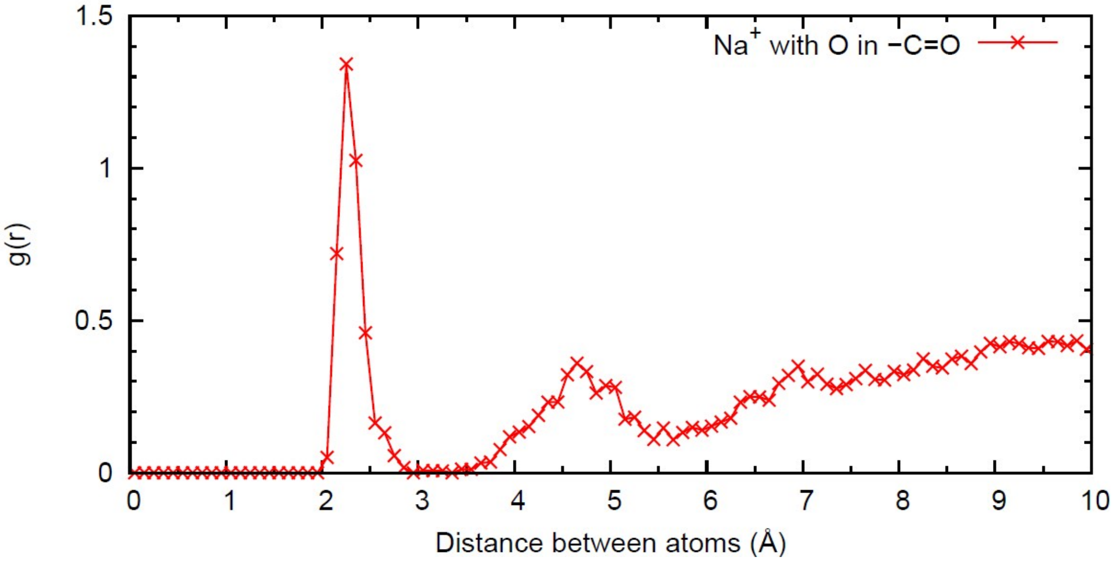

Figure SI-3: Radial distribution function between Na$^+$ ions and oxygen atoms from amide groups in PNIPAM obtained in simulation S1 (25ºC).

We have also computed the radial distribution function g(r) for the Na$^+$ and Cl$^-$ ions with PNIPAM atoms. In the case of Na$^+$, we observe a interaction with the oxygen atom in the amide group in PNIPAM, characterized by a peak in the g(r) function shown in Figure SI-3. As mentioned in the main text, this has been previously reported in the literature. We do not observe any clear features in the g(r) function for Cl$^-$ with any atom in the PNIPAM chains.

3. Electrical charge distribution for the tetraphenyl ions

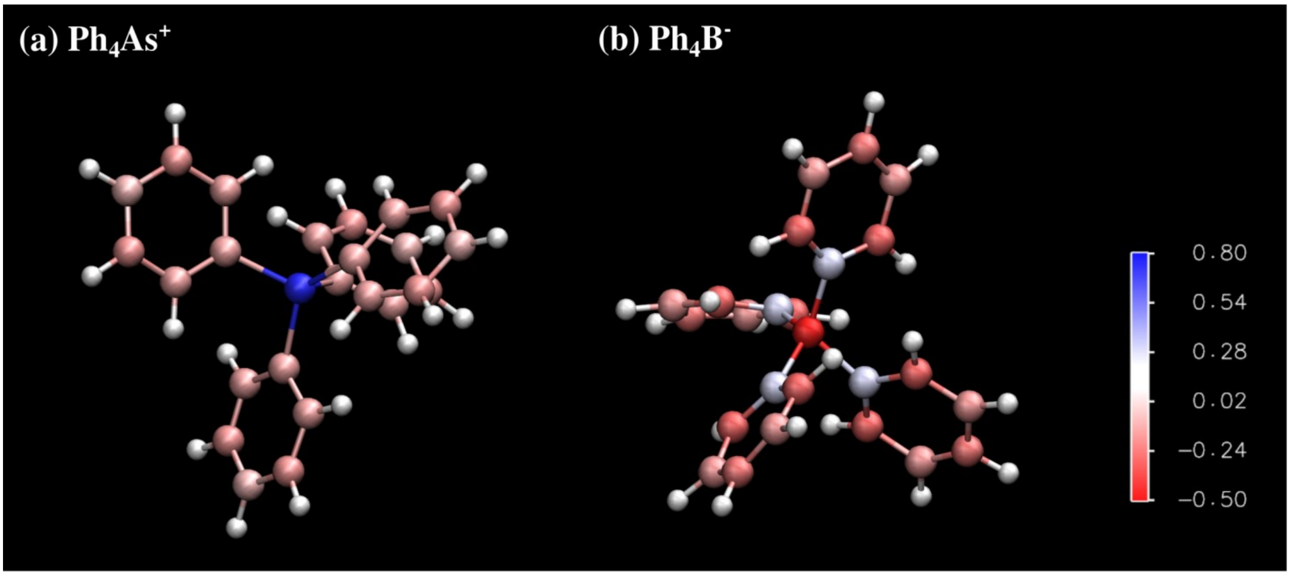

Figure SI-4: Electrical charge distribution for (a) the Ph_4As^+ cation and (b) the Ph_4B^- anion (see Table SI-T2 for more details). The ions are shown in CPK representation.

Table SI-T2: Electrical charge for each atom of the tetraphenyl ions. The position of each atom is shown in Figure SI-5

Atom	**Q_e (Ph_4As^+)**	**Q_e (Ph_4B^-)**
X (central atom)	0.76	-0.48
C_1	-0.12	-0.29
C_2	-0.16	-0.15
C_3	-0.07	-0.24
C_4	-0.16	-0.15
C_5	-0.12	-0.29
C_6	-0.12	0.30
H_1	0.15	0.14
H_2	0.18	0.13
H_3	0.15	0.15
H_4	0.18	0.13
H_5	0.15	0.14

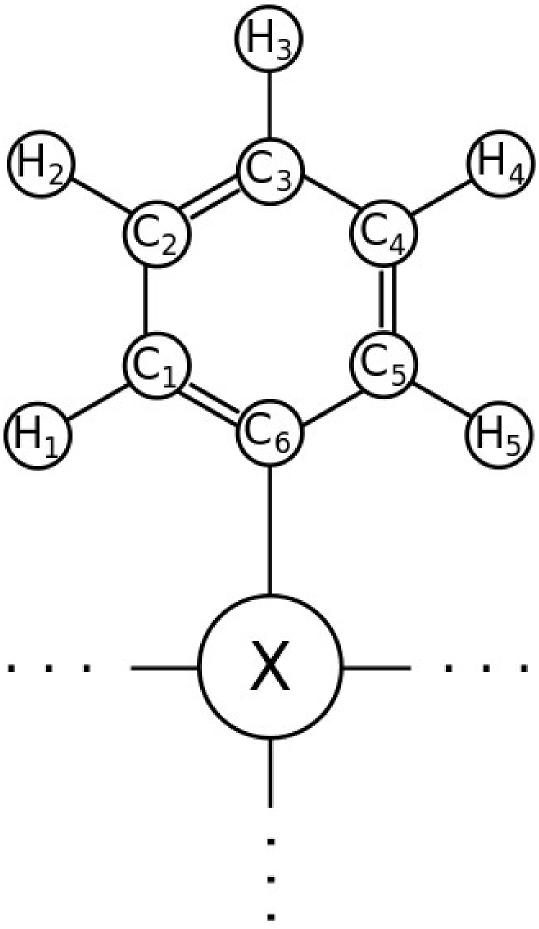

Figure SI-5: Position and assigned number of each atom of the tetraphenyl ions (see Table SI-T2).

4. Characterization of PNIPAM microgels: TEM images

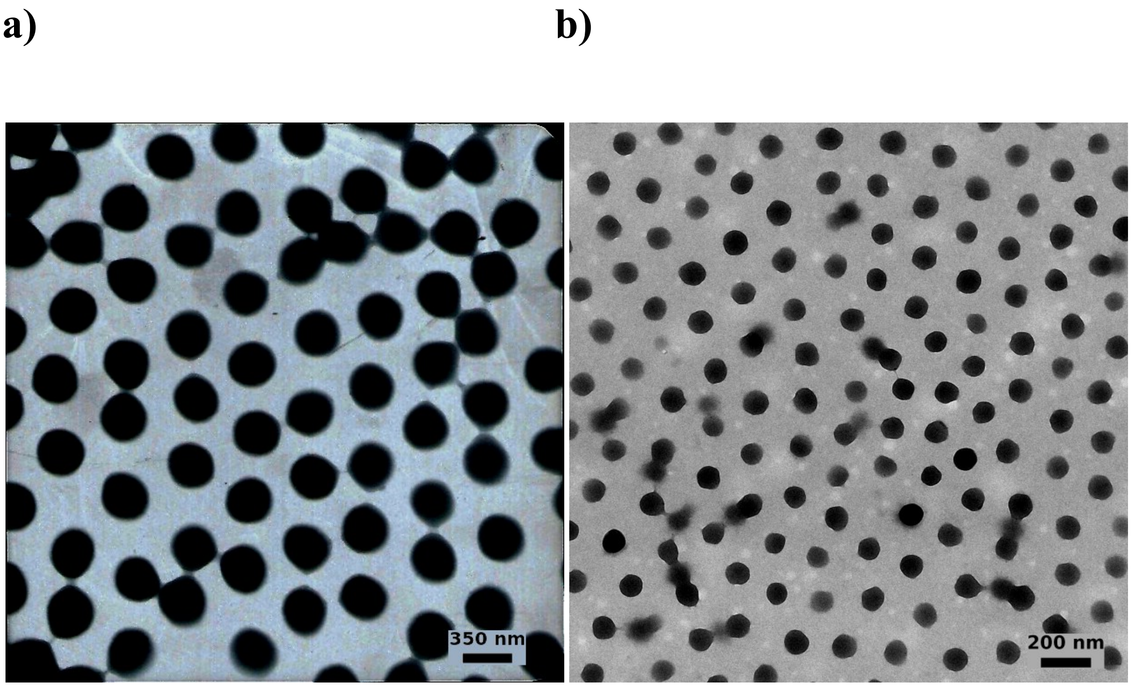

Figure SI-6: TEM images for a) anionic and b) cationic PNIPAM microgels

5. Additional AFM Images

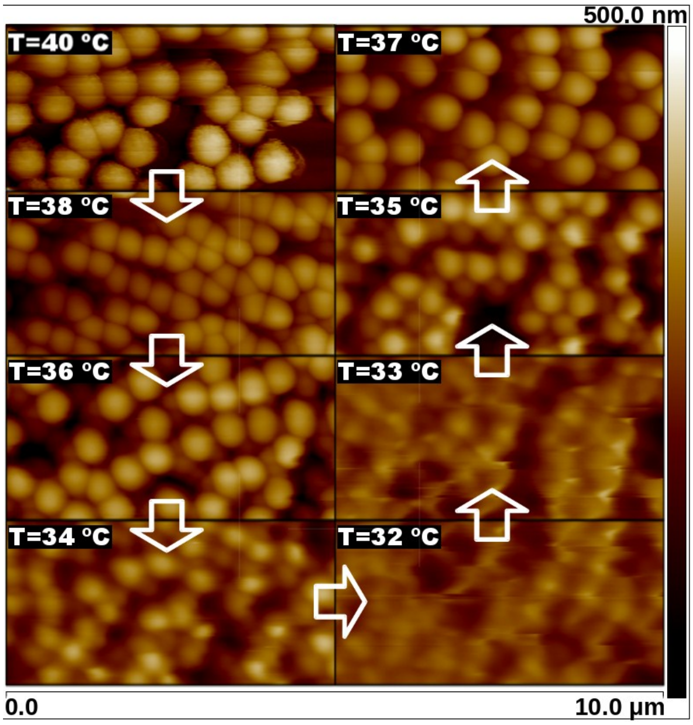

Figure SI-7: AFM micrographs of the adsorbed anionic PNIPAM microgel in salt-free water at pH 4 at different temperatures

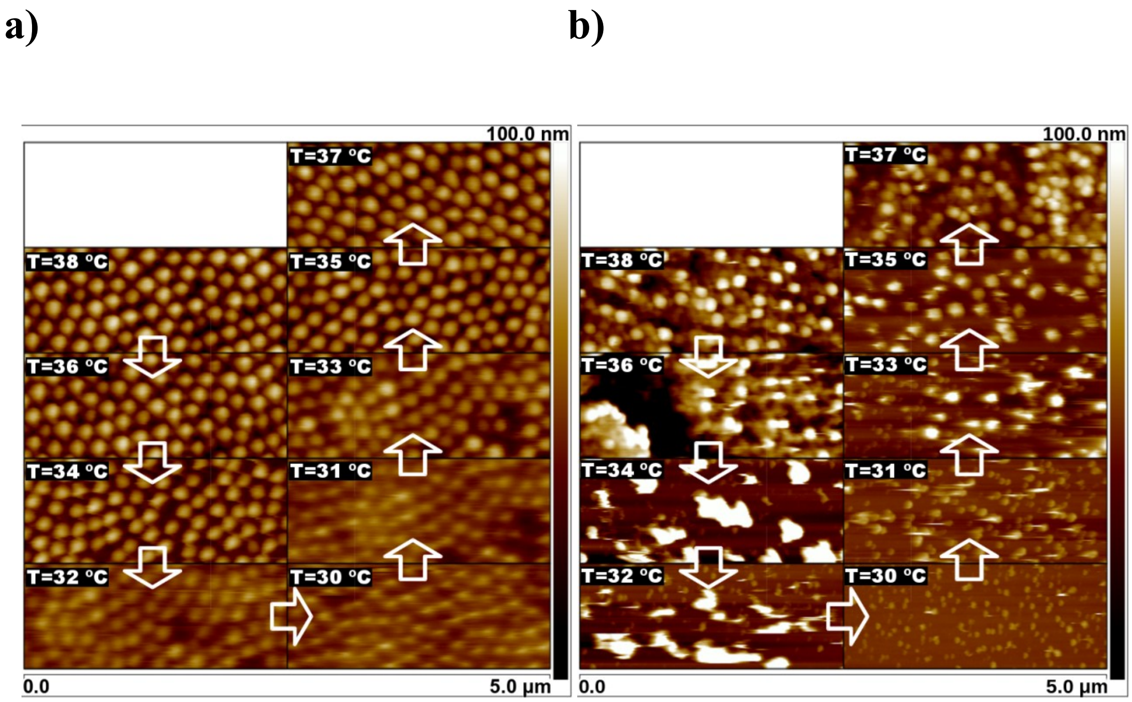

Figure SI-8: AFM micrographs of the adsorbed cationic PNIPAM microgel at different temperatures and 1 mM of a) Ph_4AsCl and b) Ph_4BNa.