Supporting information

Solvation dynamics of N-substituted acrylamide polymers and its importance on the phase transition behavior

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Equation S1: General CHARMM FF equation

$$E_{pot} = \sum_{bonds} k_b (b - b_0)^2 + \sum_{angles} k_\theta (\theta - \theta_0)^2 + \sum_{dihedrals} k_\varphi [1 + coscos (n\varphi - \delta)]$$
$$+ \sum_{impropers} k_\omega (\omega - \omega_0)^2 + \sum_{dihedral} \frac{q_i q_j}{4\pi D r_{ij}} + \varepsilon_{ij} \left[\left(\frac{R_{min;ij}}{r_{ij}}\right)^{12} - 2 \left(\frac{R_{min;ij}}{r_{ij}}\right)^6 \right]$$

Equation S1

The first four terms of Equation S1 represent the bonded interactions: bond stretching, angle bending, dihedral angles, and improper dihedral angles, respectively. equilibrium values for bond, angle, The and improper terms are b_0 , θ_0 , and ω_0 , respectively, and n and δ are the dihedral multiplicity and phase, respectively. The Coulombic electrostatic forces and van der Waals (vdW) interactions are described in the last two terms, respectively. The partial atomic charges of atoms iand j are described as q_i and q_j , respectively. In the Lennard-Jones (LJ) 12-6 term, ε_{ij} is the well depth; $R_{min;ij}$ is the distance at which the energy is minimum; and r_{ij} is the instantaneous distance between atoms i and j. [1]

C-O _w van der Waals interactions parameters				
	Standard parameters		Modified parameters	
Atom type	$arepsilon_{ij}$	$R_{min;ij/2}$	ε_{ij}	R _{min;ij/2}
Isopropyl				
methyl groups	-0.1089	3.3202	-0.1252	3.8182
(C8,C9)				
Extra methyl				
in PNIPMAm	-0.1089	3.3202	-0.1252	3.8182
(C20)				
Backbone	-0.0923	3.2854	-0.1061	3.7782
(C2,C3)				
Center of				
isopropyl	0.0698	3 2767	-0.0803	3 7682
group	0.0070	5.2101	0.0005	5.7002
(C7)				

 Table S1: Modified van der Waals Non-bonded interactions parameters

Generation of 30-mer oligomers

The generation of 30-mer oligomeric chains for the three compounds studied in this work started from a monomeric unit of each of them. We describe here the structure generation process for PNIPMAm. A monomeric unit was generated and repeated to create the complete oligomeric chain. One end of the chain was closed with a methyl group (CH_3) and the other with a hydrogen atom. Monomers were connected and placed in a 90 Å side cubic simulation cell for equilibration during 100 ps.



Figure S1: End-to-end distance distribution for PNIPAM and PNIPMAm single chains after 50 ns stabilized at 295 K.



Figure S2: PNIPAm monomer scheme emphasizing the two atoms considered for backboneisopropyl distance

References

[1] K. Vanommeslaeghe, E. Hatcher, C. Acharya, S. Kundu, S. Zhong, J. Shim, E. Darian, O.

Guvench, P. Lopes, I. Vorobyov, A.D.J. MacKerell, CHARMM General Force Field (CGenFF): A force field for drug-like molecules compatible with the CHARMM all-atom additive biological force fields(NIH Public Access), 31 (2011) 671–690. doi:10.1002/jcc.21367.