Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Molecular dynamics study of coil-to-globule transition in thermo-responsive oligomer bound to various surfaces: hydrophilic surfaces stabilize the coil form.

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Electronic Supplementary Information

MD simulations with durations of 200 ps were performed, using the same conditions reported in the experimental section, starting from a configuration characterized by the polymer placed with the backbone orientation orthogonal to surfaces.

The box size is 13.0 x 7.5 x 13.0 nm for GO and 13.0 x 7.5 x 16.0 nm for SiO_2, water molecules were added to solvate the systems at a density = 1 g/cc.

During the last 50 ps 5 structures were randomly sampled and optimized, hence it was calculated the energy of interaction (E_i) for such configurations, with E_i defined as follows:

$$E_i = E_{system} - (E_{surface} + E_{water})$$

where

$$E_{system} = E_{surface} + E_{PNIPAM} + E_{water} + E_{surface\text{-}water} + E_{PNIPAM\text{-}water} + E_{surface\text{-}PNIPAM}$$

therefore

$$E_i = E_{PNIPAM} + E_{surface\text{-}water} + E_{PNIPAM\text{-}water} + E_{surface\text{-}PNIPAM}$$

The same calculations were performed for the starting configuration (backbone orientation almost parallel to the surfaces). Differences between the lowest values of the E_i for each case are reported below ($\Delta E_i = E_{i\text{-}parallel} - E_{i\text{-}orthogonal}$):

Surface	T(K)	ΔE_i (kcal mol^{-1})	standard deviation (par/orth)

SiO_2	305	-36.81	0.97/1.12
SiO_2	300	-34.58	1.21/0.89
GO	305	-23.98	1.15/1.33
GO	300	-21.63	0.93/1.02

The results reported above suggest that a backbone orientation parallel to surface is the favored configuration; this leads us to hypothesize that long MD simulations, starting from an orthogonal orientation of the backbone, bring to the parallel orientation of the backbone; in this case the chain is affected by the interactions with surfaces (in turn temperature changes affect these interactions) whereas a negligible effect, due to the surface, is expected when the chain is orthogonal.

It is also to point out that E_{water} is missing in the analysis reported above. Suppose that surface-water and PNIPAM-water H-bonds are broken due to the formation of surface-PNIPAM H-bonds, in that case water molecules would be released from the surface and PNIPAM to the bulk followed by the recovery of water-water H-bond. Hence, there are more water-water H-bonds near the surface and PNIPAM for the parallel configuration. In other words if E_{water} was included in the calculation, by considering a huge amount of water molecules, the parallel configuration would become even more favorable in terms of the system energy.