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

SUPPORTING INFORMATION

Complex role of chemical nature and tacticity on adsorption free energy of carboxylic acid polymers at oil-water interface: Molecular dynamics simulations

Raviteja Kurapati, Upendra Natarajan*

Macromolecular Modeling and Simulation Laboratory

Department of Chemical Engineering,

Indian Institute of Technology (IIT) Madras, Chennai 600036, India

Ph: 91-44-22574184, Fax: 91-44-22574150, 22574152

*Corresponding Author: E-mail: unatarajan@iitm.ac.in

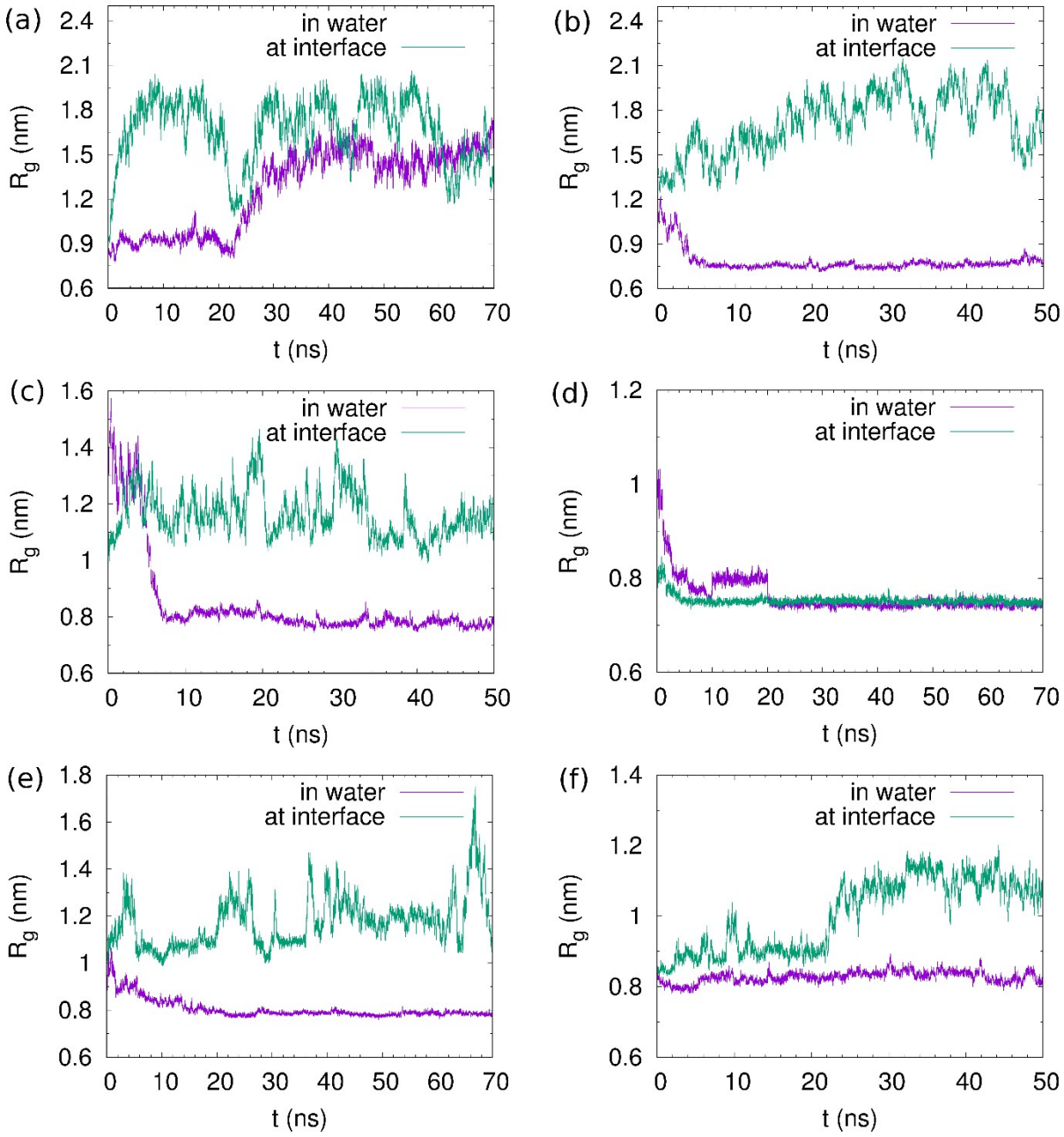


Figure S1. Radius of gyration of polymer as a function of time for umbrella sampling windows taken from end-points of reaction coordinate (i. e., polymer at the interface and in bulk aqueous phase): (a) i-PAA (b) s-PAA (c) i-PMA (d) s-PMA (e) a-PEA and (f) s-PEA.

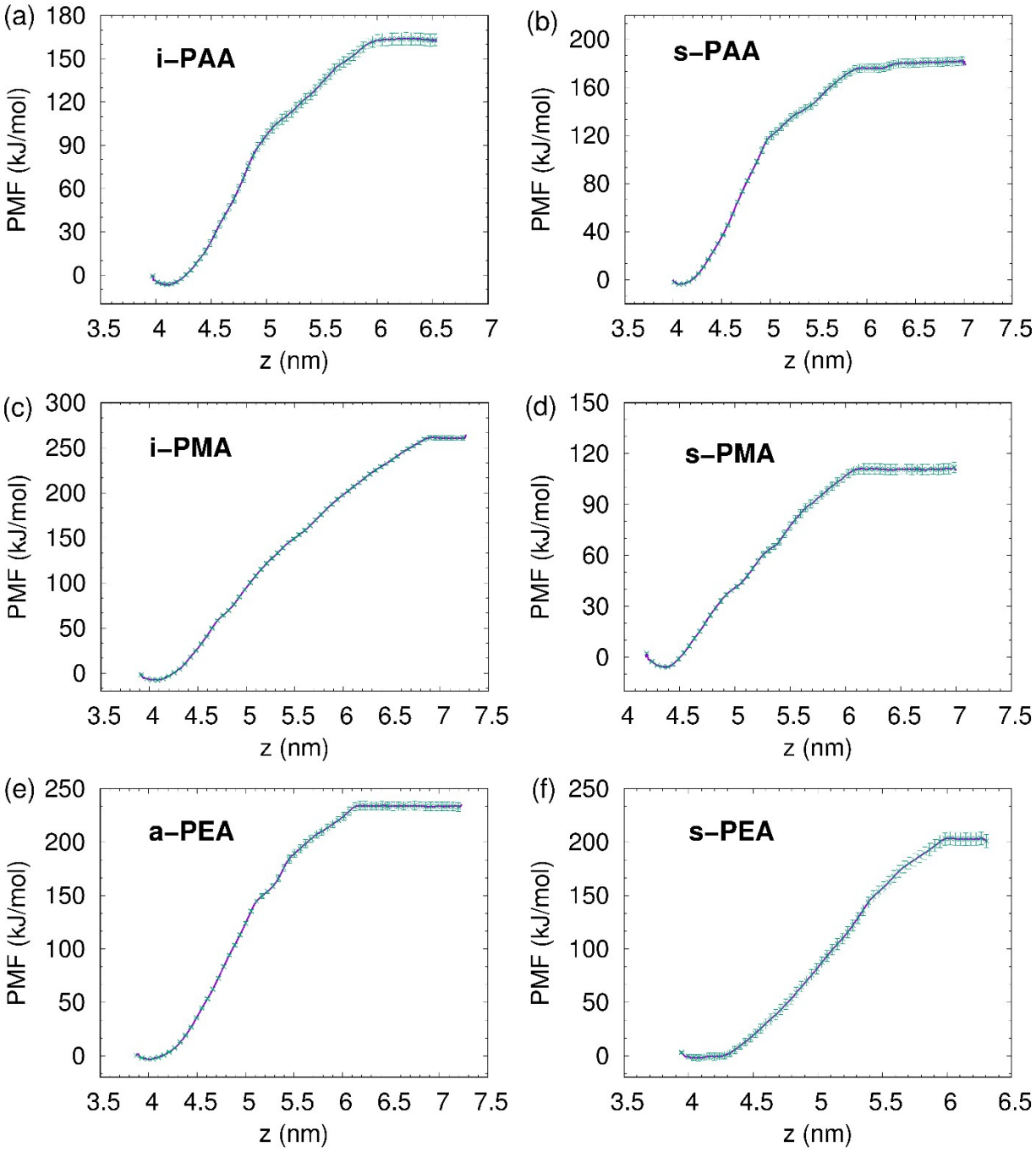


Figure S2. Error estimates for the PMF curves of adsorption of (a) i-PAA (b) s-PAA (c) i-PMA (d) s-PMA (e) a-PEA and (f) s-PEA at CCl4-water interface from aqueous phase. z-coordinate close to 4 nm indicate position of interface and close to 7 nm indicate bulk aqueous phase.

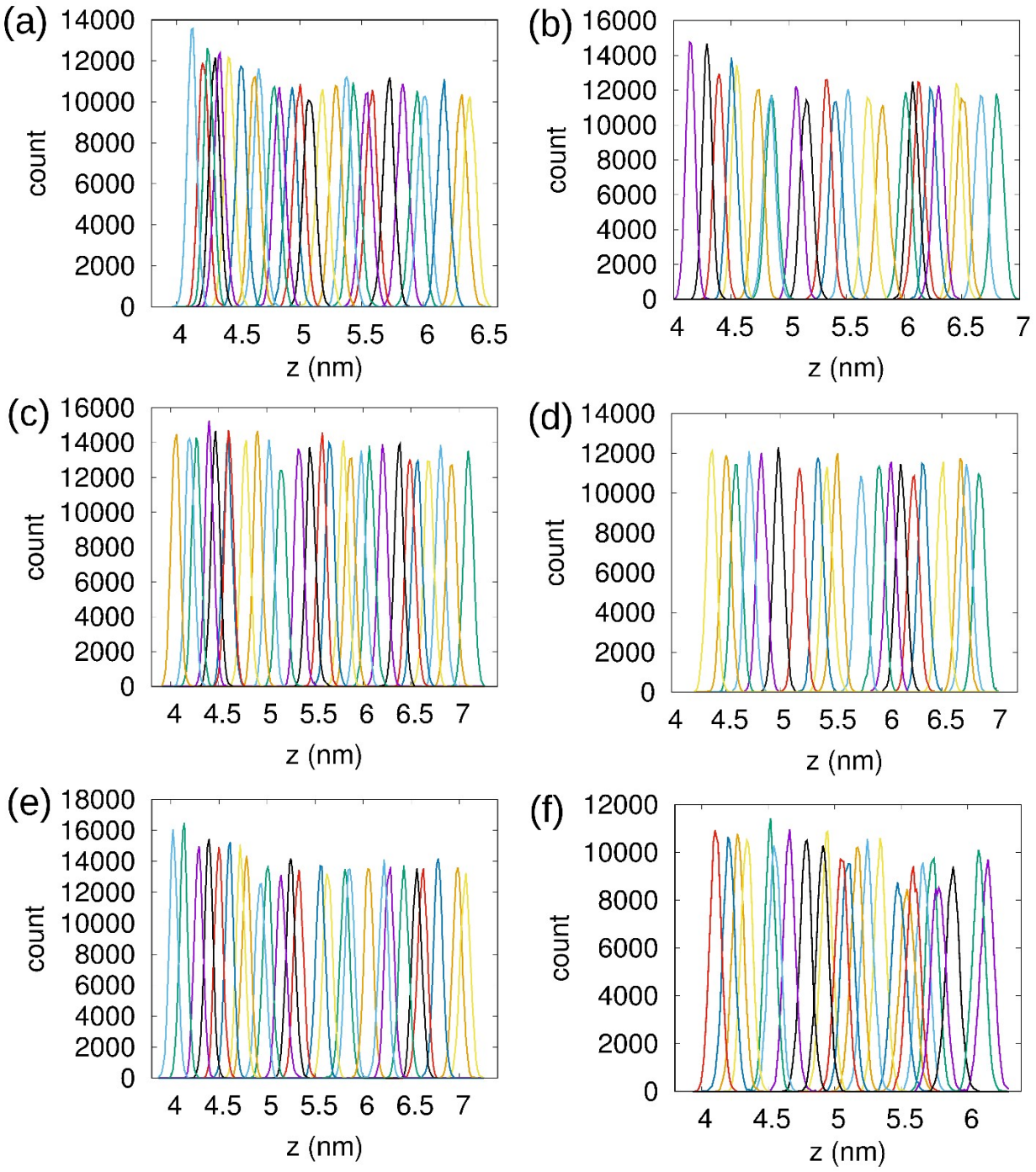


Figure S3. Histogram of umbrella sampling windows. Reaction coordinate (z) is the distance between center of mass of polymer and the center of CCl_4 phase. (a) i-PAA (b) s-PAA (c) i-PMA (d) s-PMA (e) a-PEA and (f) a-PEA.

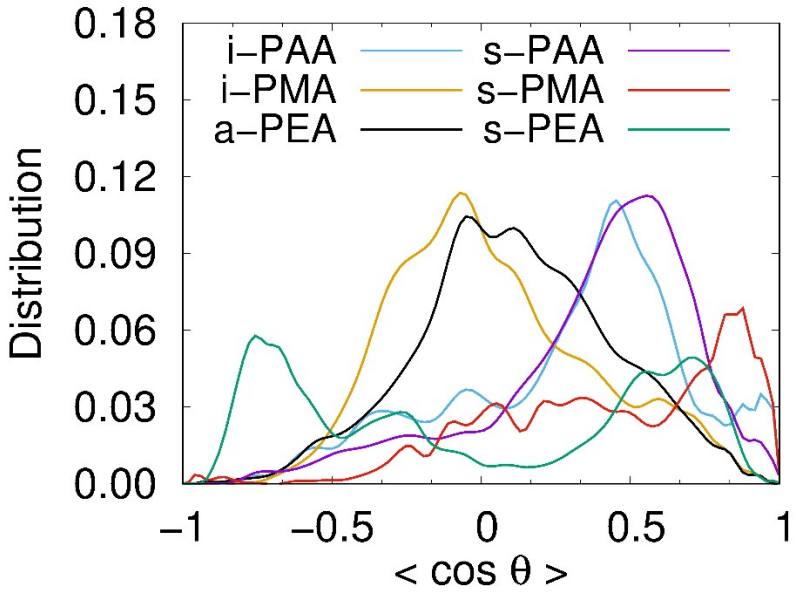


Figure S4. Orientation distribution of backbone C-C* bonds. C* represent substituted carbon. θ is angle made by bond with respect to the interface normal pointed towards aqueous phase.

Table S1. Change in Gibbs free energy (ΔG_{ads}), enthalpy (ΔH_{ads}) and entropy (ΔS_{ads}) due to adsorption of polymer at the CCl_4-water interface.

Polymer	ΔG_{ads} (kJ/mol)	ΔH_{ads} (kJ/mol)	ΔS_{ads} (kJ/mol)
i-PAA	-170.33 ± 4.15	-396.86 ± 42.93	-0.76 ± 0.14
s-PAA	-184.97 ± 3.52	-480.15 ± 52.58	-0.98 ± 0.18
i-PMA	-268.96 ± 2.28	-578.48 ± 15.68	-1.03 ± 0.05
s-PMA	-116.48 ± 3.02	-256.85 ± 57.85	-0.47 ± 0.19
a-PEA	-236.63 ± 4.04	-660.08 ± 48.67	-1.41 ± 0.16
s-PEA	-203.25 ± 5.95	-483.94 ± 54.97	-0.94 ± 0.18

Table S2. Probability of backbone torsion angles for transition between *trans*, *gauche positive* and *gauche negative* states.

Polymer	Probability for transition
i-PAA	0.023
s-PAA	0.017
i-PMA	0.005
s-PMA	0.012
a-PEA	0.022
s-PEA	0.020

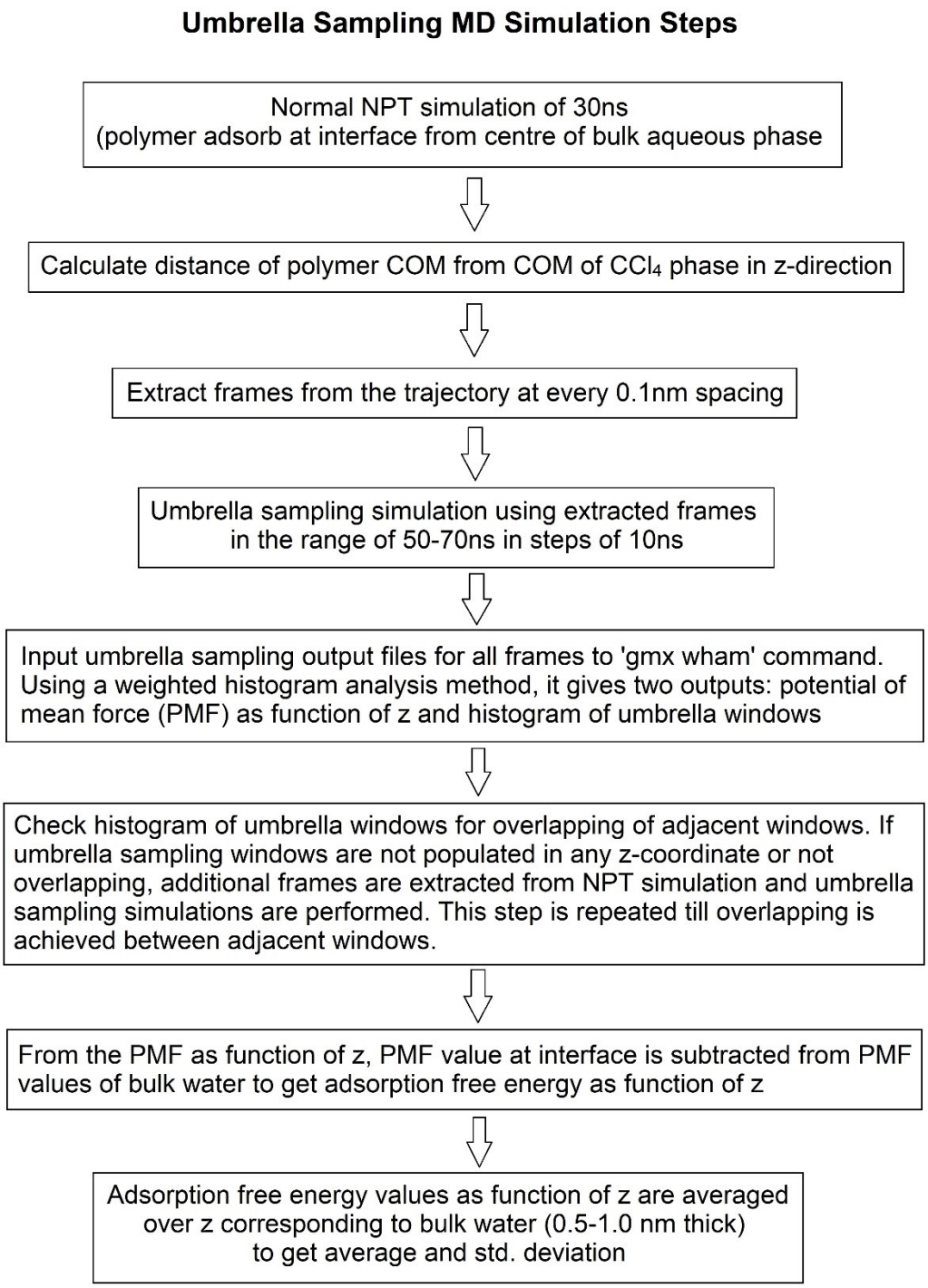
The probability for transition of dihedral between different states is obtained by counting number of dihedral transitions out of total number of frames used for sampling (5000 frames).

Table S3. Average fraction of backbone dihedrals of adsorbed polymer in different dihedral states.

Polymer	*trans*	*g*+ ($0°<\phi<120°$)	*g*- ($-120°<\phi<0°$)
i-PAA	0.73	0.17	0.10
s-PAA	0.83	0.11	0.06
i-PMA	0.96	0.01	0.03
s-PMA	0.94	0.04	0.02
a-PEA	0.77	0.15	0.08
s-PEA	0.47	0.32	0.21

Table S4. Change in number of hydrogen bonds per chain (ΔN_{HB}) between different pairs: Intrachain (P-P), polymer-water (P-W) and water-water (W-W).

Polymer	ΔN_{HB} (P-P)	ΔN_{HB} (P-W)	ΔN_{HB} (W-W)
i-PAA	-0.33 ± 0.82	-2.12 ± 1.75	14.50 ± 3.37
s-PAA	-1.12 ± 0.35	-0.44 ± 0.92	21.70 ± 2.15
i-PMA	1.84 ± 0.01	-8.25 ± 0.20	19.29 ± 2.29
s-PMA	1.28 ± 0.13	-5.61 ± 0.46	14.25 ± 1.54
a-PEA	-0.72 ± 0.52	-4.29 ± 0.94	33.62 ± 1.11
s-PEA	-2.46 ± 0.61	1.64 ± 1.27	13.95 ± 3.70



Scheme 1. Flowchart showing the steps followed for carrying out umbrella sampling MD simulations.