Supplementary Information for:

Anisotropic Surface Functionalization of Au Nanorods Driven by Molecular Architecture and Curvature Effects

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<u>Table S1:</u> Molecular details of the polymers

# of Branches	Segments in each branch	Segments in backbone	Total segments	Position of the branches *	Code
0	0	20	20	0	20l
		25	25	0	25l
		30	30	0	30l
		35	35	0	35l
		40	40	0	40l
		45	45	0	45l
		50	50	0	50l
		55	55	0	55l
		113	113	0	113l
1	5	10	15	9	15-1b
		15	20	14	20-1b
		20	25	19	25-1b
		25	30	24	30-1b
		30	35	29	35-1b
		35	40	34	40-1b
		40	45	39	45-1b
2	5	20	30	14, 19	30-2b
		25	35	19, 24	35-2b
		30	40	24, 29	40-2b
		35	45	29, 34	45-2b
		40	50	34, 39	50-2b
3	5	20	35	9, 14, 19	35-3b
		20	35	5, 10, 15	35-3b*
		25	40	14, 19, 24	40-3b
		30	45	19, 24, 29	45-3b
		35	50	24, 29, 34	50-3b
		40	55	29, 34, 39	55-3b

* Segments are numerated starting from the surface.

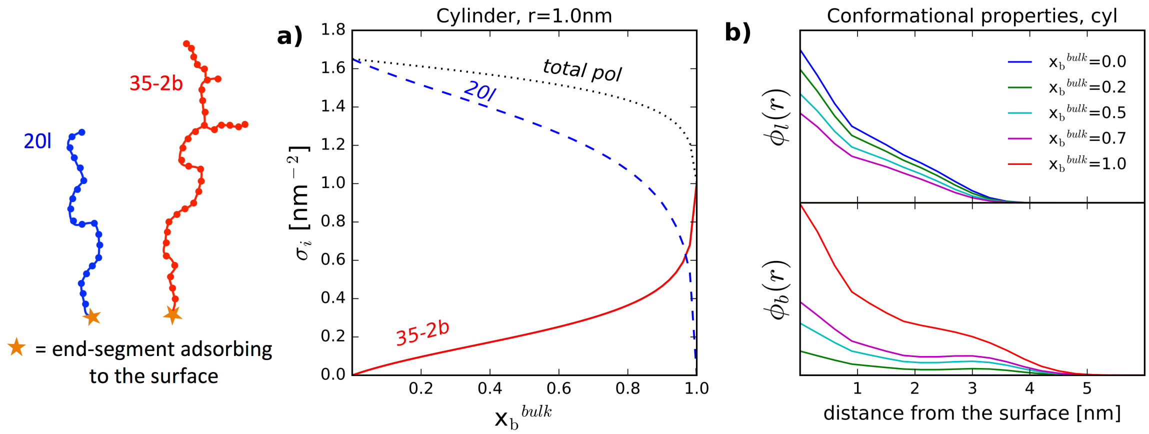

Figure S1: a) Density of surface adsorbed polymers as a function of the molar fraction of the branched polymer in the bulk for a mixture comprising a linear polymer of 20 monomers (blue line dashed) and a branched polymer of 35 total monomers, 25 segments in the backbone and 2 branches of 5 segments each (red solid line) on a cylinder of R =1 nm. **b)** Volume fraction of the surface adsorbed polymers as a function of the distance from the tethering surface. Results correspond to a cylindrical surface of radius 1 nm. Upper and lower plots show the volume fraction of the linear and the branched polymer, respectively. Colors correspond to different composition of the bulk solution, as indicated in the legend.

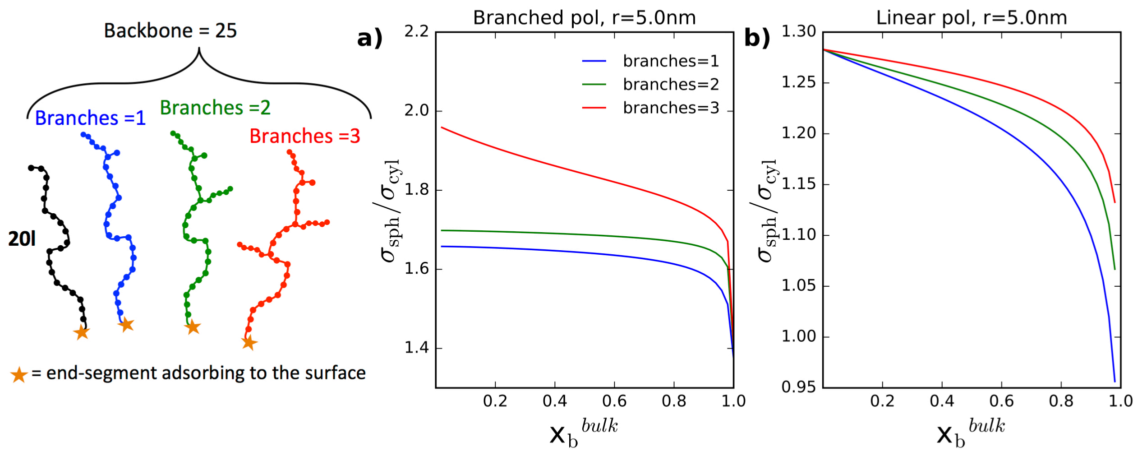

Figure S2: Effect of polymer branching on the curvature-induced partitioning between a sphere and a cylinder of R = 5 nm for a polymer mixture comprising a linear polymer of 20 monomers (20l) and a branched polymer with backbone length = 25 segments and one, two or three branches (colors blue, green, and red respectively, see scheme on the left). The plot shows the sphere-cylinder partition for the branched (panel **a**) and linear (panel **b**) polymer in the mixture as a function of the bulk molar fraction of the branched polymer.

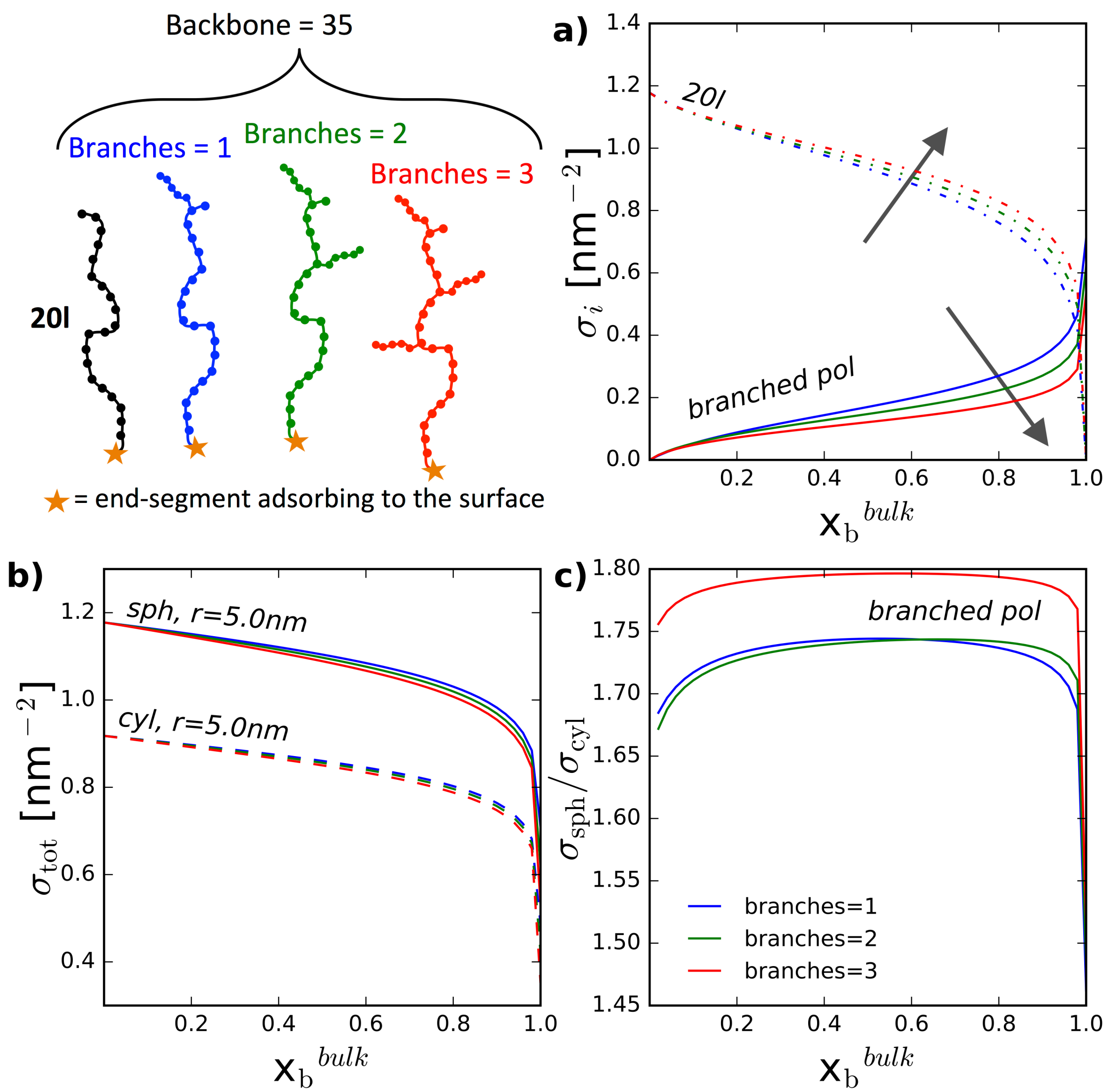

Figure S3: Effect of polymer branching on the adsorption for polymer mixtures comprising a linear polymer of 20 monomers (20l) and a branched polymer with backbone length = 35 segments and one, two or three branches (colors blue, green and red respectively, as shown in legend in panel c and in scheme on the upper left panel). All results correspond to curved surfaces of R = 5 nm. **a)** Surface density of the adsorbed linear (dash-dot lines) and branched (full lines) polymer as a function of the bulk molar fraction of the branched polymer on a spherical surface. **b)** Total surface density of adsorbed polymers ($\sigma_{tot} = \sigma_l + \sigma_b$) as a function of the bulk molar fraction of the branched polymer for spherical (full lines) and cylindrical (dashed lines) surfaces. **c)** Sphere-cylinder partition for the branched polymer in the mixture as a function of the bulk molar fraction of the branched polymer.

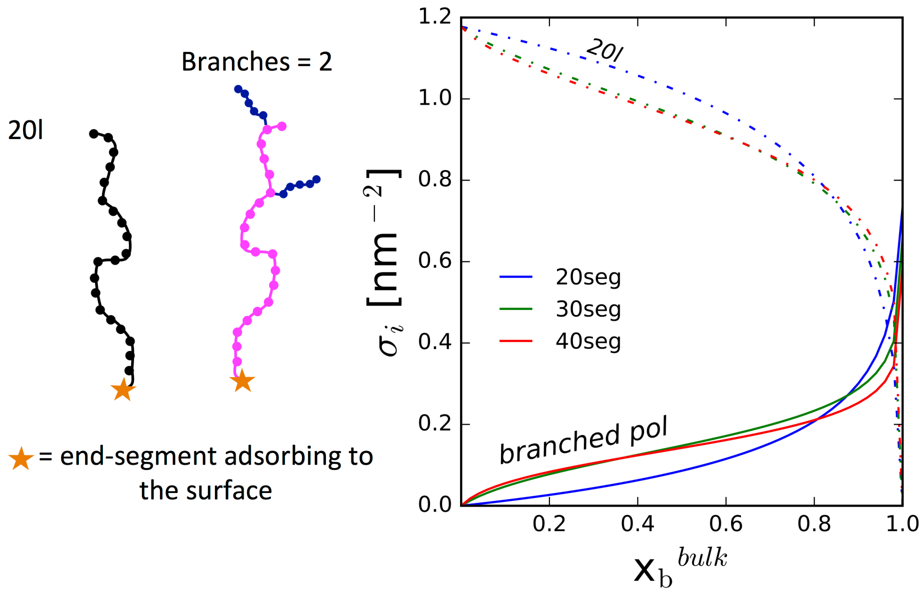

Figure S4: Surface density of adsorbed polymers as a function of the bulk molar fraction of the branched polymer for mixtures comprising a linear (20l, dash-dot lines) and a branched polymer (full lines) with different backbone length (20, 30, 40 monomers in blue, green, and red lines respectively) and containing two branches (see scheme on the left). Results correspond to a spherical surface of R = 5 nm.

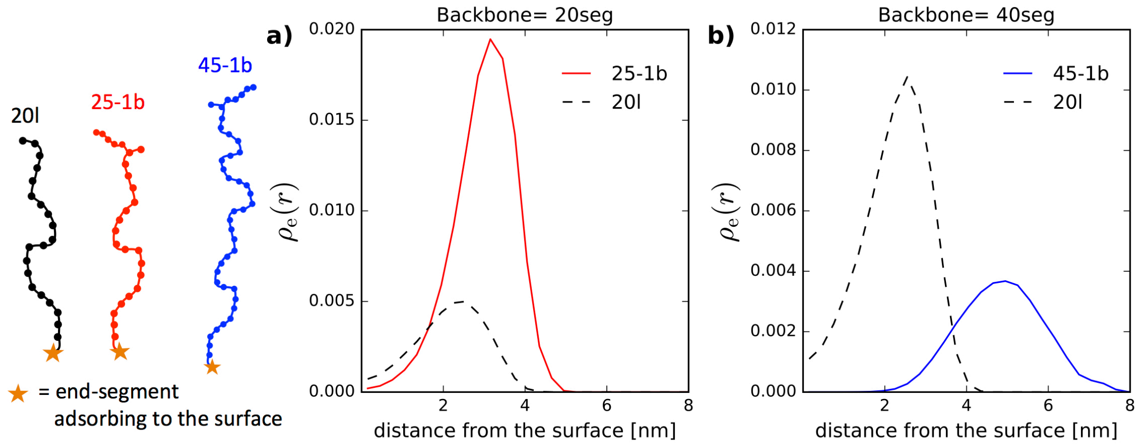

Figure S5: Density of free ends as a function of the distance from the tethering surface for a spherical surface of R = 5 nm. Plots correspond to a mixture of a linear polymer of 20 monomers (20l) and a branched polymer with one branch and backbone length of 20 (25-1b) and 40 (45-1b) segments, in panels **a** and **b**, respectively (see scheme on the left). Dashed lines correspond to the end segment of the backbone of the linear polymer. Full lines correspond to the end segment of the backbone and branches for the branched polymer. All the cases are for a fixed bulk composition with $x_b^{bulk} = 0.9$.

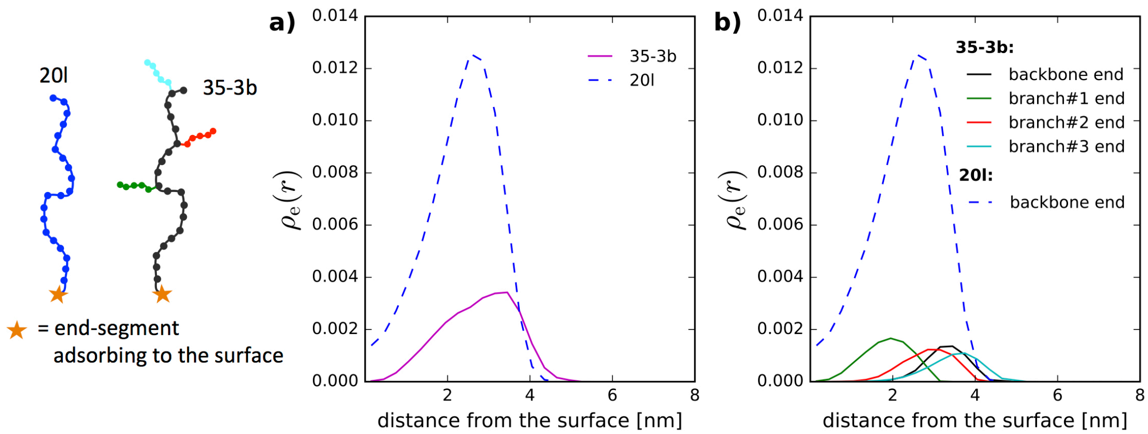

Figure S6: Density of free ends as a function of the distance from the tethering surface for a spherical surface of *R* = 5 nm. Plots correspond to a mixture of a linear polymer of 20 monomers (20l) and a branched polymer with 3 branches and backbone length of 20 segments (35-3b, see scheme on the left). All the cases are for a fixed bulk composition with x_b^{bulk} = 0.9. Dashed lines show the end-segment density of the backbone of the linear polymer (panels **a** and **b**). Full lines show the sum of the end-segment densities of the backbone and each branch of the branched polymer in panel a and a detail of the individual densities of each type of end segment in panel **b**.

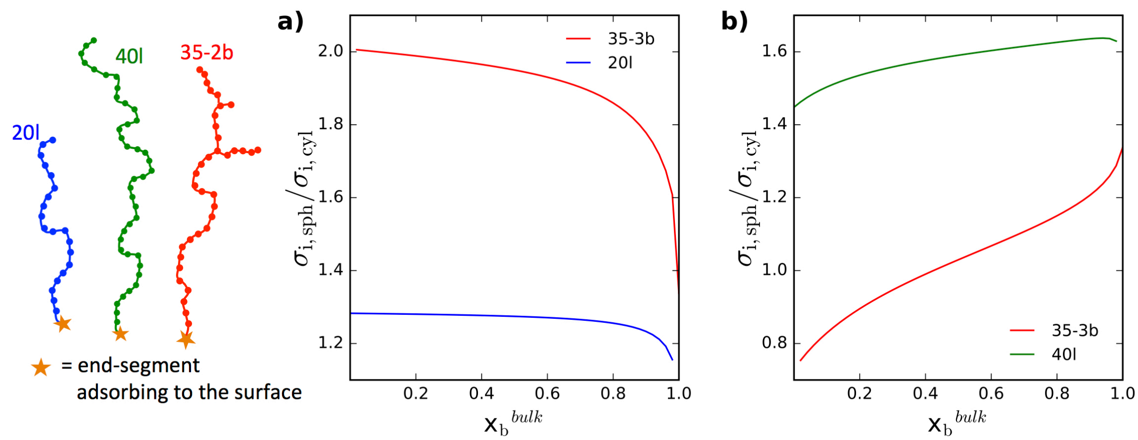

Figure S7: Effect of length of the linear backbone on the sphere-cylinder partition for the branched and linear polymer in the mixture as a function of the bulk molar fraction of the branched polymer. The mixtures contain a branched polymer with backbone length = 20 segments and three branches (35-3b, red line in panels a and b) and linear polymers of 20 (panel **a**, blue line) or 40 (panel **b**, green line). Results correspond to R=5nm and a bulk composition with x_b^{bulk} = 0.9.

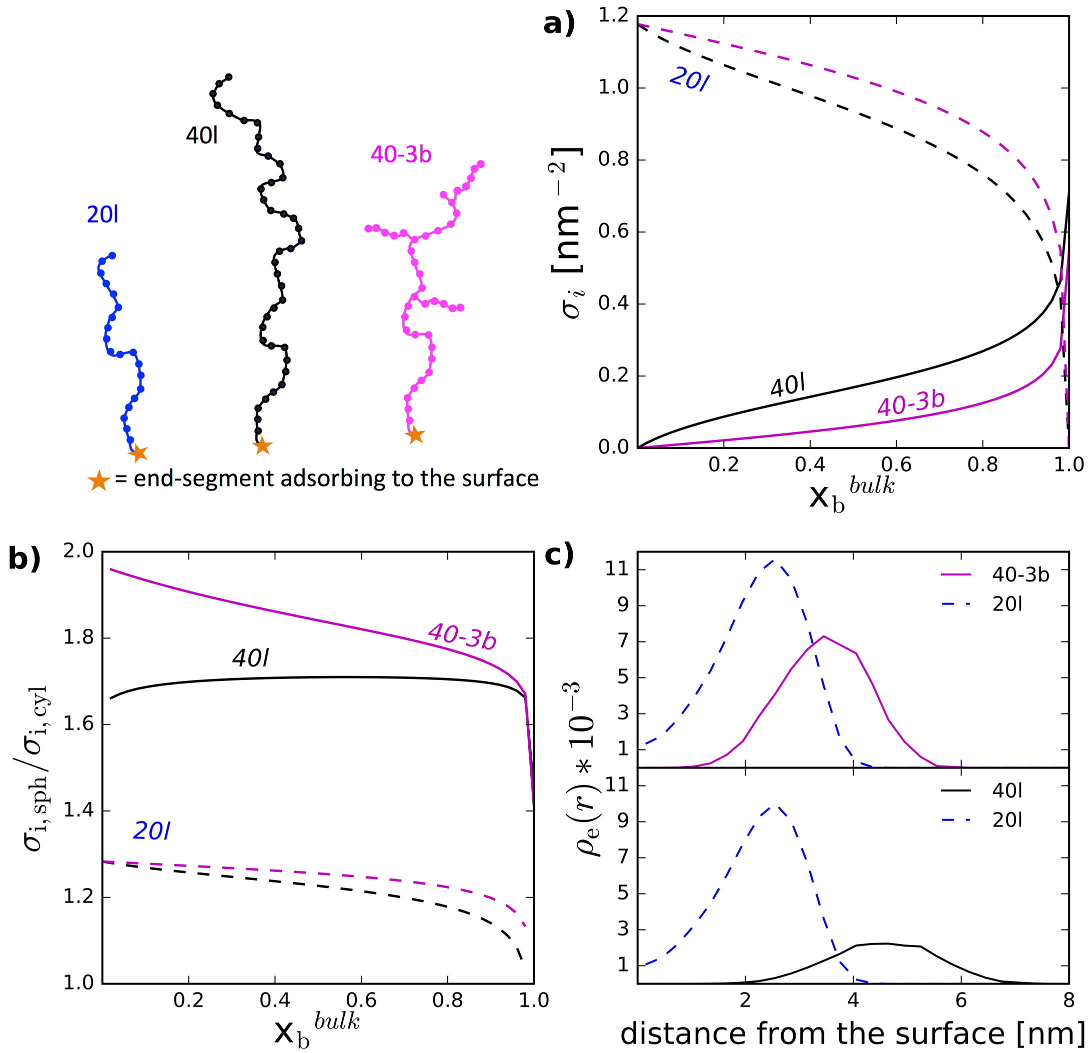

Figure S8: Effect of the intramolecular connectivity on the competitive adsorption of binary mixtures. **a**) Molar fraction of the branched polymer in the adsorbed layer as a function of the bulk molar fraction of the branched polymer. The full magenta and full black lines correspond to the 40l and 40-3b polymers respectively (see scheme on the upper left panel). The dashed magenta and dashed black lines correspond to the 20l polymer in the 20l/40l and in the 20l/40-3b mixtures, respectively. Results correspond to a spherical surface of *R* = 5 nm. **b)** Partition of the linear and branched polymers between a sphere and a cylinder of *R* = 5 nm for the 20l/40l (magenta) and the 20l/40-3b (black) mixtures. **c)** Total density of free ends as a function of the distance from the tethering surface for a spherical surface of *R* = 5 nm. All the cases are for a fixed bulk composition with $x_b{}^{bulk}$ = 0.9. Lines and colors are indicated in the legend.

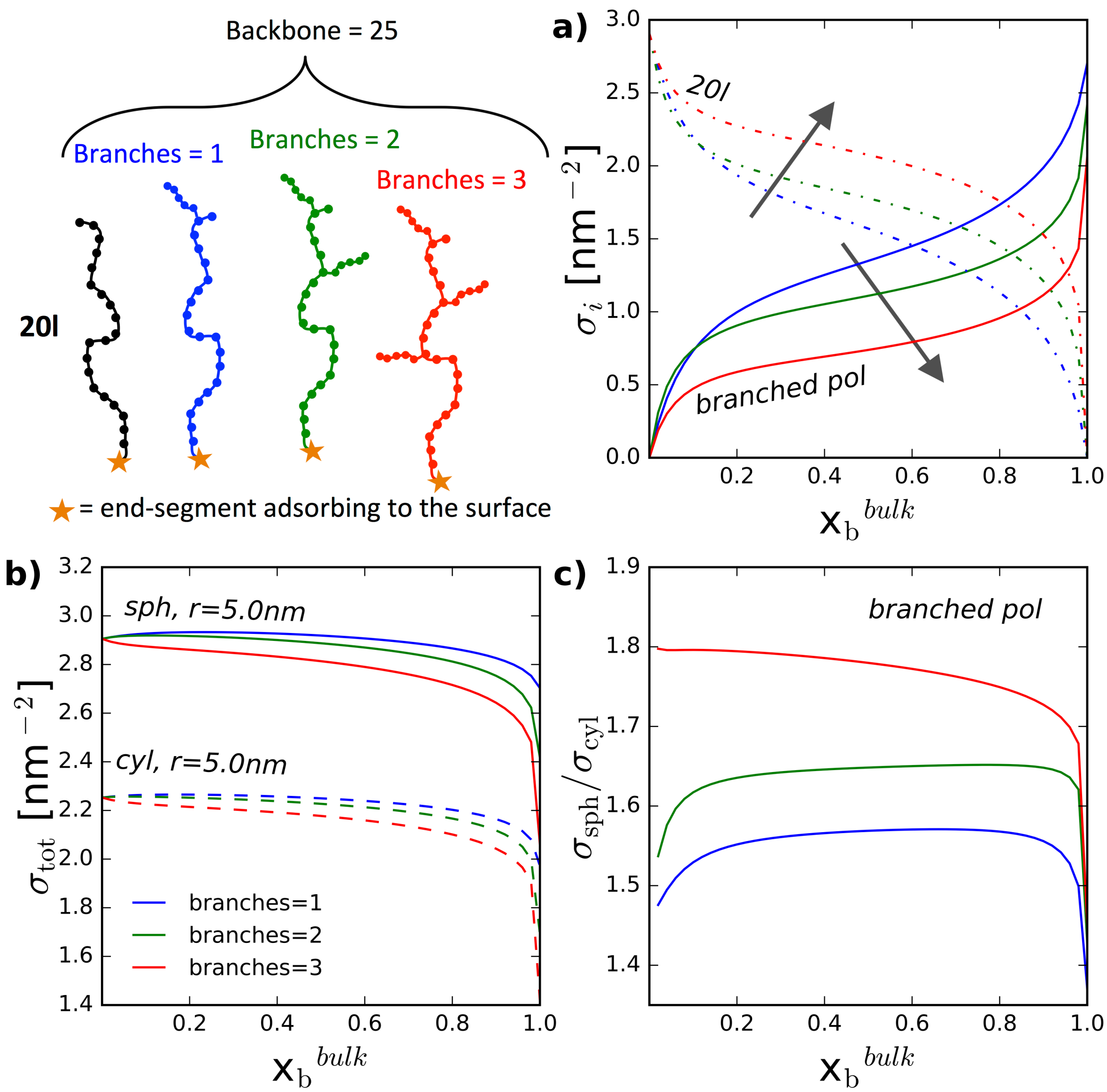

Figure S9: Effect of polymer branching on the adsorption for polymer mixtures comprising a linear polymer of 20 monomers (20l) and a branched polymer with backbone length = 25 segments and one, two or three branches (colors blue, green and red respectively, as shown in legend in panel d and in upper left scheme). All results correspond to curved surfaces of *R* = 5 nm and to poor-solvent conditions (χ_c/χ = 0.8). **a)** Surface density of the adsorbed linear (dash-dot lines) and branched polymer (full lines) as a function of the bulk molar fraction of the branched polymer **b)** Total surface density of adsorbed polymers ($\sigma_{tot} = \sigma_l + \sigma_b$) as a function of the bulk molar fraction of the branched polymer for spherical (full lines) and cylindrical (dashed lines) surfaces. **c)** Sphere-cylinder partition for the branched polymer in the mixture as a function of the bulk molar fraction of the branched polymer.