Electronic Supplementary Information

Amphiphilic Microgels Adsorbed at Oil-Water Interface as Mixers of Two Immiscible Liquids

Rustam A. Gumerov, [†,‡] Sergei A. Filippov, [†] Walter Richtering, [‡,#] Andrij Pich, [‡,§] Igor I. Potemkin[†,‡,≠,*]

[†]Physics Department, Lomonosov Moscow State University, Moscow 119991, Russian Federation

[‡]DWI - Leibniz Institute for Interactive Materials, Aachen 52056, Germany

[#]Institute of Physical Chemistry, RWTH Aachen University, Aachen 52056, Germany

[§]Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Aachen 52056, Germany

[≠]National Research South Ural State University, Chelyabinsk 454080, Russian Federation

The models of amphiphilic microgel particles

Table S1. Characteristics of microgel models

Subchain length N	Total number of beads, M_{tot}	Crosslinking Fraction, %
3	100017	14
4	100050	11.1
5	100052	9
6	100013	7.7
7	100173	6.7

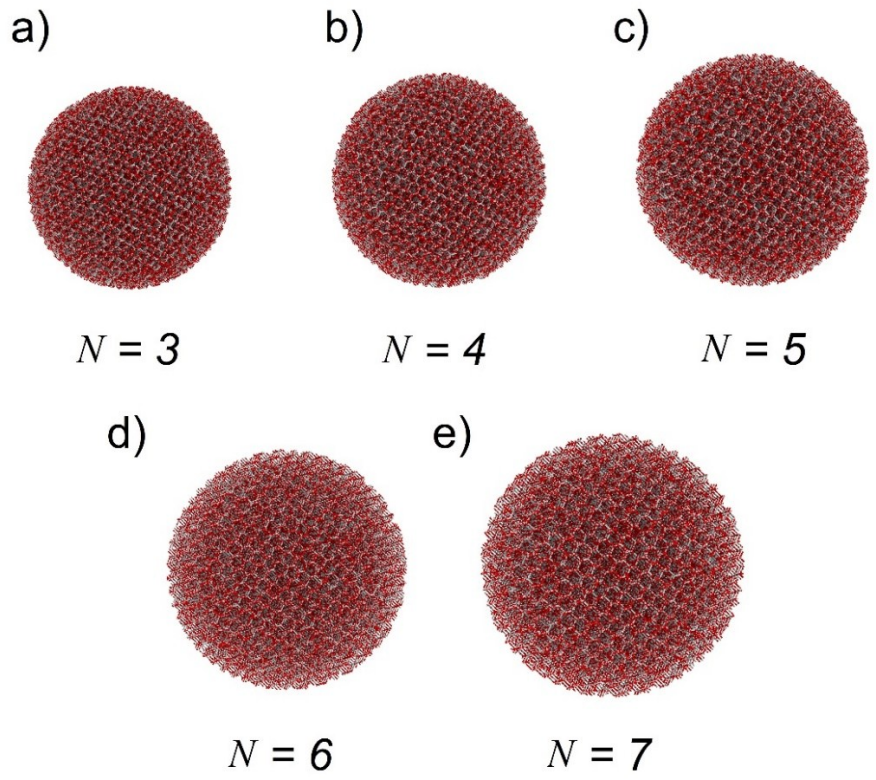

Fig. S1. Initial (before annealing) structures of microgels having equal molecular weight and different length of the subchains (cross-linking density): $N = 3$ (a), 4 (b), 5 (c), 6 (d) and 7 (e) beads per subchain. Average fractions of hydrophobic (red) and hydrophilic (gray) beads are equal in each microgel.

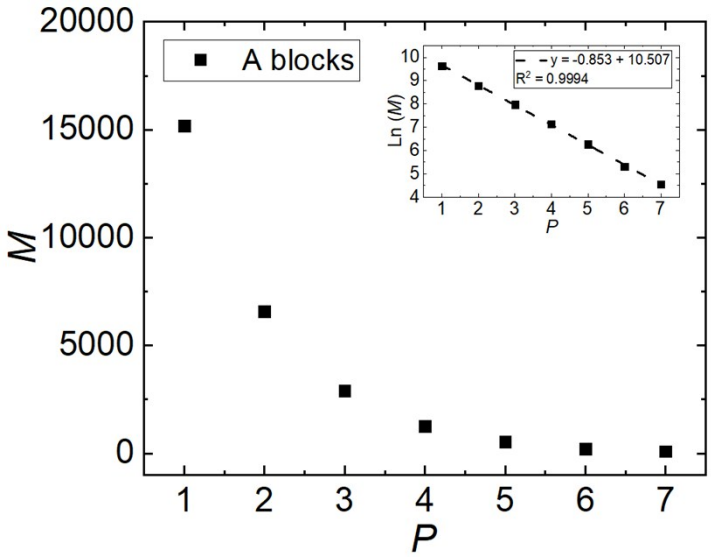

Fig. S2. The average number M of mono- ($P = 1$), di- ($P = 2$), … and heptamers ($P = 7$) of type A in the subchains of the microgel, $N = 7$. The inset shows ln(M) vs. P, and the dashed line corresponds to the linear approximation.

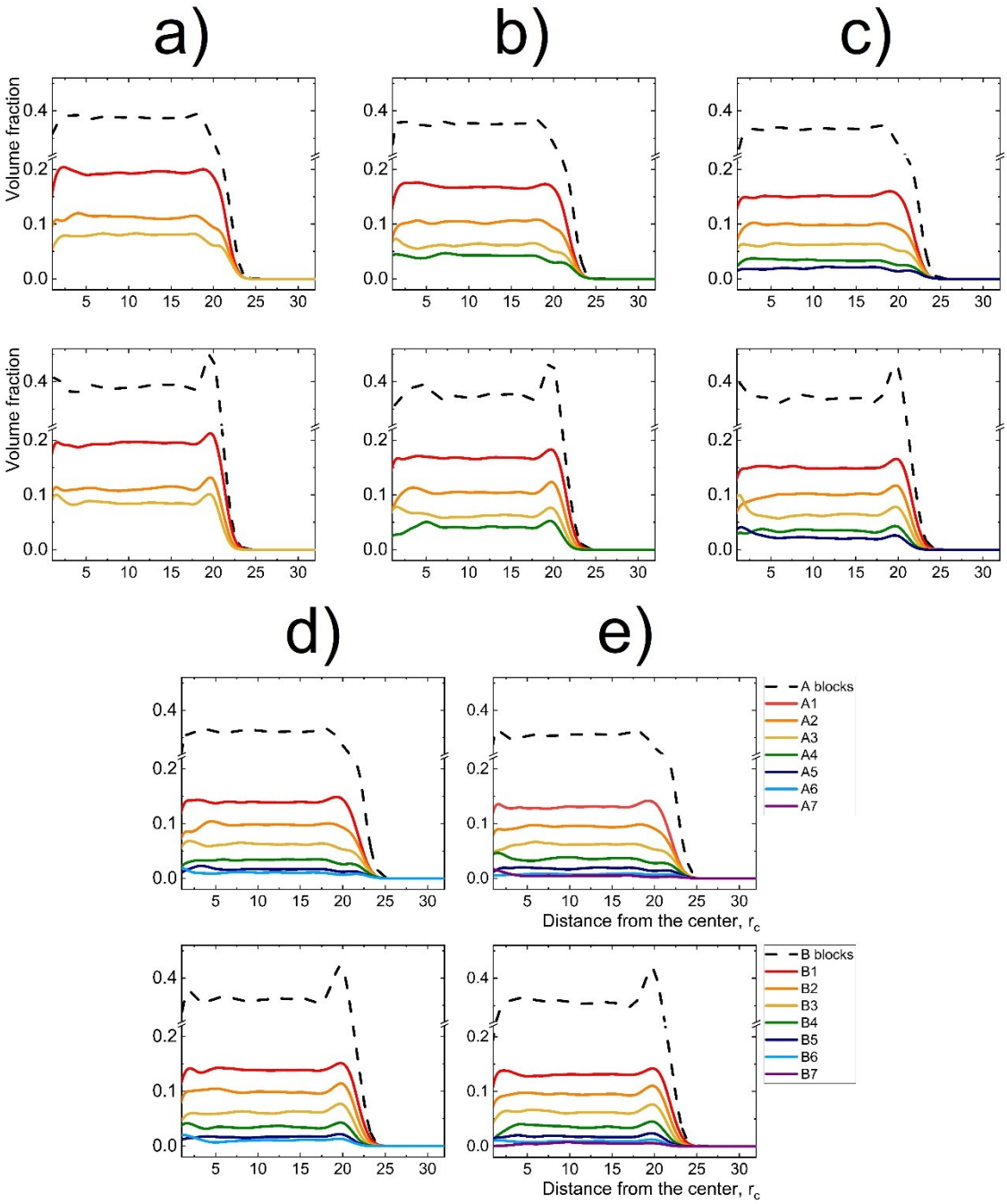

Fig. S3. Radial concentration profiles of the blocks of different lengths P of hydrophilic (upper plots in columns, A1, A2, …) and hydrophobic (bottom plots in columns, B1, B2, …) beads within amphiphilic microgels in a water. Different columns correspond to different lengths of the subchains: $N = 3$ (a), 4 (b), 5 (c), 6 (d) and 7 (e) beads per subchain. The set of the interaction parameters: $a_{AW} = 25$, $a_{BW} = 40$, $a_{AB} = 35$. The dashed curves in each plot corresponds to the total concentration.

The set of the concentration profiles of amphiphilic microgels at the liquid interface

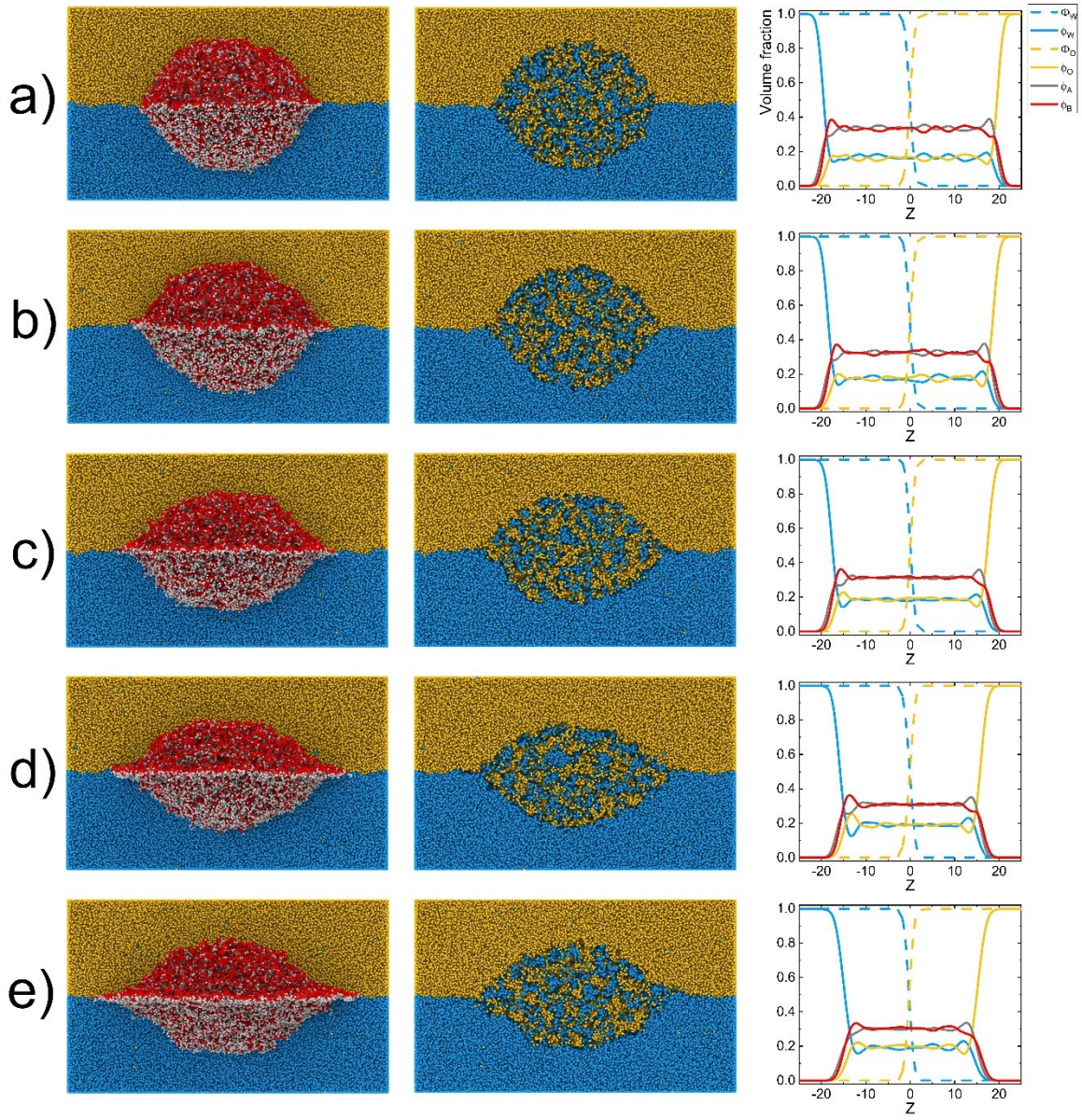

Fig. S4. Side views of the adsorbed microgels (left column), cross-section of the microgels through the center of mass and visualization of oil (yellow) and water (blue) beads only (middle column), concentration profiles along the normal to the interface, z-axis (right column). Solid and dashed lines correspond to the concentrations inside and outside the microgel, respectively. Gray, red, blue and yellow lines are concentrations of hydrophilic (A), hydrophobic (B), water and oil beads, respectively. Different columns correspond to different lengths of the subchains: $N = 3$ (a), 4 (b), 5 (c), 6 (d) and 7 (e) beads per subchain. The set of the interaction parameters: $a_{OW} = 50$, $a_{AW} = a_{BO} = 25$, $a_{AO} = a_{BW} = 40$, $a_{AB} = 35$.

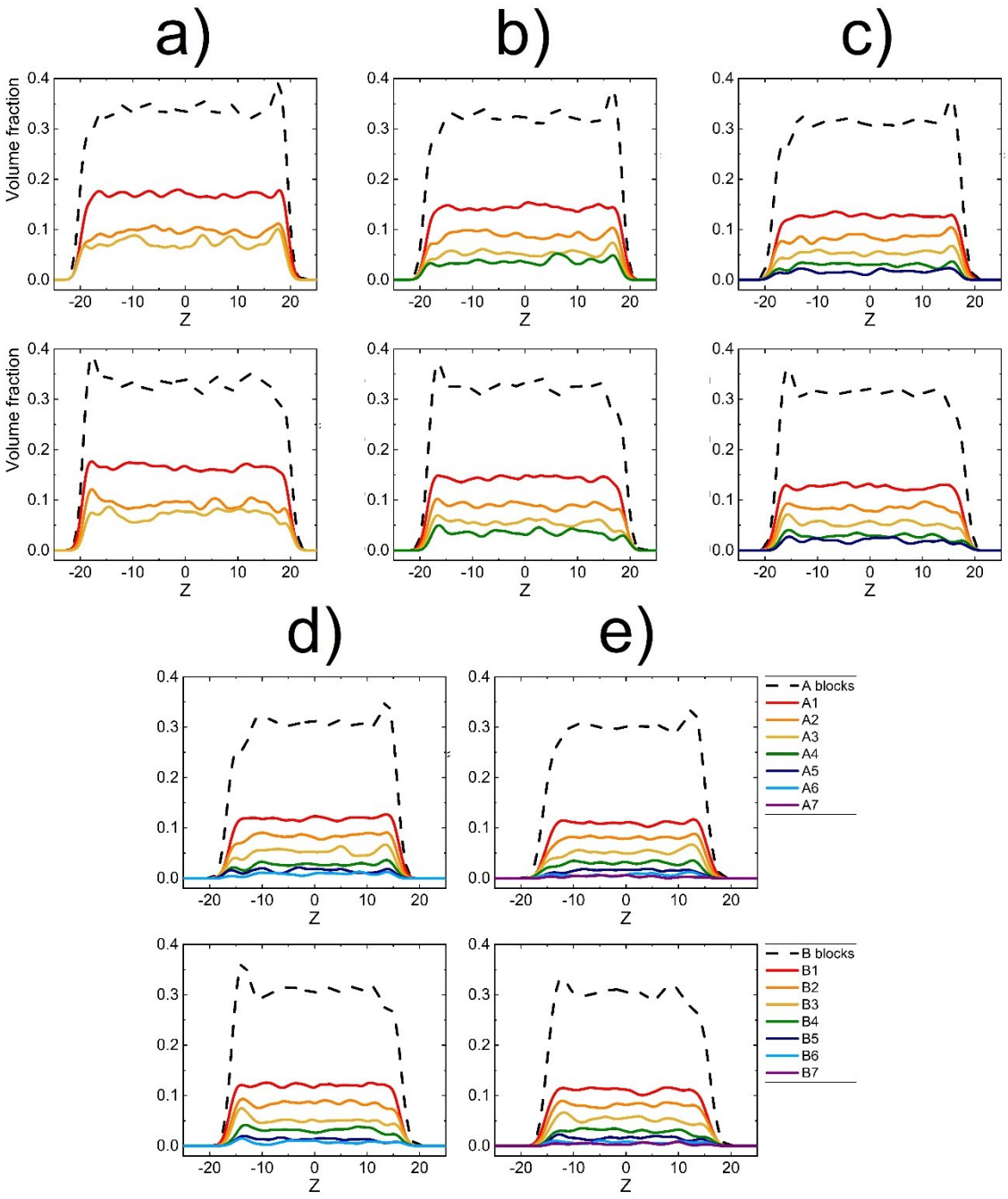

Fig. S5. Concentration profiles along the normal to the interface, z-axis of blocks of different lengths *P* of hydrophilic (upper plots in columns) and hydrophobic (bottom plots in columns) polymers within amphiphilic microgels at the liquid interface. Different columns correspond to different lengths of the subchains: $N = 3$ (a), 4 (b), 5 (c), 6 (d) and 7 (e) beads per subchain. The set of the interaction parameters: $a_{OW} = 50$, $a_{AW} = a_{BO} = 25$, $a_{AO} = a_{BW} = 40$, $a_{AB} = 35$. The dashed curves in each plots corresponds to the total concentration.

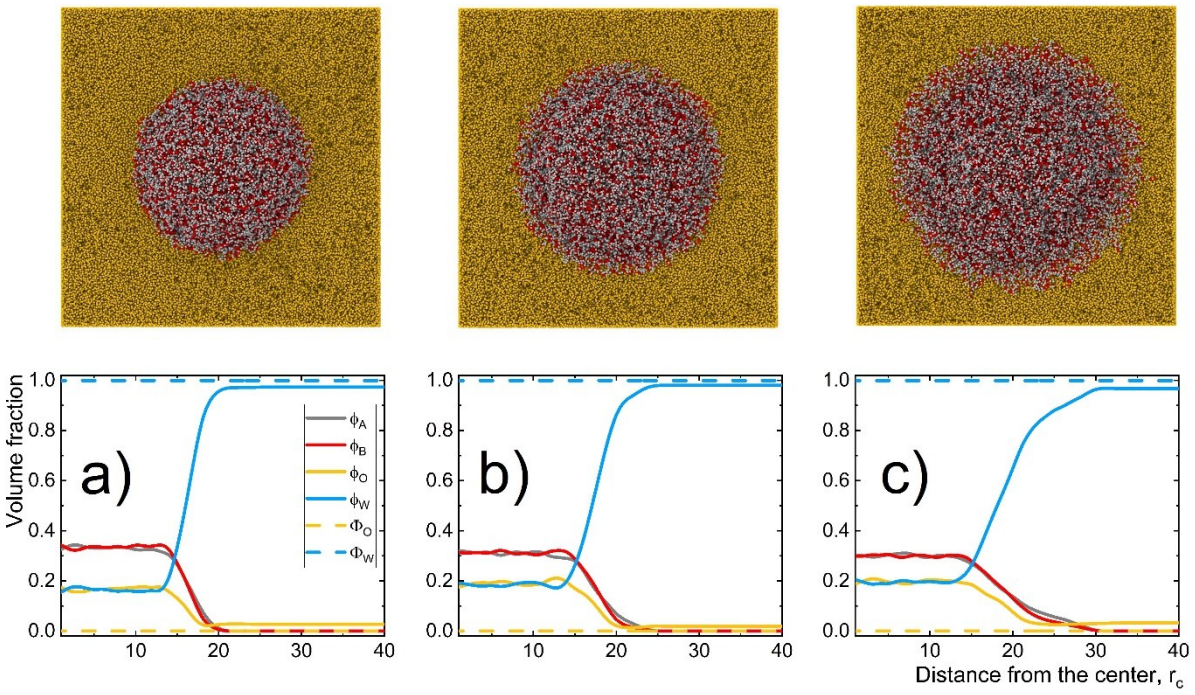

Fig. S6. Bottom views of the adsorbed microgels (upper row), radial concentration profiles in water phase close to the interface $z = 0$ (lower row). Different rows correspond to different lengths of the subchains: $N = 3$ (a), 5 (b) and 7 (c). The set of the interaction parameters: $a_{OW} = 50$, $a_{AW} = a_{BO} = 25$, $a_{AO} = a_{BW} = 40$, $a_{AB} = 35$.

Calculation of microgels volume and surface area

The geometric properties of copolymer microgels were calculated using the modifier implemented in the OVITO[1] software. First, we selected the mirogels beads (A and B beads) for all systems and performed the Delaunay tetrahedrization. Then, rom the resulting tetrahedra, all elements are removed whose circumsphere does not fit into the virtual probe sphere of radius R_{probe}. The remaining tetrahedra form the solid region, and the closed surface mesh can be extracted, which consists of the triangular faces of the tessellation that divide the solid from the open region (i.e. the microgels inner region from the outer water or the water/oil media in the solution and the interface respectively). Here we chose the default value of the probe radius as R_{probe}= 3. The example of the constructing surface mesh for microgel with N = 5 in solution and at the interface are presented in Fig. S7.

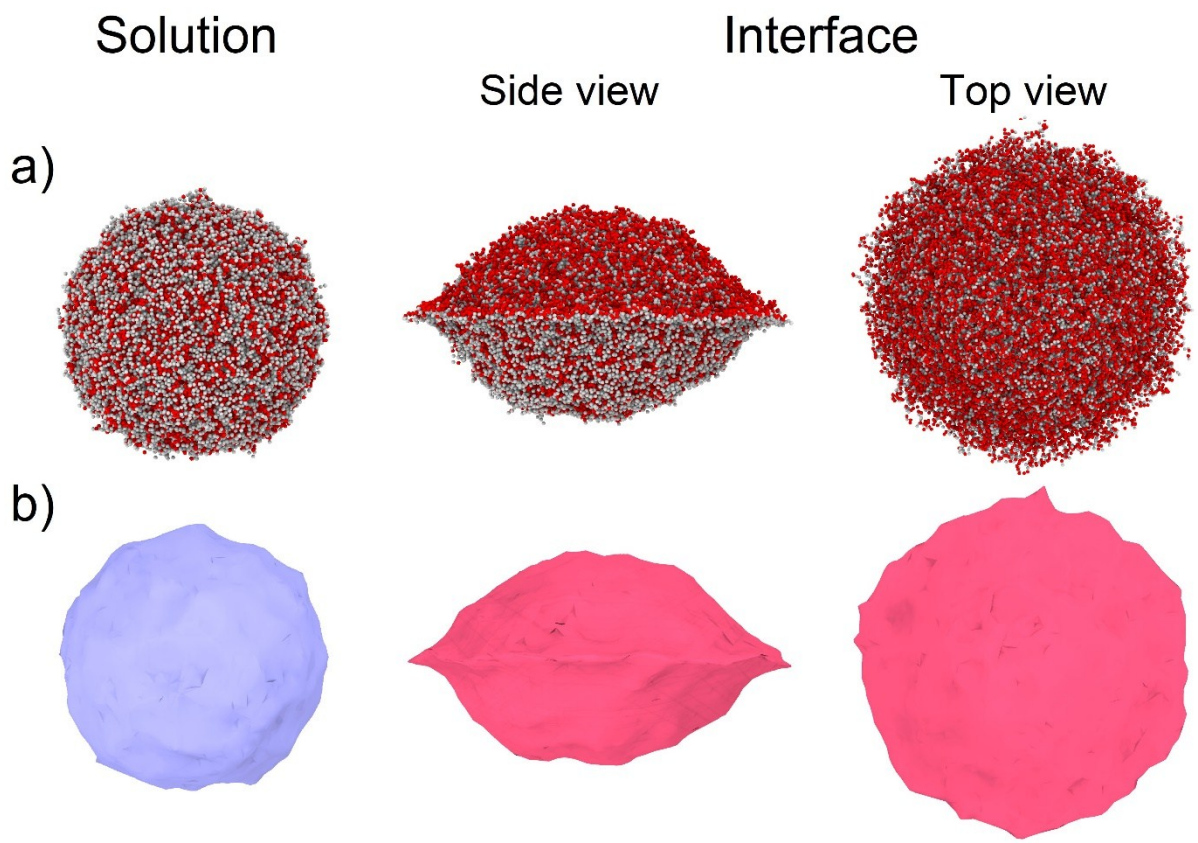

Fig. S7. (a) Simulation snapshots of microgel in water and at the oil/water interface; (b) corresponding isosurfaces. N = 5. The set of the interaction parameters: a_{OW} = 50, a_{AW} = a_{BO} = 25, a_{AO} = a_{BW} = 40, a_{AB} = 35.

Asphericity ratio of the microgels at the liquid interface

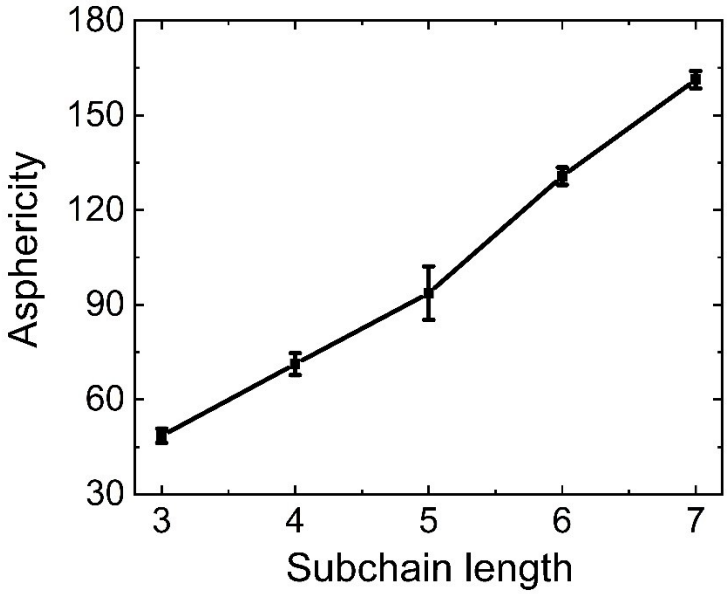

Fig. S8. Asphericity ratio of adsorbed microgels as functions of the subchain length N. The set of the interaction parameters: $a_{OW} = 50$, $a_{AW} = a_{BO} = 25$, $a_{AO} = a_{BW} = 40$, $a_{AB} = 35$.

Calculation of the number of contacts between the water and oil

To determine the mean number of contacts between the immiscible liquids with and without microgel we performed the following procedure. First, for each type of microgel (with particular value of N) in each snapshot a lateral gyration radius[2] R_g^r and the center of mass (COM) of the microgel are determined. Then, we count the number of contacts between oil and water beads within a cylindrical region of a height $40r_c$ and the radius $R_{cyl} = 0.5R_g^r$, where the axis of the cylinder is normal to the interface and passes through the COM of the microgel. The chosen height exceeds the microgel height. The same procedure (counting of the contacts within the cylindrical volume) was done for the bare interface (without the microgel). Then we expanded R_{cyl} up to $0.75R_g^r$ and decreased the height of the cylinder, $30r_c$ (still exceeding the microgel height) and made sure that the ratio of the mean numbers of the contacts does not depend on the choice of the volume.

References

1. A. Stukowski, *JOM*, 2014, **66**, 399–407.
2. R. A. Gumerov, A. A Rudov, W. Richtering, M. Möller and I. I. Potemkin, *ACS Appl. Mater. Interfaces*, 2017, **9**, 31302−31316.