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

Electronic Supplementary Information for:

Hydrophilic dangling chain interfacial segregation in polyurethane networks at aqueous interface and its underlying mechanisms: Molecular dynamics simulation

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1 - Coarse-Grained (CG) Parameters

The bond and angle interactions were defined using equation SI-1 and SI-2 based on MARTINI method. Equilibrium values and force constants for bond and angle potentials were obtained by the following procedure. Initially, 5 ns *NPT* simulation (P = 1 bar, T = 227 °C) were done with a 0.5 fs time step at the atomistic level by OPLS-AA force field. For this step, we used a modified Berendsen thermostat and Parrinello-Rahman barostat. Then, the distributions of the bonds and angles connecting the center of the mass of the atoms of a bead were averaged over these 5 ns. These distribution functions were converted to the probability and the potential values obtained by equation SI-3. The force constants for bonds and angle and equilibrium values were obtained by fitting equation SI-1 and SI-2, respectively. The equilibrium values and force constants for all bonded interactions at the CG level are listed in table SI-1 and SI-2. For simplicity, we ignored dihedral potentials at the CG level.

$$U_{\text{bond}} = \frac{1}{2} K_{\text{bond}} (l - l_0)^2 \quad \text{(SI-1)}$$

$$U_{\text{angle}} = \frac{1}{2} K_{\text{angle}} [\cos(\theta) - \cos(\theta_0))]^2 \quad \text{(SI-2)}$$

$$U = -\ln(p)\, kT \quad \text{(SI-3)}$$

Table SI-1 Bond type parameters at CG level.

Bond	l_0 (nm)	K_{bond} (kJ/mol.nm^2)
Triisocyanate Cross-linker		
NCO-CC1	0.2963	15732
CC1-CC1	0.2408	32040
CC1-NCC	0.2817	12484
NCC-CONH	0.2780	13600
CONH-CC1	0.2779	16366
PTMG		
COH-CC1	0.2399	29340
CC1-COC	0.2836	11446
mPEG		
COH-COC	0.2692	7686
COC-COC	0.3119	4810
COC-COM	0.3130	5140
Urethane		
UOH-UNCO	0.4000	10000
CC1-UNCO	0.2963	15732
COC-UOH	0.2692	7686

CC1-UOH	0.2399	29340
Ethyl acetate		
OCOM-CC3	0.2949	23120

Table SI-2 Angle type parameters at CG level.

angle	θ_0 (°)	K_{angle} (kJ/mol.rad^2)
Triisocyanate Cross-linker		
NCO-CC1-CC1	109.73	41.62
CC1-CC1-NCC	163.94	152.56
CC1-NCC-CONH	136.12	197.84
NCC-CONH-CC1	120.73	566.60
CONH-CC1-CC1	118.91	73.22
CC1-CC1-CC1	157.00	474.80
CONH-NCC-CONH	74.00	122.00
PTMG		
COH-CC1-COC	153.00	170.00
CC1-COC-CC1	133.00	55.80
COC-CC1-COC	150.08	78.62
mPEG		
COH-COC-COC	114.24	38.10
COC-COC-COC	121.43	35.42
COC-COC-COM	119.90	38.50
Urethane		
COC-CC1-UOH	153.00	170.00
CC1-UOH-UNCO	150.00	100.00
UOH-UNCO-CC1	150.00	100.00
UNCO-CC1-CC1	109.73	41.62
COC-COC-UOH	114.24	38.10
COC-UOH-UNCO	150.00	100.00

2 - Probability distribution of products of first step of reaction

Based on the number of dangling chains connected to one cross-linker molecule, four different structures could form at first step of polymerization, i.e. the reaction of cross-linker and mPEG. The probability of these structures is illustrated at Figure SI-1 both for short and long mPEG chains.

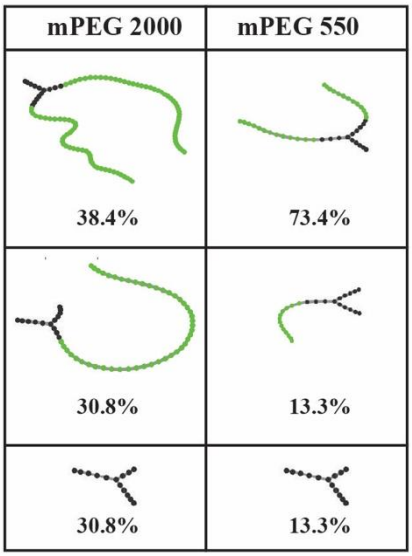

Figure SI-1. The probability of different structures formed at first step of polymerization reaction.

3. Water density profile in y direction

To recognize the height of water layer, we plotted the density profile of the water beads in y direction for case 4 as a representative. The inflection point of the curve shows the place of water/polymer interface.

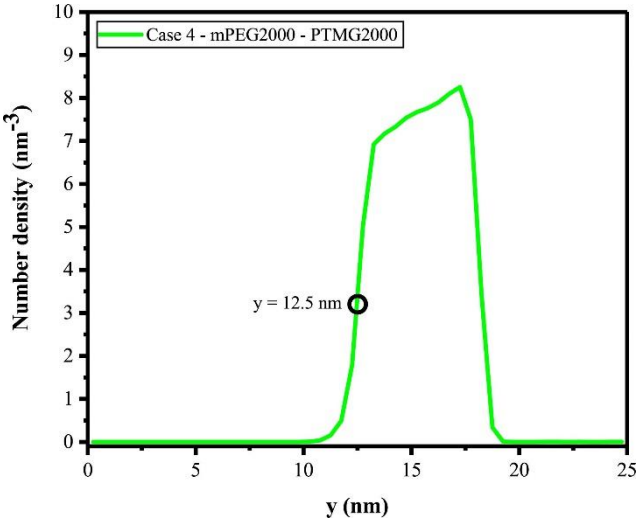

Figure SI-2. Density profile of the water in y direction for case 4. The open dot on the curve shows the inflection point.

4 – mPEG density profile at interface in x direction

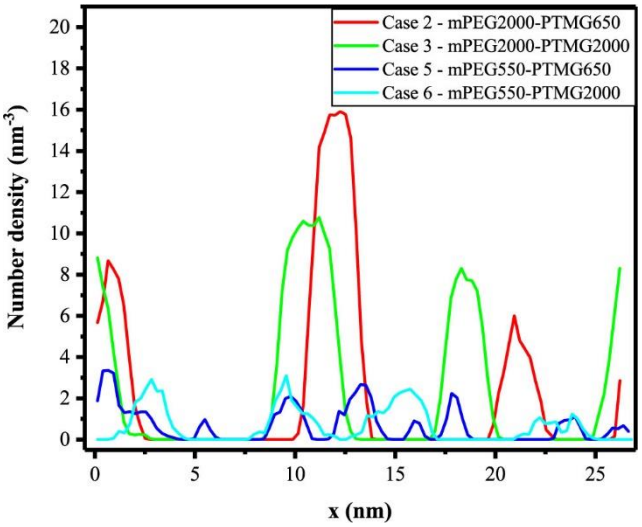

Figure SI-3. The profile density of mPEG chains in x direction.

5 – mPEG density profile at the interface in y direction

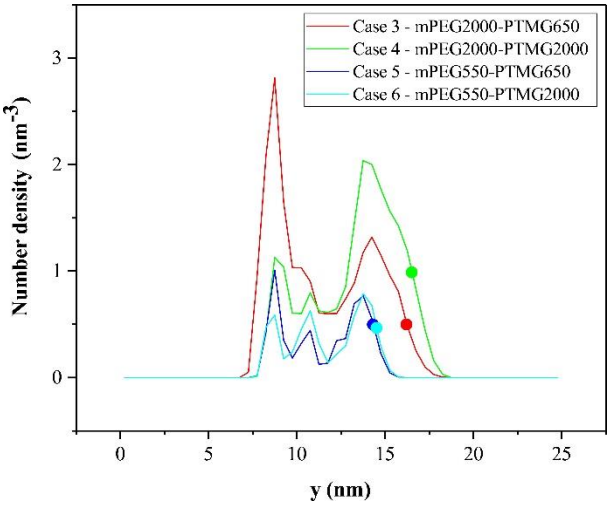

Figure SI-4. The density profile of mPEG chains in y direction. The marks on the curve show the inflection points.

6 – Dangling chain density profile at water layer in x direction for case 4

To study the lateral spread of dangling chains at the interfacial layer, we plotted the dangling chains density profile in the x direction at two time steps: First about the time that the lateral spreading begins and second is the end of simulation. This first time step for Grunewald et al. interaction type is 9 ns and for attractive type interaction is 3 ns. Figure SI-5 shows the height of the peaks decreases with time. This graph shows the dangling chain lateral spreading at the interfacial layer.

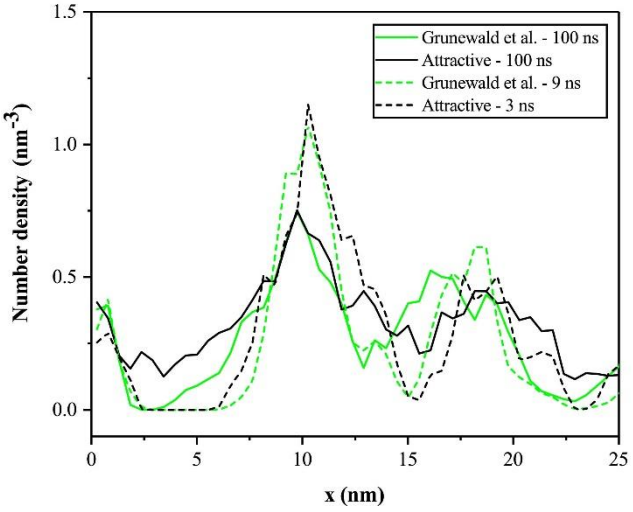

Figure SI-5. Density profile of the dangling chains in x direction for case 4 with Grunewald et al. and attractive types interactions.

7 – Radius of gyration (R_g) of the mPEG in water

To obtain R_g of a single mPEG chain in water for mPEG560 (Grunewald et al.) and for mPEG2000 (various types of interactions), we ran an *NPT* simulation for 20 ns at 25 °C and 1 bar. V-rescale and Berendsen were used as thermostat and barostat, respectively. The average of the R_g during the last 10 ns was reported in table 3. Figure SI-6 shows the snapshots of a

single mPEG560 in water for Grunewald et al. interaction and a single mPEG2000 in water for different types of interactions.

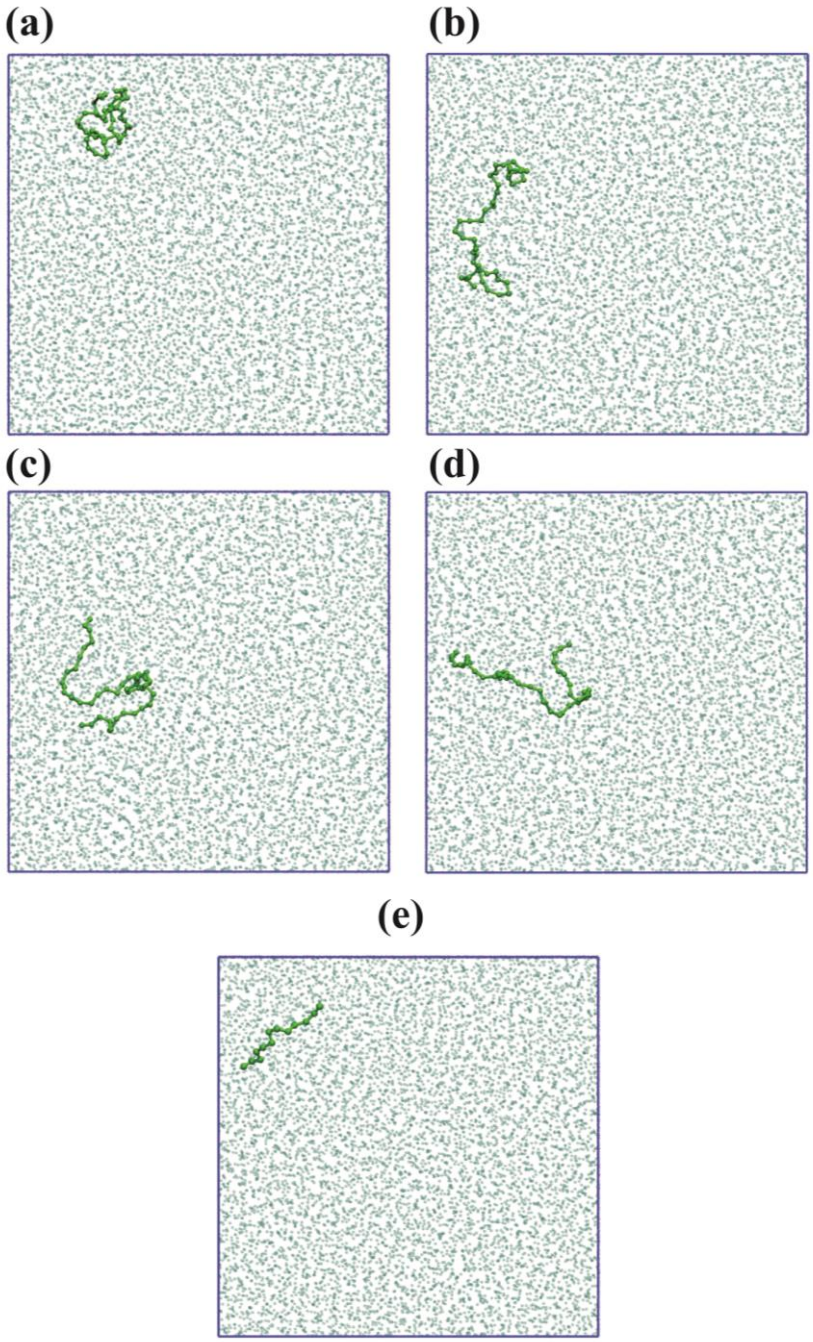

Figure SI-6. Snapshots of a single mPEG2000 chain in water with various types of interaction: a) almost intermediate, b) Grunewald et al., c) semi attractive, d) attractive. e) snapshot of a single mPEG560 chain in water with Grunewald et al. interaction.

8 – Height of the dangling chains in water layer

To recognize the height of the dangling chains in water layer for various interactions, we plotted the time-average of density profile of the dangling chains in y direction at the final steps (90-100 ns), see Figure SI-7. The thickness of the brush-like layer , i.e., the maximum coordinates of the dangling chain in y direction, was obtained from the inflection points as shown in Figure SI-7. Also, the water/polymer interface (y = 12.5 nm) was obtained from the inflection point of the water density profile (Figure SI-8). The difference between these two y coordinates was considered as the height of the dangling chain.

The inflection point for all cases is marked on the corresponding curves in Figure SI-4, and the same procedure has been done to calculate the height of the brush for other cases.

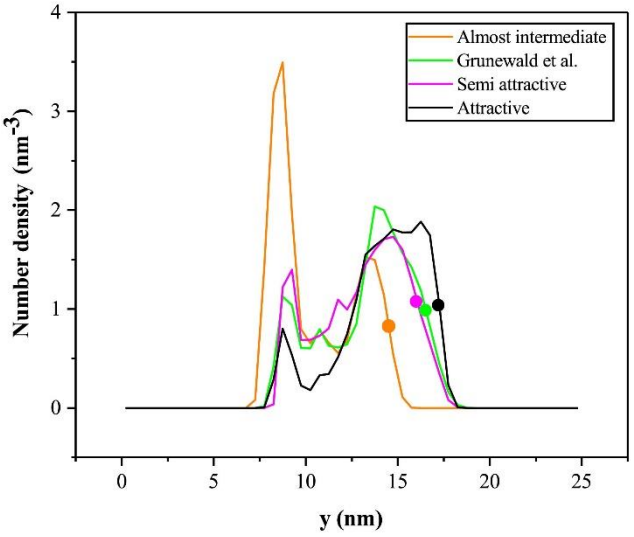

Figure SI-7. Density profile of the dangling chains in y direction for case 4 with different types of interactions. The marks on the curve show the inflection points.

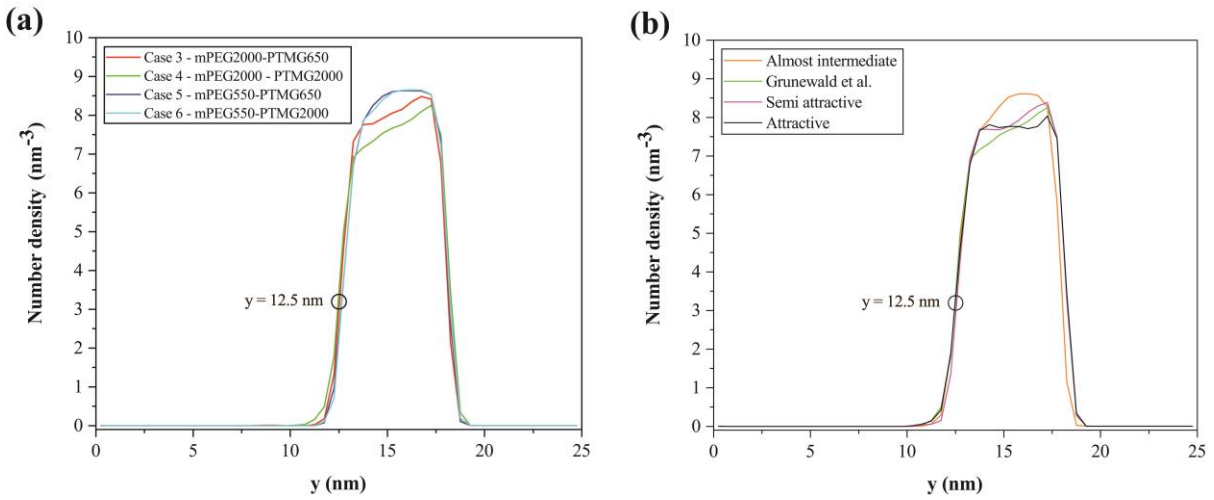

Figure SI-8. Density profile of the water in y direction. a) cases containing mPEG with Grunewald et al. interaction type and b) case 4 with different types of interactions. The marks on the curves show the inflection points.

9 – Radial distribution function

To find the first layer of hydration layer we performed the radial distribution function (*RDF*) for all cases containing mPEG. Figure SI-9 shows the *g*(r). All cases use similar mPEG-water interaction, so *RDF* graph for all of them is similar. This reveals the radius of hydration shell only depends on the type of mPEG-water interaction and is independent of the structural features of the polymeric network.

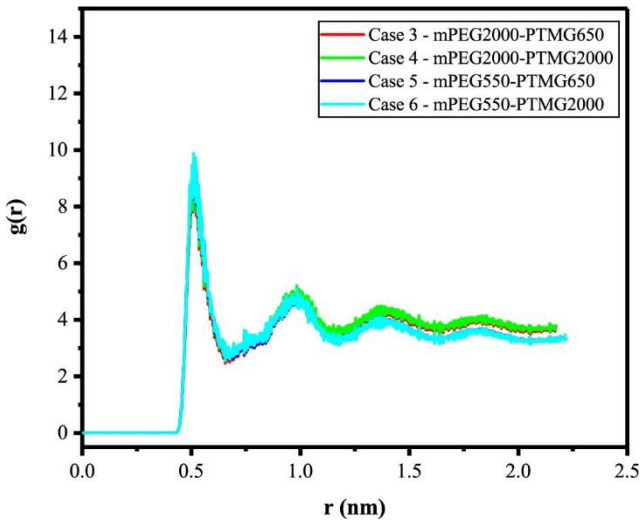

Figure SI-9. The *RDF* for cases containing mPEG with Grunewald et al. type interaction.

10 – Simulation trajectories

We made a movie of the 100 ns *NVT* water slab simulations of two cases based on Grunewald et al. and attractive interaction parameters. The movies are attached as web enhance objects and called as Attractive.avi and Grunewald.avi.

11 – Mean square displacement of water

To obtain the self-diffusion coefficient of the water an *NPT* simulation was done for 5 ns with 10 fs time step at 25 °C and 1 bar. The temperature and the pressure was controlled by V-rescale thermostat and Berendsen barostat. The mean square displacement analysis was done for the last 1 ns. Figure SI-10 shows the original data of the *MSD* analysis. We used equation 3 to calculate the self-diffusion coefficient of water beads.

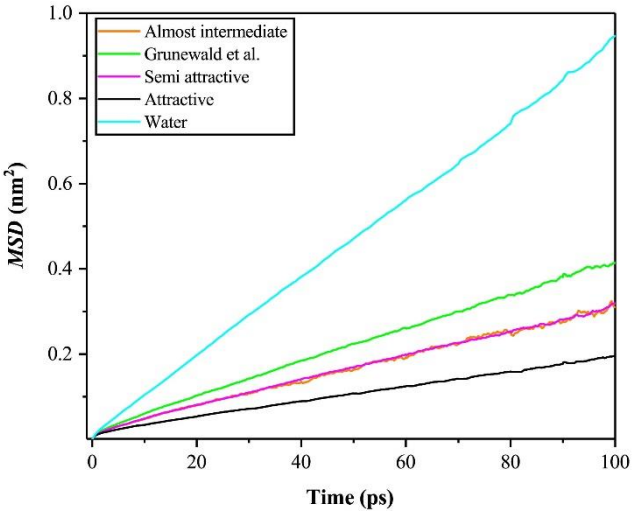

Figure SI-10. The *MSD* analysis of case 4 for different types of interactions and water beads.