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

Supplementary Information

Unravelling the molecular interactions behind the formation of PEG/PPG aqueous two-phase systems

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Experimental Data

Table S1. Binodal curve data obtained in this study at 298K and 323K, in weight percentage (wt%).

298K			323K					
PEG600 (wt%)	**PPG400 (wt%)**	**H_2O (wt%)**	**PEG600 (wt%)**	**PPG400 (wt%)**	**H_2O (wt%)**	**PEG600 (wt%)**	**PPG400 (wt%)**	**H_2O (wt%)**
53.56	12.06	34.39	17.60	64.53	17.86	9.93	16.72	73.35
45.86	12.22	41.93	19.24	62.03	18.74	7.04	18.64	74.31
43.25	12.40	44.35	26.55	52.93	20.52	8.55	73.67	17.78
41.95	13.33	44.73	28.35	50.53	21.11	6.89	74.22	18.89
40.14	13.62	46.24	31.29	46.61	22.10	5.73	74.41	19.86
28.43	20.26	51.31	34.55	42.72	22.74	2.77	20.54	76.69
22.45	26.95	50.59	36.86	39.73	23.41	2.26	20.16	77.58
19.86	31.32	48.82	39.00	36.95	24.05	0.00	23.88	76.12
16.43	39.36	44.20	40.82	34.59	24.59	0.00	52.05	47.95
14.85	44.66	40.49	42.38	32.62	25.01	1.79	63.66	34.54
13.66	48.34	38.00	43.93	30.69	25.38	3.54	71.47	24.99
11.12	54.86	34.02	45.06	29.06	25.88	0.00	20.74	79.26
9.96	58.53	31.51	46.89	26.40	26.72	1.33	56.99	41.67
8.65	62.32	29.03	48.21	24.31	27.48			
6.92	68.74	24.34	50.38	20.99	28.64			
58.97	17.04	23.99	51.48	17.52	31.00			
53.59	25.63	20.78	51.68	15.69	32.63			
38.60	44.17	17.22	51.85	13.73	34.42			
44.65	36.88	18.47	50.39	11.73	37.88			
48.85	31.86	19.28	37.97	9.86	52.17			
28.24	56.71	15.05	35.33	10.51	54.16			
21.14	64.67	14.19	32.61	10.72	56.68			
14.39	72.29	13.32	29.60	11.54	58.86			
11.37	74.69	13.94	40.49	9.98	49.53			
8.62	76.33	15.04	32.34	10.49	57.17			
7.09	76.83	16.08	27.82	11.80	60.39			
57.75	18.85	23.40	22.02	12.90	65.08			
59.45	14.83	25.72	18.12	13.81	68.07			
59.86	12.86	27.28	14.53	14.90	70.57			

Table S2. Binodal curve data retrieved for Malmsten et al. [12] at 298K and 323K, in weight percentage (wt%).

298K			323K					
PEG600 (wt%)	**PPG400 (wt%)**	**H_2O (wt%)**	**PEG600 (wt%)**	**PPG400 (wt%)**	**H_2O (wt%)**	**PEG600 (wt%)**	**PPG400 (wt%)**	**H_2O (wt%)**
13.00	72.00	15.00	0.00	70.00	30.00	0.00	25.00	75.00
20.00	64.00	16.00	4.00	71.00	25.00	0.00	33.00	67.00
25.00	60.00	15.00	8.00	70.00	22.00	0.00	40.00	60.00
29.00	54.00	17.00	12.00	68.00	20.00	0.00	48.00	52.00
32.00	49.00	19.00	17.00	63.00	20.00	0.00	56.00	44.00
37.00	44.00	19.00	20.00	59.00	21.00	0.00	62.00	38.00
39.00	40.00	21.00	25.00	55.00	20.00			
44.00	35.00	21.00	28.00	49.00	23.00			
47.00	31.00	22.00	31.00	45.00	24.00			
50.00	27.00	23.00	35.00	41.00	24.00			
54.00	23.00	23.00	38.00	38.00	24.00			
56.00	19.00	25.00	40.00	32.00	28.00			
54.00	15.00	31.00	42.00	28.00	30.00			
49.00	14.00	37.00	45.00	25.00	30.00			
42.00	13.00	45.00	48.00	21.00	31.00			
36.00	16.00	48.00	47.00	15.00	38.00			
32.00	18.00	50.00	41.00	12.00	47.00			
29.00	20.00	51.00	31.00	12.00	57.00			
27.00	22.00	51.00	26.00	13.00	61.00			
25.00	25.00	50.00	21.00	13.00	66.00			
23.00	29.00	48.00	18.00	13.00	69.00			
20.00	32.00	48.00	13.00	13.00	74.00			
20.00	37.00	43.00	11.00	13.00	76.00			
17.00	42.00	41.00	9.00	14.00	77.00			
15.00	46.00	39.00	5.00	14.00	81.00			
10.00	59.00	31.00	3.00	16.00	81.00			
6.00	69.00	25.00	2.00	17.00	81.00			
8.00	72.00	20.00	1.00	18.00	81.00			
			0.00	20.00	80.00			

Table S3. Binodal curve data obtained in this study at 298K and 323K, in mol fraction (mol%).

298K			323K					
PEG600 (mol%)	**PPG400 (mol%)**	**H_2O (mol%)**	**PEG600 (mol%)**	**PPG400 (mol%)**	**H_2O (mol%)**	**PEG600 (mol%)**	**PPG400 (mol%)**	**H_2O (mol%)**
4.40	1.48	94.12	2.48	13.64	83.88	0.40	1.01	98.59
3.14	1.25	95.61	2.61	12.63	84.76	0.28	1.11	98.61
2.81	1.21	95.98	3.36	10.05	86.59	1.20	15.52	83.28
2.70	1.29	96.01	3.51	9.38	87.11	0.92	14.88	84.20
2.51	1.28	96.22	3.73	8.34	87.92	0.74	14.32	84.94
1.61	1.72	96.68	4.03	7.48	88.48	0.11	1.19	98.70
1.28	2.31	96.41	4.20	6.80	89.00	0.09	1.16	98.76
1.17	2.77	96.05	4.35	6.18	89.46	0.00	1.39	98.61
1.06	3.81	95.13	4.47	5.69	89.84	0.00	4.66	95.34
1.04	4.68	94.28	4.58	5.29	90.13	0.14	7.65	92.21
1.01	5.36	93.63	4.69	4.92	90.39	0.38	11.36	88.26
0.91	6.70	92.39	4.74	4.58	90.68	0.00	1.16	98.84
0.87	7.65	91.49	4.80	4.05	91.15	0.09	5.79	94.12
0.81	8.74	90.45	4.82	3.64	91.54			
0.75	11.19	88.06	4.86	3.04	92.10			
6.67	2.89	90.44	4.63	2.37	93.00			
6.83	4.90	88.27	4.44	2.02	93.53			
5.69	9.76	84.55	4.25	1.69	94.06			
6.24	7.73	86.03	3.79	1.32	94.89			
6.61	6.46	86.93	2.12	0.83	97.06			
4.59	13.83	81.57	1.90	0.85	97.25			
3.58	16.41	80.01	1.68	0.83	97.49			
2.54	19.14	78.32	1.47	0.86	97.66			
1.93	19.05	79.02	2.37	0.88	96.75			
1.38	18.33	80.29	1.66	0.81	97.54			
1.08	17.50	81.42	1.35	0.86	97.79			
6.67	3.27	90.06	1.00	0.88	98.13			
6.33	2.37	91.30	0.79	0.90	98.32			
6.06	1.95	91.99	0.61	0.94	98.46			

	PEG600/H_2O						PPG400/H_2O					
x_W	Total H^E	H^E (MF)	H^E (HB)	H^E VDW)	Total G^E	γ	Total H^E	H^E (MF)	H^E (HB)	H^E VDW)	Total G^E	γ
1.00E-08	0.0000	0.0000	0.0000	0.0000	0.0000	0.2677	0.0000	0.0000	0.0000	0.0000	0.0000	1.5376
1.00E-05	0.0000	0.0000	0.0000	0.0000	0.0000	0.2677	0.0000	0.0000	0.0000	0.0000	0.0000	1.5376
0.001	-0.0013	-0.0002	-0.0010	-0.0001	-0.0008	0.2679	-0.0003	0.0002	-0.0005	-0.0001	0.0003	1.5347
0.01	-0.0128	-0.0018	-0.0103	-0.0006	-0.0078	0.2693	-0.0036	0.0018	-0.0046	-0.0007	0.0025	1.5097
0.02	-0.0257	-0.0037	-0.0207	-0.0012	-0.0155	0.2708	-0.0075	0.0034	-0.0095	-0.0015	0.0049	1.4840
0.05	-0.0644	-0.0093	-0.0520	-0.0031	-0.0386	0.2756	-0.0213	0.0078	-0.0254	-0.0037	0.0115	1.4172
0.1	-0.1299	-0.0190	-0.1048	-0.0062	-0.0763	0.2842	-0.0487	0.0136	-0.0550	-0.0073	0.0207	1.3315
0.15	-0.1964	-0.0288	-0.1583	-0.0093	-0.1129	0.2936	-0.0799	0.0180	-0.0868	-0.0110	0.0281	1.2672
0.2	-0.2640	-0.0390	-0.2126	-0.0124	-0.1484	0.3037	-0.1132	0.0213	-0.1199	-0.0146	0.0340	1.2177
0.25	-0.3325	-0.0494	-0.2676	-0.0155	-0.1826	0.3149	-0.1476	0.0239	-0.1533	-0.0182	0.0385	1.1789
0.3	-0.4020	-0.0602	-0.3233	-0.0186	-0.2153	0.3272	-0.1822	0.0260	-0.1863	-0.0219	0.0419	1.1482
0.35	-0.4723	-0.0711	-0.3796	-0.0216	-0.2463	0.3409	-0.2159	0.0277	-0.2182	-0.0254	0.0443	1.1241
0.4	-0.5434	-0.0824	-0.4364	-0.0247	-0.2754	0.3562	-0.2480	0.0293	-0.2483	-0.0290	0.0458	1.1054
0.45	-0.6150	-0.0938	-0.4935	-0.0277	-0.3022	0.3735	-0.2777	0.0309	-0.2760	-0.0325	0.0466	1.0911
0.5	-0.6869	-0.1055	-0.5506	-0.0307	-0.3264	0.3932	-0.3039	0.0326	-0.3004	-0.0360	0.0468	1.0807
0.55	-0.7584	-0.1173	-0.6074	-0.0337	-0.3473	0.4158	-0.3256	0.0346	-0.3207	-0.0394	0.0465	1.0735
0.6	-0.8289	-0.1290	-0.6632	-0.0367	-0.3644	0.4423	-0.3415	0.0370	-0.3357	-0.0428	0.0458	1.0690
0.65	-0.8970	-0.1406	-0.7169	-0.0396	-0.3767	0.4737	-0.3502	0.0400	-0.3442	-0.0460	0.0449	1.0668
0.7	-0.9606	-0.1515	-0.7666	-0.0424	-0.3827	0.5119	-0.3499	0.0437	-0.3445	-0.0491	0.0440	1.0662
0.75	-1.0156	-0.1612	-0.8092	-0.0451	-0.3805	0.5593	-0.3385	0.0482	-0.3347	-0.0520	0.0430	1.0663
0.8	-1.0544	-0.1682	-0.8385	-0.0477	-0.3669	0.6202	-0.3131	0.0533	-0.3120	-0.0544	0.0420	1.0657
0.85	-1.0613	-0.1698	-0.8418	-0.0498	-0.3362	0.7012	-0.2706	0.0588	-0.2732	-0.0561	0.0407	1.0623
0.9	-0.9989	-0.1589	-0.7890	-0.0510	-0.2782	0.8120	-0.2071	0.0627	-0.2137	-0.0562	0.0381	1.0523
0.95	-0.7636	-0.1167	-0.5981	-0.0488	-0.1714	0.9528	-0.1195	0.0586	-0.1271	-0.0510	0.0306	1.0298
0.98	-0.4202	-0.0569	-0.3241	-0.0391	-0.0703	1.0098	-0.0551	0.0400	-0.0579	-0.0372	0.0180	1.0089
0.99	-0.2395	-0.0288	-0.1819	-0.0288	-0.0323	1.0078	-0.0308	0.0253	-0.0308	-0.0253	0.0105	1.0026
0.999	-0.0279	-0.0027	-0.0204	-0.0049	-0.0026	1.0002	-0.0038	0.0033	-0.0033	-0.0037	0.0012	1.0000
0.99999	-0.0003	0.0000	-0.0002	-0.0001	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000
0.99999999	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000	0.0000	0.0000	0.0000	0.0000	0.0000	1.0000

Table S4. Thermodynamic properties of the binary systems PEG600/H_2O and PPG400/H_2O as function of water molar fraction (x_W). H^E (MF), H^E (HB) and H^E (VDW) correspond to the excess enthalpy of the binary mixture caused by misfit/electrostatic interactions, hydrogen bonds and Van der Waals forces, respectively. "Total H^E" and "Total G^E" correspond to the excess enthalpy and excess free Gibbs energy of the system.

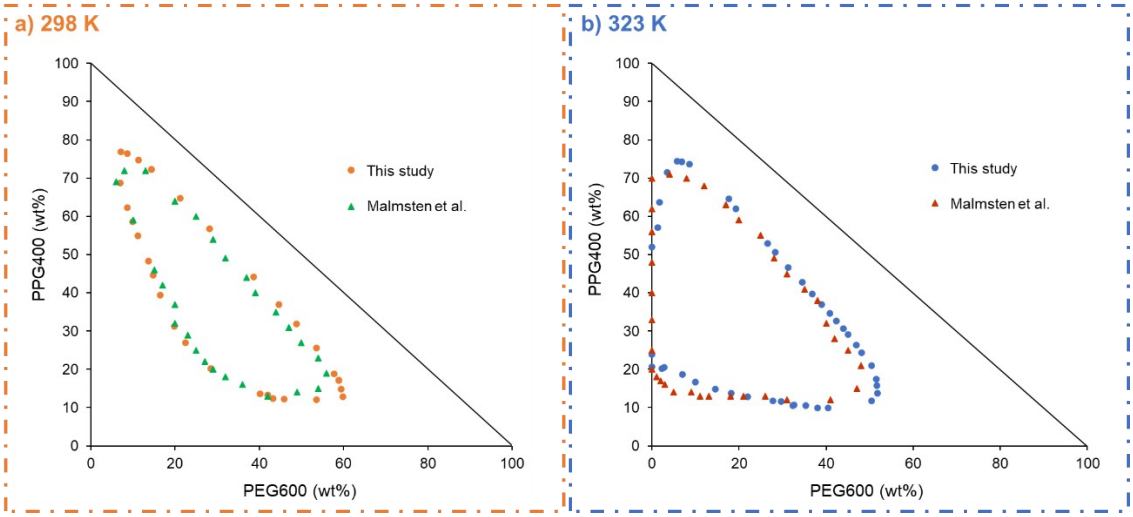

Figure S1. Experimental phase diagrams of PEG600/PPG400/H_2O at 298K (**a**) and 323K (**b**), and atmospheric pressure. The full circles correspond to the experimental data of this study and the full triangles the data retrieved from Malmsten et al.[12] by manual drawing and eye assessment of the mixture points within the equilibrium curve.

S2. Simulation Results

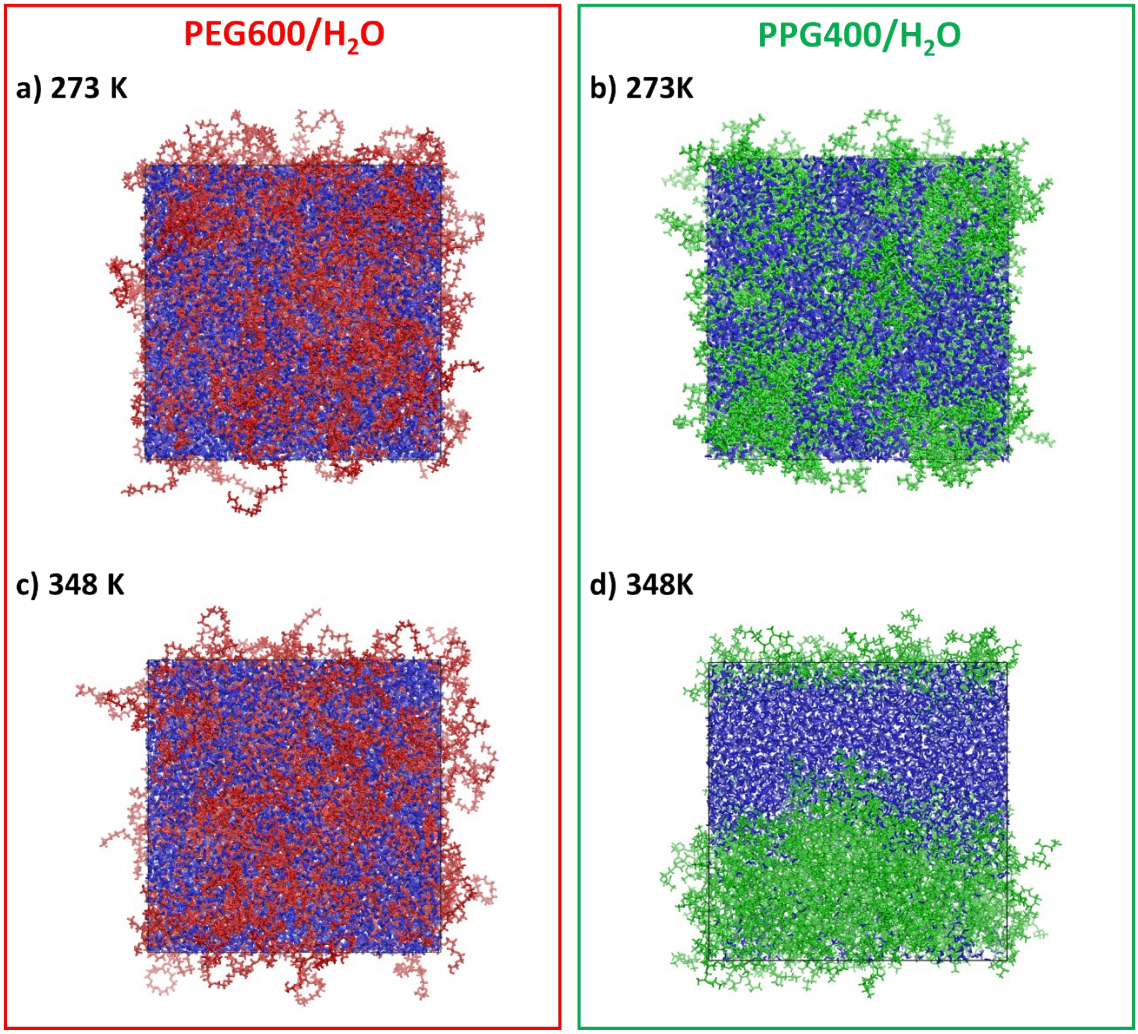

Figure S2. Snapshots from MD simulations of the binary systems containing 1:1 mass ratio of PEG600 and H_2O (**a** and **c**), and PPG400 and H_2O (**c** and **d**), at 273 K and 348 K. PEG600, PPG400 and water are represented by red, green and blue colors, respectively.

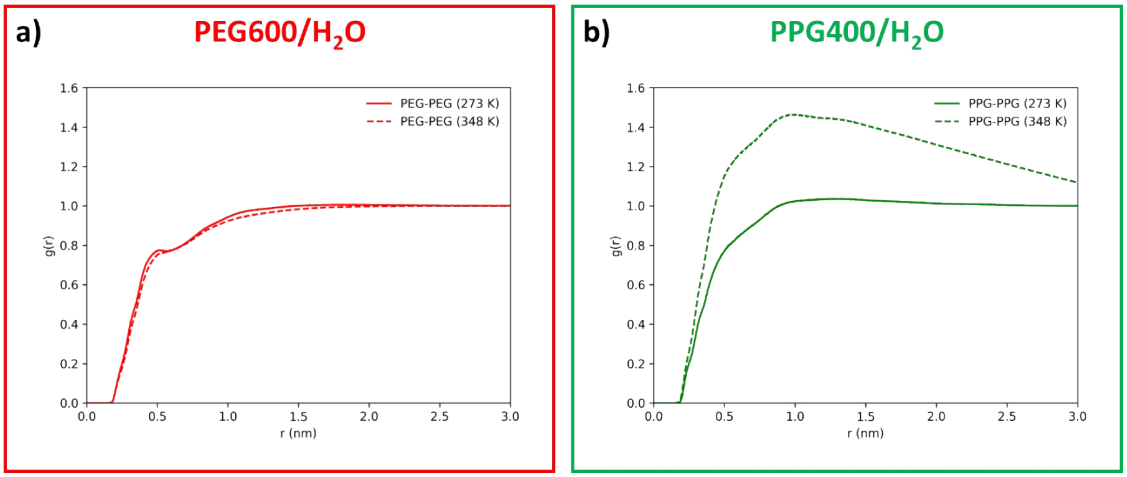

Figure S3. Radial distribution functions between the polymeric moieties obtained from MD simulations of the binary systems containing 1:1 mass ratio of PEG600 and H_2O (**a**), and PPG400 and H_2O (**b**), at 273 K (solid lines) and 348 K (dashed lines). The red and green curves correspond to PEG600-PEG600 and PPG400-PPG400 pairs, respectively.

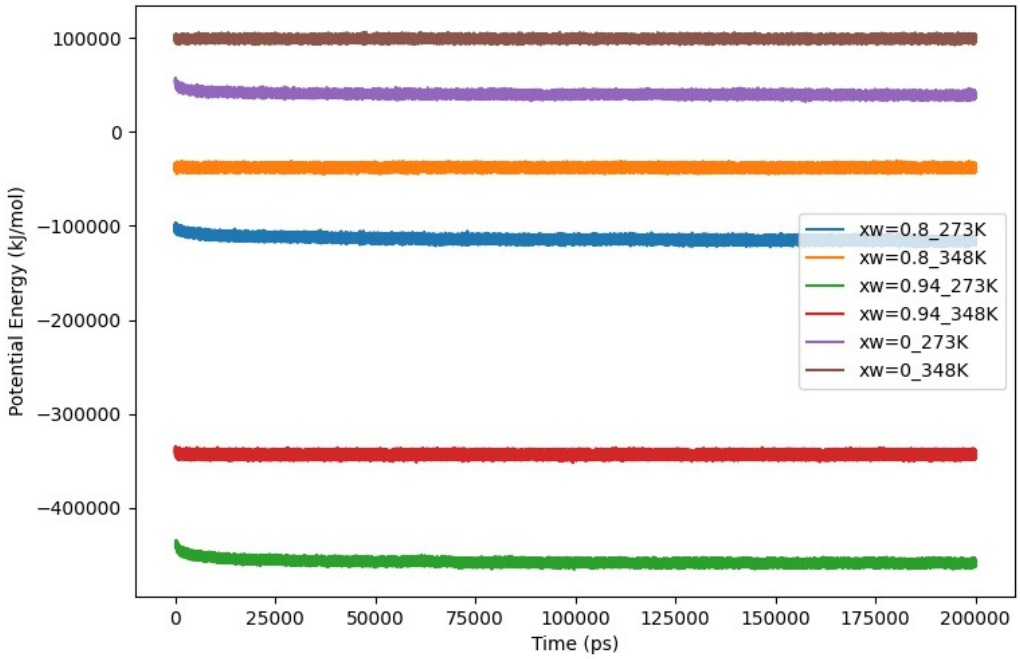

Figure S4. Evolution of the total potential energy throughout the time length of each simulation.

S3. Simulation Details

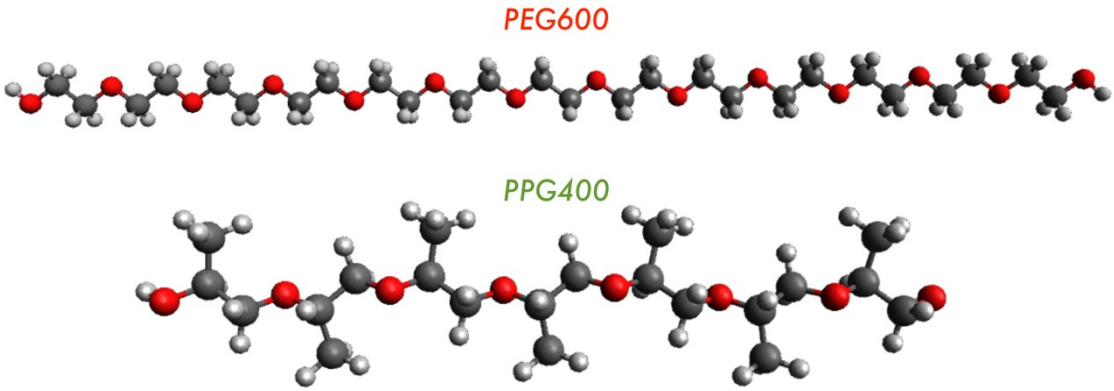

Figure S5. Molecular structure of PEG600 ($C_{26}H_{54}O_{14}$) and PPG400 ($C_{21}H_{44}O_8$). Color scheme: hydrogen – white, carbon – gray and oxygen – red.

Table S5. Number of molecules used in the simulations boxes for each system.

System	PEG600	PPG400	H_2O
x_W=0	300	300	0
x_W=0.8	300	300	2400
x_W=0.94	300	300	9400
PEG600/H_2O	300	0	10000
PEG600/H_2O	0	300	7100

The input files, including topology, coordinate and control files can be found on the following repository: https://github.com/goncalosilva20/PEG600_PPG400_Water.