Table S1: Number composition of simulated H-[O-$CH_2$-$CH_2$]$_n$-OH-water systems.

| | $w_{water}$ | | | |
|---|---|---|---|---|
| n | 0.001 | 0.005 | 0.010 | 0.020 |
| | | Diethylene Glycol | | |
| 2 | 994 | 971 | 944 | 893 |
| $H_2O$ | 6 | 29 | 56 | 107 |
| | | Tetraethylene glycol | | |
| 4 | 989 | 949 | 902 | 820 |
| $H_2O$ | 11 | 51 | 98 | 180 |
| | | Hexaethylene glycol | | |
| 6 | 492 | 464 | 432 | 379 |
| $H_2O$ | 8 | 36 | 68 | 121 |
| | | PEG200 | | |
| 2 | 34 | 33 | 31 | 28 |
| 3 | 220 | 211 | 200 | 182 |
| 4 | 316 | 303 | 288 | 261 |
| 5 | 244 | 233 | 222 | 201 |
| 6 | 128 | 122 | 116 | 105 |
| 7 | 47 | 45 | 42 | 38 |
| $H_2O$ | 11 | 53 | 101 | 185 |

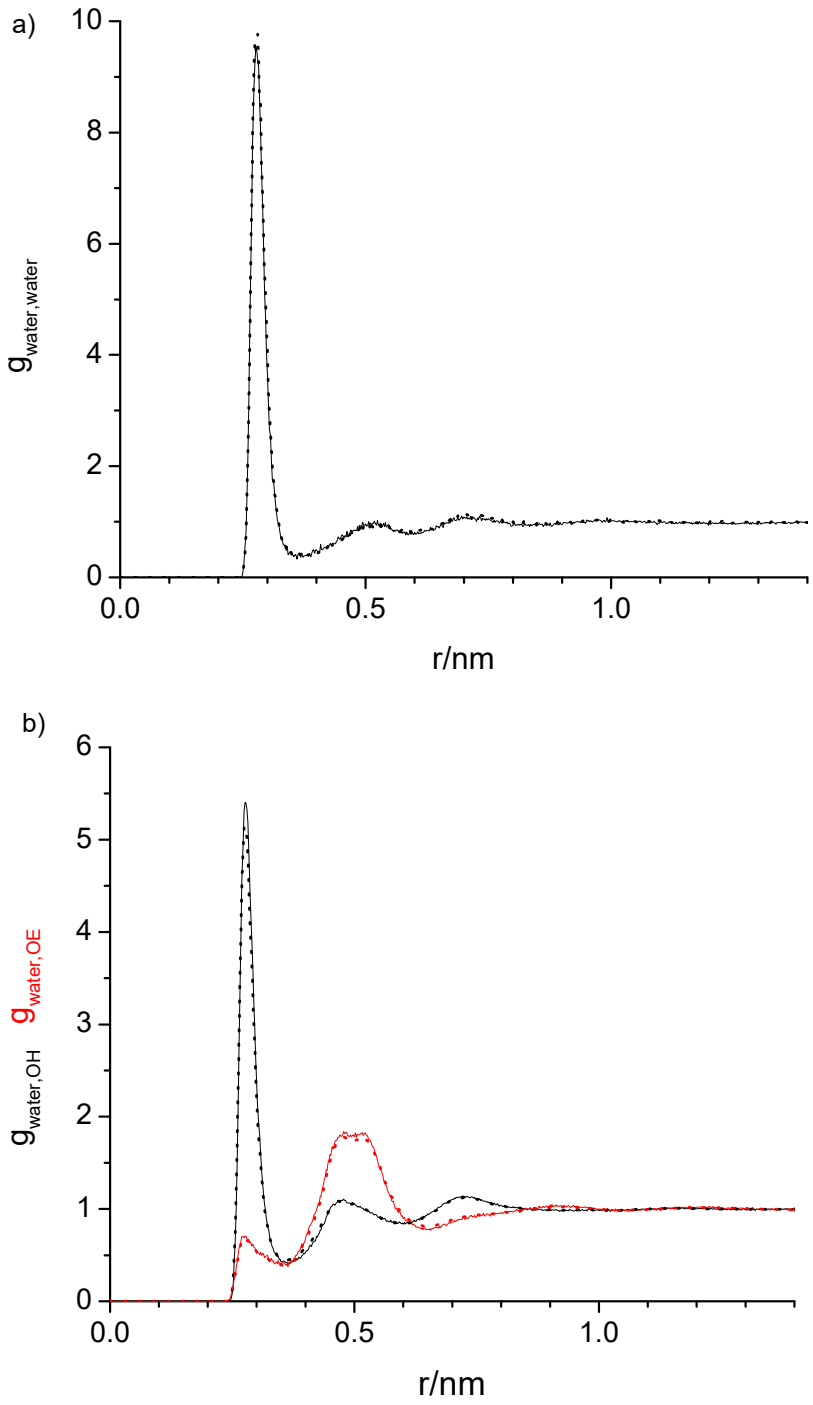


Figure S1. Radial distribution functions of water oxygen with (a) water oxygen as well as (b) oligomer hydroxy oxygen (black) and ether oxygen (red) for 0.02 mass fraction of water in diethylene glycol obtained with the water force fields TIP4P/2005 in combination with OPLS forcefield (solid) and the modified OPLS force field (dotted).

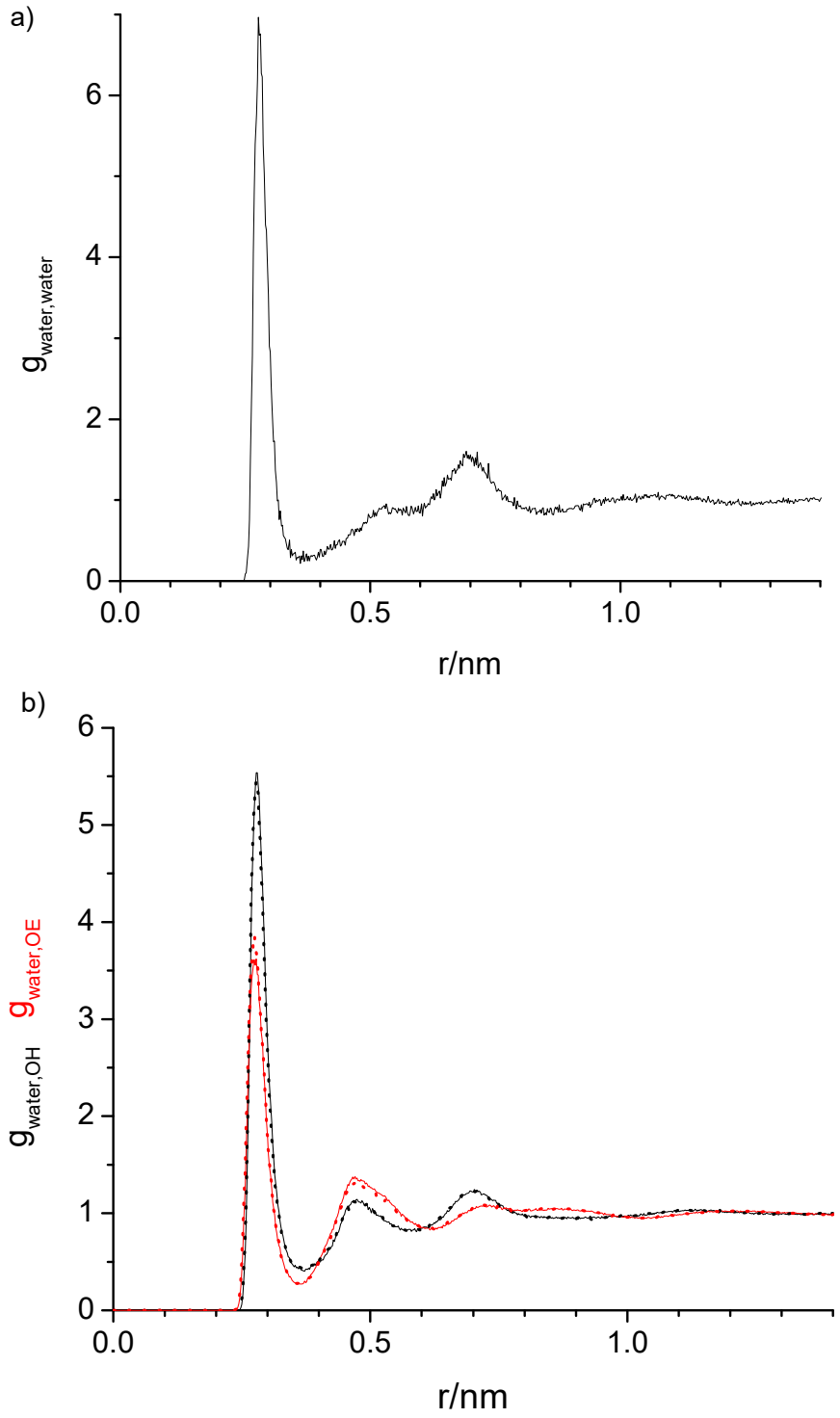


Figure S2. Radial distribution functions of water oxygen with (a) water oxygen as well as (b) oligomer hydroxy oxygen (black) and ether oxygen (red) for 0.02 mass fraction of water in tetraethylene glycol obtained with the water force fields TIP4P/2005 in combination with OPLS forcefield (solid) and the modified OPLS force field (dotted).

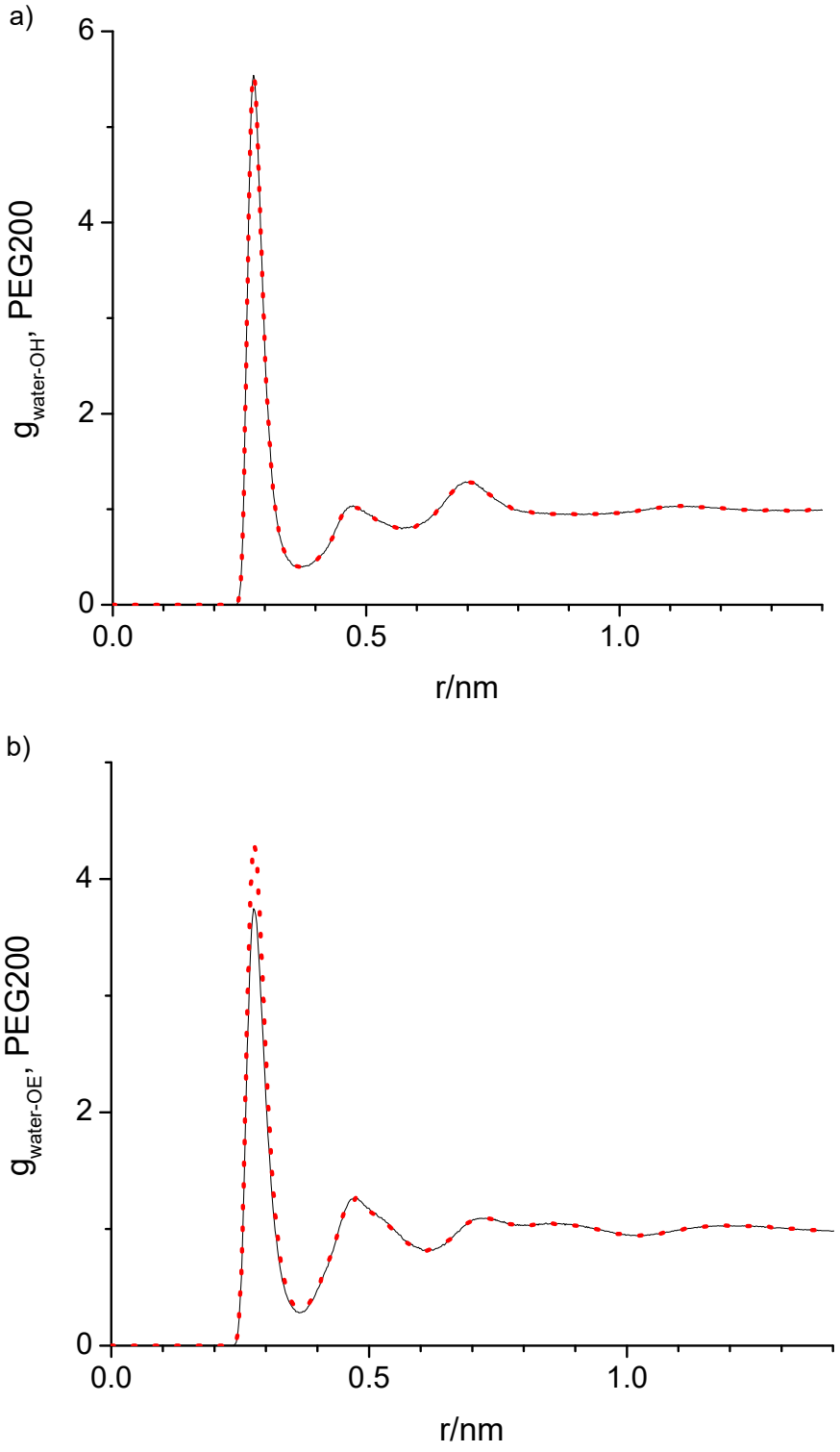


Figure S3. Calculated (solid black line) and simulated (dotted red line) radial distribution functions of water with (a) hydroxy oxygen as well as (b) ether oxygen for 0.02 mass fraction of water in PEG200 obtained with the water force fields SPC/E in combination with OPLS forcefield.

**Kinetic Theory of Gases**

For two water molecules to engage in hydrogen bonding, they must come in contact, i.e., collide. The number of collisions, $dN_{coll}$, for water behaving as an ideal gas moving through the simulation box in straight trajectories of random direction at average speed of

$$\langle u \rangle = \left(\frac{8RT}{\pi M}\right)^{1/2} \quad \text{(S1)}$$

where $T$ is the temperature in Kelvin (328 K in this case) and $M$ the molar mass of water, is calculated to be $dN_{coll} = 3.12 \times 10^{-4}$ using equation S2

$$dN_{\mathrm{coll}} = \rho\sigma\langle u \rangle dt \quad \text{(S2)}$$

In equation S2, $\rho$ is the number density (for PEG200 with $w_{water} = 0.020$ there were 185 water molecules in a cubic box of length $6.42 \times 10^{-9}$ m) and $\sigma$ is the collision cross section of water = $3.59 \times 10^{-19}$ m$^2$ calculated from the van der Waals radius of $1.69 \times 10^{-10}$ m.[1] The hydrogen bonding numbers from the MD simulations were obtained from averaging the counts across the recorded frames from the MD simulation where each frame is an image from the last simulation time increment, $dt$, of $2 \times 10^{-15}$ s. The corresponding value for $n_{HB}/n_{water}$ is then $1.68 \times 10^{-6}$.

Table S2: Simulation results at 328K for number of hydrogen bonds per number of water molecules

| | | $w_{water}$ | | | | $w_{water}$ | | | |
|---|---|---|---|---|---|---|---|---|---|
| OPLS | model[a] | 0.001 | 0.005 | 0.010 | 0.020 | 0.001 | 0.005 | 0.010 | 0.020 |
| | | Water with oligomer OH | | | | Water with water | | | |
| | | Diethylene glycol | | | | Diethylene glycol | | | |
| Unmod | SPC/E | 2.511 | 2.458 | 2.397 | 2.280 | 0.009 | 0.045 | 0.083 | 0.136 |
| Unmod | TIP4P | 2.493 | 2.444 | 2.397 | 2.320 | 0.004 | 0.034 | 0.063 | 0.138 |
| Mod | SPC/E | 2.310 | 2.251 | 2.208 | 2.091 | 0.006 | 0.048 | 0.086 | 0.100 |
| Mod | TIP4P | 2.299 | 2.271 | 2.232 | 2.159 | 0.008 | 0.032 | 0.061 | 0.097 |
| | | Tetraethylene glycol | | | | Tetraethylene glycol | | | |
| Unmod | SPC/E | 1.515 | 1.510 | 1.488 | 1.448 | 0.004 | 0.025 | 0.054 | 0.110 |
| Unmod | TIP4P | 1.535 | 1.508 | 1.498 | 1.472 | 0.003 | 0.020 | 0.043 | 0.086 |
| Mod | SPC/E | 1.544 | 1.515 | 1.494 | 1.443 | 0.005 | 0.031 | 0.062 | 0.127 |
| Mod | TIP4P | 1.581 | 1.566 | 1.548 | 1.508 | 0.006 | 0.024 | 0.047 | 0.097 |
| | | Hexaethylene glycol | | | | Hexaethylene glycol | | | |
| Unmod | SPC/E | 1.074 | 1.074 | 1.065 | 1.044 | 0.003 | 0.018 | 0.039 | 0.079 |
| Unmod | TIP4P | 1.072 | 1.049 | 1.053 | 1.037 | 0.003 | 0.012 | 0.032 | 0.063 |
| Mod | SPC/E | 0.627 | 0.635 | 0.624 | 0.611 | 0.005 | 0.029 | 0.059 | 0.124 |
| Mod | TIP4P | 0.625 | 0.631 | 0.625 | 0.620 | 0.004 | 0.020 | 0.040 | 0.085 |
| | | PEG200 | | | | PEG 200 | | | |
| Unmod | SPC/E | 1.397 | 1.389 | 1.379 | 1.356 | 0.005 | 0.020 | 0.043 | 0.087 |
| Unmod | TIP4P | 1.382 | 1.396 | 1.382 | 1.371 | 0.004 | 0.020 | 0.032 | 0.068 |
| Mod | SPC/E | 1.323 | 1.302 | 1.297 | 1.268 | 0.005 | 0.023 | 0.048 | 0.105 |
| Mod | TIP4P | 1.337 | 1.347 | 1.332 | 1.321 | 0.004 | 0.019 | 0.038 | 0.078 |
| | | Water with oligomer ether group | | | | Sum of all contributions | | | |
| | | Diethylene glycol | | | | Diethylene glycol | | | |
| Unmod | SPC/E | 0.141 | 0.145 | 0.139 | 0.156 | 2.661 | 2.648 | 2.619 | 2.572 |
| Unmod | TIP4P | 0.140 | 0.140 | 0.138 | 0.118 | 2.637 | 2.618 | 2.598 | 2.576 |
| Mod | SPC/E | 0.107 | 0.105 | 0.104 | 0.171 | 2.423 | 2.404 | 2.398 | 2.362 |
| Mod | TIP4P | 0.102 | 0.099 | 0.098 | 0.123 | 2.409 | 2.402 | 2.391 | 2.379 |
| | | Tetraethylene glycol | | | | Tetraethylene glycol | | | |
| Unmod | SPC/E | 1.171 | 1.129 | 1.101 | 1.047 | 2.690 | 2.664 | 2.643 | 2.605 |
| Unmod | TIP4P | 1.092 | 1.087 | 1.065 | 1.026 | 2.630 | 2.615 | 2.606 | 2.584 |
| Mod | SPC/E | 0.990 | 0.976 | 0.941 | 0.881 | 2.539 | 2.522 | 2.497 | 2.451 |
| Mod | TIP4P | 0.913 | 0.889 | 0.882 | 0.845 | 2.500 | 2.479 | 2.477 | 2.450 |
| | | Hexaethylene glycol | | | | Hexaethylene glycol | | | |
| Unmod | SPC/E | 1.587 | 1.560 | 1.530 | 1.472 | 2.664 | 2.652 | 2.634 | 2.595 |
| Unmod | TIP4P | 1.542 | 1.564 | 1.511 | 1.476 | 2.617 | 2.625 | 2.596 | 2.576 |
| Mod | SPC/E | 1.734 | 1.694 | 1.656 | 1.575 | 2.366 | 2.358 | 2.339 | 2.310 |
| Mod | TIP4P | 1.768 | 1.744 | 1.719 | 1.657 | 2.397 | 2.395 | 2.384 | 2.362 |
| | | PEG200 | | | | PEG200 | | | |
| Unmod | SPC/E | 1.397 | 1.389 | 1.379 | 1.356 | 2.799 | 2.798 | 2.801 | 2.799 |
| Unmod | TIP4P | 1.382 | 1.396 | 1.382 | 1.371 | 2.768 | 2.812 | 2.796 | 2.810 |
| Mod | SPC/E | 1.323 | 1.302 | 1.297 | 1.268 | 2.651 | 2.627 | 2.642 | 2.641 |
| Mod | TIP4P | 1.337 | 1.347 | 1.332 | 1.321 | 2.678 | 2.713 | 2.702 | 2.720 |

[a] The specific TIP4P model used was TIP4P/2005

Table S3: Simulation results at 328K for number of oligomer-oligomer hydrogen bonds per number of ethylene glycol oligomer molecules

| | | $w_{water}$ | | | | | $w_{water}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OPLS | model[a] | 0[2] | 0.001 | 0.005 | 0.010 | 0.020 | 0[2] | 0.001 | 0.005 | 0.010 | 0.020 |
| | | Intramolecular OH-OH Diethylene glycol | | | | | Intramolecular OH-OE Diethylene glycol | | | | |
| Unmod | SPC/E | 0.007 | 0.007 | 0.008 | 0.007 | 0.008 | 0.028 | 0.027 | 0.028 | 0.027 | 0.028 |
| Unmod | TIP4P | 0.007 | 0.008 | 0.008 | 0.008 | 0.007 | 0.028 | 0.027 | 0.028 | 0.028 | 0.028 |
| Mod | SPC/E | 0.019 | 0.020 | 0.019 | 0.020 | 0.020 | 0.055 | 0.055 | 0.054 | 0.053 | 0.052 |
| Mod | TIP4P | 0.019 | 0.021 | 0.019 | 0.020 | 0.019 | 0.055 | 0.055 | 0.055 | 0.056 | 0.053 |
| | | Tetraethylene glycol | | | | | Tetraethylene glycol | | | | |
| Unmod | SPC/E | 0.070 | 0.055 | 0.057 | 0.057 | 0.050 | 0.156 | 0.159 | 0.161 | 0.165 | 0.147 |
| Unmod | TIP4P | 0.070 | 0.061 | 0.060 | 0.052 | 0.052 | 0.156 | 0.160 | 0.166 | 0.154 | 0.144 |
| Mod | SPC/E | 0.122 | 0.121 | 0.119 | 0.110 | 0.110 | 0.332 | 0.316 | 0.328 | 0.314 | 0.309 |
| Mod | TIP4P | 0.122 | 0.120 | 0.122 | 0.119 | 0.109 | 0.332 | 0.330 | 0.332 | 0.325 | 0.310 |
| | | Hexaethylene glycol | | | | | Hexaethylene glycol | | | | |
| Unmod | SPC/E | 0.006 | 0.007 | 0.006 | 0.010 | 0.008 | 0.146 | 0.145 | 0.140 | 0.142 | 0.134 |
| Unmod | TIP4P | 0.006 | 0.006 | 0.008 | 0.009 | 0.008 | 0.146 | 0.143 | 0.140 | 0.137 | 0.131 |
| Mod | SPC/E | 0.003 | 0.003 | 0.003 | 0.002 | 0.002 | 0.075 | 0.075 | 0.075 | 0.070 | 0.072 |
| Mod | TIP4P | 0.003 | 0.002 | 0.003 | 0.003 | 0.003 | 0.075 | 0.073 | 0.074 | 0.074 | 0.074 |
| | | Intermolecular OH-OH Diethylene glycol | | | | | Intermolecular OH-OE Diethylene glycol | | | | |
| Unmod | SPC/E | 1.085 | 1.092 | 1.075 | 1.058 | 1.022 | 0.114 | 0.142 | 0.140 | 0.141 | 0.138 |
| Unmod | TIP4P | 1.085 | 1.093 | 1.077 | 1.058 | 1.022 | 0.114 | 0.142 | 0.140 | 0.140 | 0.139 |
| Mod | SPC/E | 0.829 | 0.825 | 0.817 | 0.805 | 0.788 | 0.089 | 0.089 | 0.089 | 0.088 | 0.088 |
| Mod | TIP4P | 0.829 | 0.824 | 0.818 | 0.808 | 0.791 | 0.089 | 0.089 | 0.088 | 0.086 | 0.088 |
| | | Tetraethylene glycol | | | | | Tetraethylene glycol | | | | |
| Unmod | SPC/E | 0.710 | 0.633 | 0.620 | 0.605 | 0.584 | 0.444 | 0.378 | 0.365 | 0.348 | 0.341 |
| Unmod | TIP4P | 0.710 | 0.628 | 0.618 | 0.612 | 0.584 | 0.444 | 0.379 | 0.362 | 0.361 | 0.348 |
| Mod | SPC/E | 0.164 | 0.164 | 0.163 | 0.168 | 0.160 | 0.064 | 0.080 | 0.063 | 0.070 | 0.063 |
| Mod | TIP4P | 0.164 | 0.165 | 0.160 | 0.159 | 0.162 | 0.064 | 0.066 | 0.059 | 0.061 | 0.064 |
| | | Hexaethylene glycol | | | | | Hexaethylene glycol | | | | |
| Unmod | SPC/E | 0.520 | 0.515 | 0.507 | 0.489 | 0.467 | 0.498 | 0.497 | 0.479 | 0.452 | 0.410 |
| Unmod | TIP4P | 0.520 | 0.518 | 0.505 | 0.492 | 0.469 | 0.498 | 0.499 | 0.485 | 0.461 | 0.422 |
| Mod | SPC/E | 0.138 | 0.138 | 0.136 | 0.134 | 0.131 | 0.166 | 0.166 | 0.159 | 0.157 | 0.143 |
| Mod | TIP4P | 0.138 | 0.138 | 0.136 | 0.134 | 0.130 | 0.166 | 0.168 | 0.160 | 0.153 | 0.139 |

[a] The specific TIP4P model used was TIP4P/2005

Table S4: Simulation results at 328K for end-to-end distances and radii of gyration

| | | $w_{water}$ | | | | | $w_{water}$ | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| OPLS | Model[a] | $0^2$ | 0.001 | 0.005 | 0.010 | 0.020 | $0^2$ | 0.001 | 0.005 | 0.010 | 0.020 |
| | | End-to-end distances/nm | | | | | Radii of gyration/nm | | | | |
| | | Diethylene glycol | | | | | Diethylene glycol | | | | |
| Unmod | SPC/E | 0.5672 | 0.5563 | 0.5563 | 0.5562 | 0.5555 | 0.2254 | 0.2237 | 0.2237 | 0.2237 | 0.2236 |
| Unmod | TIP4P | 0.5672 | 0.5563 | 0.5559 | 0.5553 | 0.5544 | 0.2254 | 0.2237 | 0.2236 | 0.2235 | 0.2234 |
| Mod | SPC/E | 0.4746 | 0.4742 | 0.4741 | 0.4740 | 0.4740 | 0.2112 | 0.2112 | 0.2112 | 0.2112 | 0.2112 |
| Mod | TIP4P | 0.4746 | 0.4742 | 0.4741 | 0.4739 | 0.4738 | 0.2112 | 0.2112 | 0.2112 | 0.2111 | 0.2111 |
| | | Tetraethylene glycol | | | | | Tetraethylene glycol | | | | |
| Unmod | SPC/E | 0.8163 | 0.8181 | 0.8152 | 0.8123 | 0.8052 | 0.3415 | 0.3418 | 0.3414 | 0.3411 | 0.3403 |
| Unmod | TIP4P | 0.8163 | 0.8171 | 0.8149 | 0.8110 | 0.8036 | 0.3415 | 0.3416 | 0.3414 | 0.3409 | 0.3401 |
| Mod | SPC/E | 0.6715 | 0.6676 | 0.6658 | 0.6634 | 0.6612 | 0.3209 | 0.3205 | 0.3204 | 0.3203 | 0.3203 |
| Mod | TIP4P | 0.6715 | 0.6670 | 0.6669 | 0.6648 | 0.6625 | 0.3209 | 0.3204 | 0.3205 | 0.3204 | 0.3204 |
| | | Hexaethylene glycol | | | | | Hexaethylene glycol | | | | |
| Unmod | SPC/E | 1.1765 | 1.1729 | 1.1639 | 1.1485 | 1.1216 | 0.4638 | 0.4633 | 0.4618 | 0.4594 | 0.4549 |
| Unmod | TIP4P | 1.1765 | 1.1715 | 1.1622 | 1.1497 | 1.1225 | 0.4638 | 0.4630 | 0.4616 | 0.4595 | 0.4551 |
| Mod | SPC/E | 1.1487 | 1.1428 | 1.1329 | 1.1231 | 1.1054 | 0.4619 | 0.4609 | 0.4591 | 0.4574 | 0.4542 |
| Mod | TIP4P | 1.1487 | 1.1431 | 1.1340 | 1.1232 | 1.1027 | 0.4619 | 0.4610 | 0.4593 | 0.4575 | 0.4538 |

[a] The specific TIP4P model used was TIP4P/2005

References cited in the Supportive Information


1. Edward, J. T., Molecular Volumes and the Stokes-Einstein Equation. *J. Chem. Educ.* **1970**, *47*, 261-270.
2. Hoffmann, M. M.; Too, M. D.; Paddock, N. A.; Horstmann, R.; Kloth, S.; Vogel, M.; Buntkowsky, G., On the Behavior of the Ethylene Glycol Components of Polydisperse Polyethylene Glycol PEG200. *J. Phys. Chem. B* **2023**, *127*, 1178−1196.
3. Hoffmann, M. M.; Horowitz, R. H.; Gutmann, T.; Buntkowsky, G., Densities, Viscosities, and Self-Diffusion Coefficients of Ethylene Glycol Oligomers. *J. Chem. Eng. Data* **2021**, *66*, 2480-2500.
4. Hoffmann, M. M.; Kealy, J. D.; Gutmann, T.; Buntkowsky, G., Densities, Viscosities, and Self-Diffusion Coefficients of Several Polyethylene Glycols. *J. Chem. Eng. Data* **2021**, *67*, 88-103.
5. Pokorný, V.; Serra, P. B. P.; Fulem, M.; Lima, C. F. R. A. C.; Santos, L. M. N. B. F.; Růžička, K., Heat Capacity and Phase Behavior of Selected Oligo(Ethylene Glycol)S. *J. Chem. Eng. Data* **2019**, *64*, 2742-2749.