Supplemental Information for "Does freezing induces self-assembly of polymers? A molecular dynamics study"

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Abstract

The supporting information contains the system details and the force field parameters that were used for modeling the polymers. This document also contains the tables and figures that support the explanations and conclusions in the main paper i.e., the snapshots of the simulation box during the FISA as well as in the supercooled solution, the diffusivity of the polymers in the supercooled solution, and the PMF curves for the polymer-water interactions.

Force Field Parameters

The polymers were modeled using the force field parameters developed by Naullage and Molinero.[1] The non-bonded parameters for the Lennard Jones interactions between the polymer

Table S1: The system details for the simulations.

Degree of polymerization (DP)	Type	Solute concentration (wt%)	No. of polymer molecules	No. of mW water molecules
4-mer	Hydrophilic	0.5	25	49217
		1.0	50	48969
		2.5	125	48227
		5.0	250	46991
	Amphiphilic	0.5	25	48126
		1.0	50	47884
		2.5	125	47159
		5.0	250	45950
	Hydrophobic	0.5	25	47037
		1.0	50	46800
		2.5	125	46091
		5.0	250	44909
8-mer	Hydrophilic	0.5	25	97880
		1.0	50	97388
		2.5	125	95913
		5.0	250	93453
	Amphiphilic	0.5	25	95699
		1.0	50	95219
		2.5	125	93776
		5.0	250	91371
	Hydrophobic	0.5	25	93520
		1.0	50	93050
		2.5	125	91640
		5.0	250	89291
20-mer	Hydrophilic	0.5	10	97546
		1.0	20	97056
		2.5	50	95585
		5.0	100	93135
	Amphiphilic	0.5	10	95365
		1.0	20	94886
		2.5	50	93449
		5.0	100	91052
	Hydrophobic	0.5	10	93186
		1.0	20	92718
		2.5	50	91313
		5.0	100	88972

chains and water are mentioned in Table S2. The bonded parameters for the bonds, angles, and dihedrals of the polymers are mentioned in Table S3 and Table S4 respectively. The bond lengths and angles were constrained using the harmonic bond and angle potentials; $U = k_r (r - r_0)^2$ and $U = k_\theta (\theta - \theta_0)^2$, respectively. The dihedral potentials were the same for all the cases; $U = k_1[1+cos\phi]/2+k_2[1-cos(2\phi)]/2+k_3[1+cos(3\phi)]/2+k_4[1-cos(4\phi)]/2$

Table S2: The non-bonded parameters $\varepsilon(kcal\ mol^{-1})$ and σ(Å) for polymer chains and mW water molecules.

	CH_3	CH_2	CH	OH	H_2O
CH_3	0.175, 3.905	—	—	—	—
CH_2	0.118, 3.877	0.118, 3.905	—	—	—
CH	0.144, 3.905	0.097, 3.877	0.080, 3.850	—	—
OH	0.170, 3.536	0.170, 3.536	0.170, 3.536	mW	—
H_2O	0.204, 3.536	0.204, 3.536	0.204, 3.536	mW	mW

Table S3: The bonded parameters for the bonds and angles of the polymeric chains.

	$k_r(kcal\ mol^{-1}$Å$^{-2})$	r_0(Å)		$k_\theta(kcal\ mol^{-1}radian^{-2})$	$\theta_0(^o)$
$C1-C2$	30	1.53	$C3-C1-C2$	30	108
$C1-C3$	30	1.53	$C3-C1-O$	30	108
$C2-C2$	30	1.53	$C2-C1-C2$	30	108
$C2-C3$	30	1.53	$C2-C1-O$	30	112
$C1-O$	30	1.43	$C1-C2-C1$	30	112
$C2-O$	30	1.43	$C2-C1-O$	30	112

Table S4: The bonded parameters for the dihedrals of the polymeric chains.

$k_1\ (kcal\ mol^{-1})$	$k_2\ (kcal\ mol^{-1})$	$k_3\ (kcal\ mol^{-1})$	$k_4\ (kcal\ mol^{-1})$
1.411	-0.271	3.145	0.0

Asphericity and radius of gyration

The morphology of the self-assembled structures was analyzed by evaluating the ashpericity and radius of gyration of the assembled aggregates. The gyration tensor T of a molecule

Table S5: The aggregation distribution of 20-mer polymer chains in a cluster with an initial concentration of 5 wt% after FISA and in supercooled solutions. For aggregation number, the term in the parentheses is the number of aggregates for the respective aggregation number.

Polymer type	Temperature (K)	No. of clusters	Aggregation number
		In FISA	
Hydrophilic	263	39	24(1), 8(1), 6(2), 5(1), 4(2), 3(3), 2(5), 1(24)
	253	53	10(1), 8(1), 6(1), 5(3), 4(2), 3(1), 2(6), 1(38)
	240	66	5(4), 3(4), 2(10), 1(48)
Amphiphilic	263	17	53(1), 11(1), 10(1), 4(1), 3(1), 2(2), 1(10)
	253	28	20(1), 11(1), 10(1), 8(1), 6(2), 4(2), 3(3), 2(5), 1(12)
	240	37	16(1), 11(1), 6(1), 5(2), 4(4), 3(2), 2(9), 1(17)
Hydrophobic	263	12	63(1), 12(1), 9(1), 3(2), 2(3), 1(4)
	253	22	31(1), 13(1), 10(1), 9(1), 7(1), 6(1), 4(1), 3(1), 2(3), 1(11
	240	35	11(2), 9(1), 7(2), 6(1), 4(1), 3(5), 2(7), 1(16)
		In supercooled solution	
Hydrophilic	263	73	5(1), 4(2), 3(3), 2(11), 1(56)
	253	77	3(7), 2(9), 1(61)
	240	81	4(1), 3(2), 2(12), 1(66)
Amphiphilic	263	35	8(4), 5(4), 4(3), 3(2), 2(8), 1(14)
	253	44	7(1), 6(2), 5(1), 4(6), 3(5), 2(8), 1(11)
	240	56	7(1), 6(1), 5(2), 4(3), 3(2), 2(12), 1(35)
Hydrophobic	263	17	39(1), 13(1), 11(1), 5(4), 3(1), 2(5), 1(4)
	253	22	19(1), 14(1), 12(1), 8(1), 7(1), 5(2), 4(2), 3(3), 2(3), 1(7
	240	30	13(2), 9(2), 7(1), 5(3), 4(2), 3(1), 2(4), 1(15)

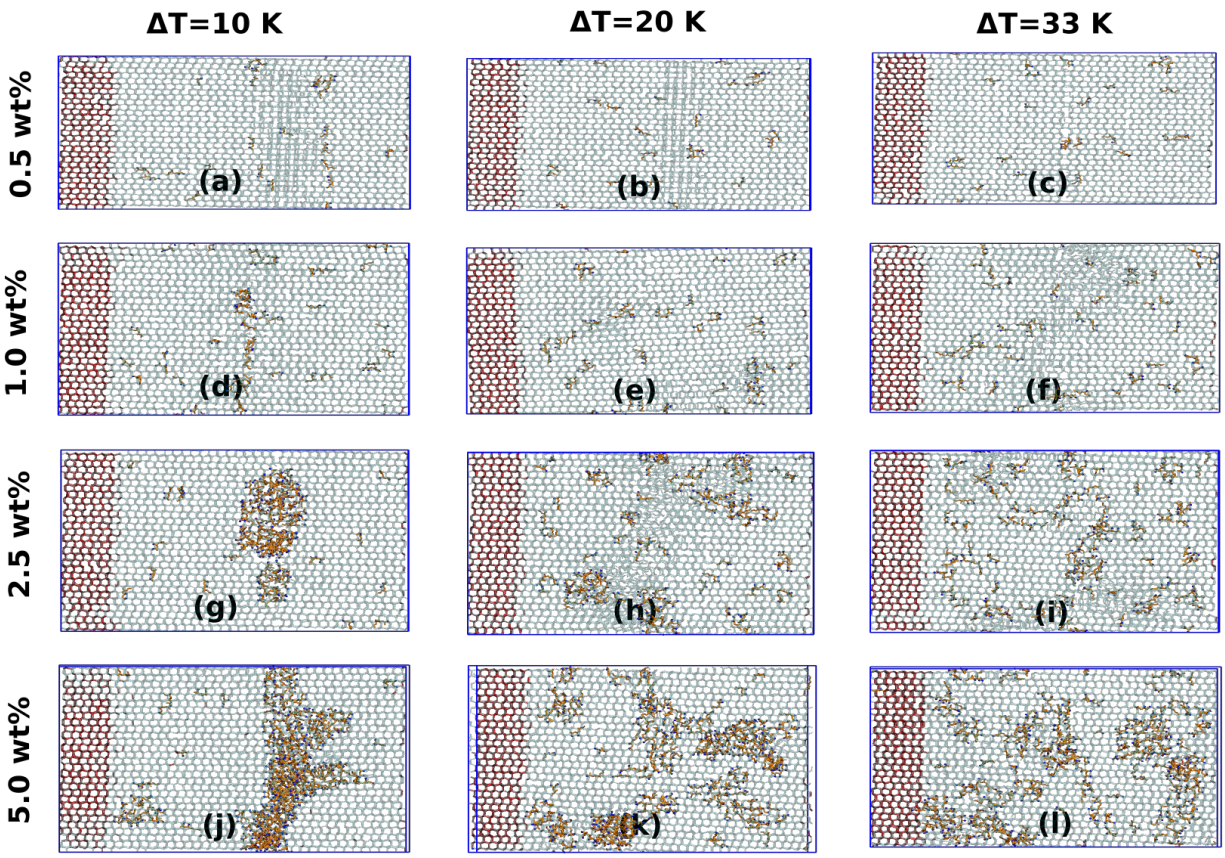

Figure S1: The snapshots of the simulation box after a production run of 100 ns for the amphiphilic 4-mer polymer chains at varying DoS (vertical columns) and different initial concentrations (horizontal rows). The orange, blue, cyan, and red colours represent the polymer backbone, the hydroxyl groups of the polymers, the frozen water molecules, and the ice slab, respectively.

consisting of N (spherical) atoms at cartesian positions $r_i, i = 1, ..., N$, can be represented as,

$$T_{\alpha\beta} = \frac{1}{2N^2} . \sum_{i,j=1}^{N} (r_{i,\alpha} - r_{j,\alpha}).(r_{i,\beta} - r_{j,\beta}) \tag{S1}$$

Where, $r_{i,\alpha}$ is the α^{th} component of the r_i and α, β span over 3d components of the cartesian coordinates. Using the gyration tensor T, the asphericity of a aggregate can be calculated as,[2,3]

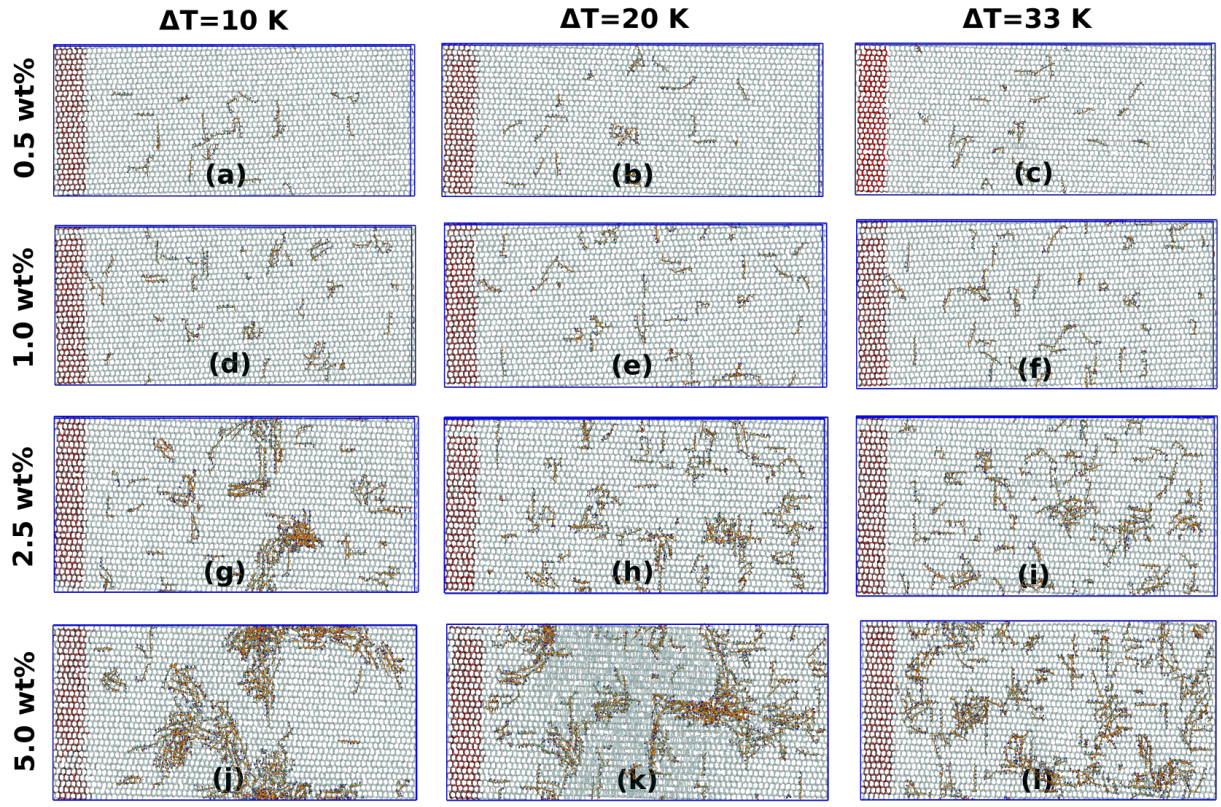

Figure S2: The snapshots of the simulation box after a production run of 100 ns for the amphiphilic 8-mer polymer chains at varying DoS (vertical columns) and different initial concentrations (horizontal rows). The orange, blue, cyan, and red colours represent the polymer backbone, the hydroxyl groups of the polymers, the frozen water molecules, and the ice slab, respectively.

$$\Delta = \frac{3\sum_{i=1}^{3}(\gamma_i - \bar{\gamma})^2}{2(trT)^2} \tag{S2}$$

Where, γ_i are the eigenvalues of the tensor T and $trT = \sum_{i=1}^{3}\gamma_i = R_g^2$ with $\bar{\gamma} = trT/3$. The components of the gyration tensor were evaluated using *cluster analysis* module in the OVITO[4] package.

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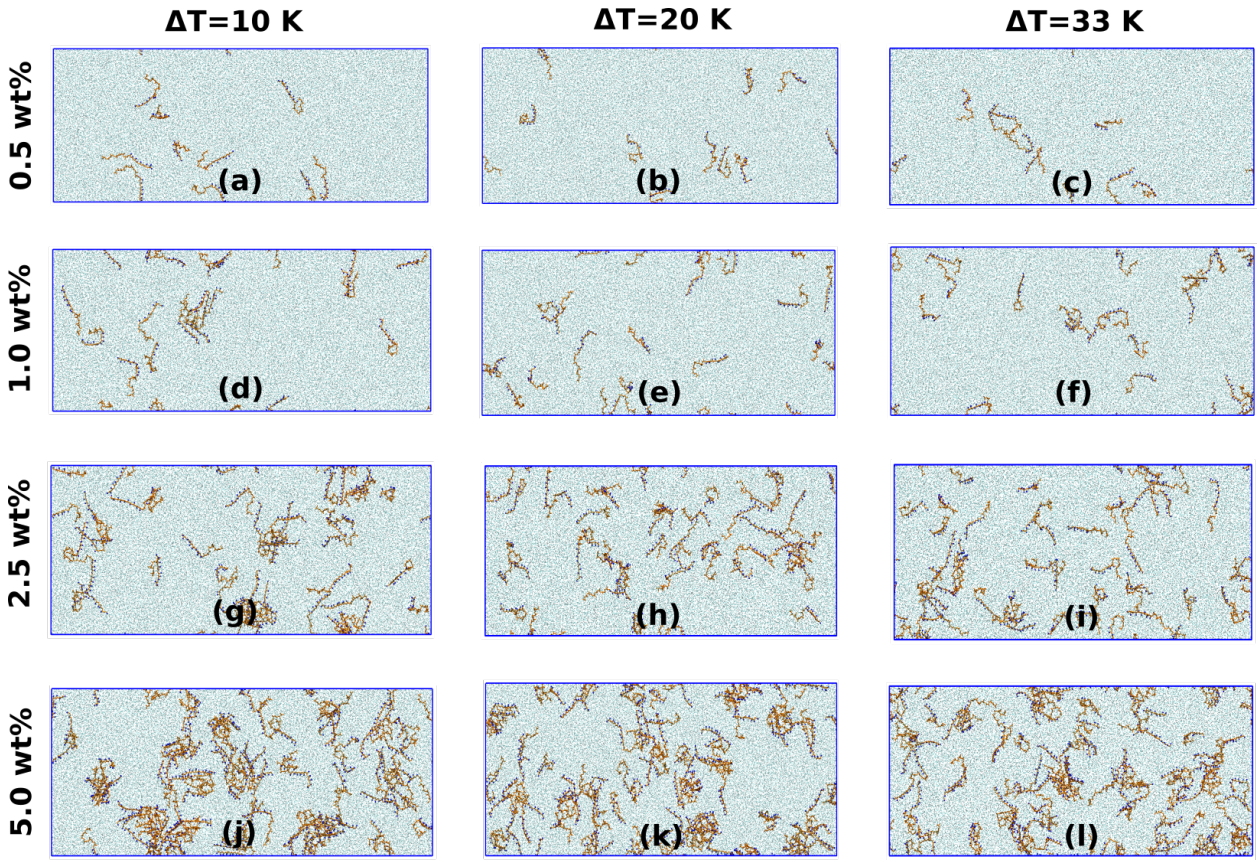

Figure S3: The snapshots of the simulation box after a production run of 100 ns for amphiphilic 20-mer polymer chain in the supercooled solution at varying DoS (vertical columns) and different initial concentrations (horizontal rows) in the supercooled solution. The orange, blue, and cyan colours represent the polymer backbone, the hydroxyl groups of the polymers, and the water molecules, respectively.

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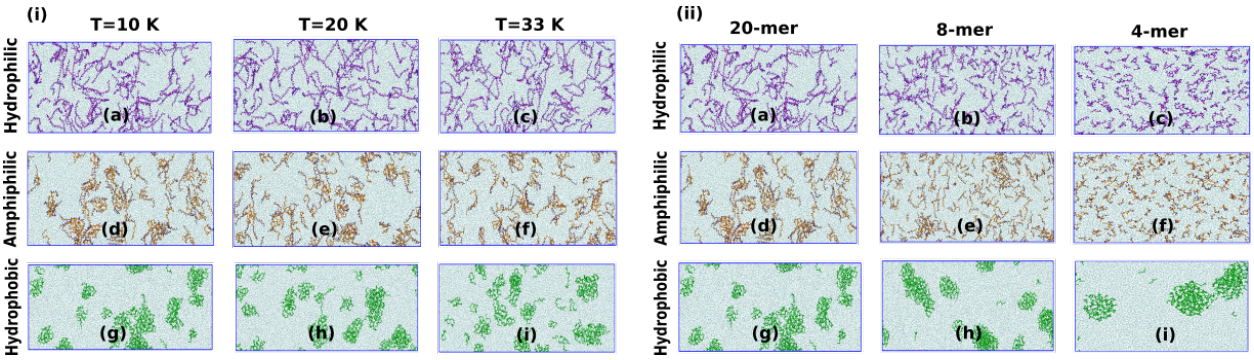

Figure S4: The snapshots of the simulation box after a production run of 100 ns at 5 wt% concentration of the polymer chains in the supercooled solution. (i) The vertical columns and horizontal rows represent the data at a constant DoS and polymer type respectively for 20-mer polymer chains. (ii) The vertical columns and horizontal rows represent the data at a constant DP and polymer type respectively at a DoS of 10 K. The purple, orange, green, blue, and cyan colours represent the hydrophilic polymer backbone, the amphiphilic polymer backbone, the hydrophobic polymer backbone, the hydroxyl groups of the polymers, and the water molecules, respectively.

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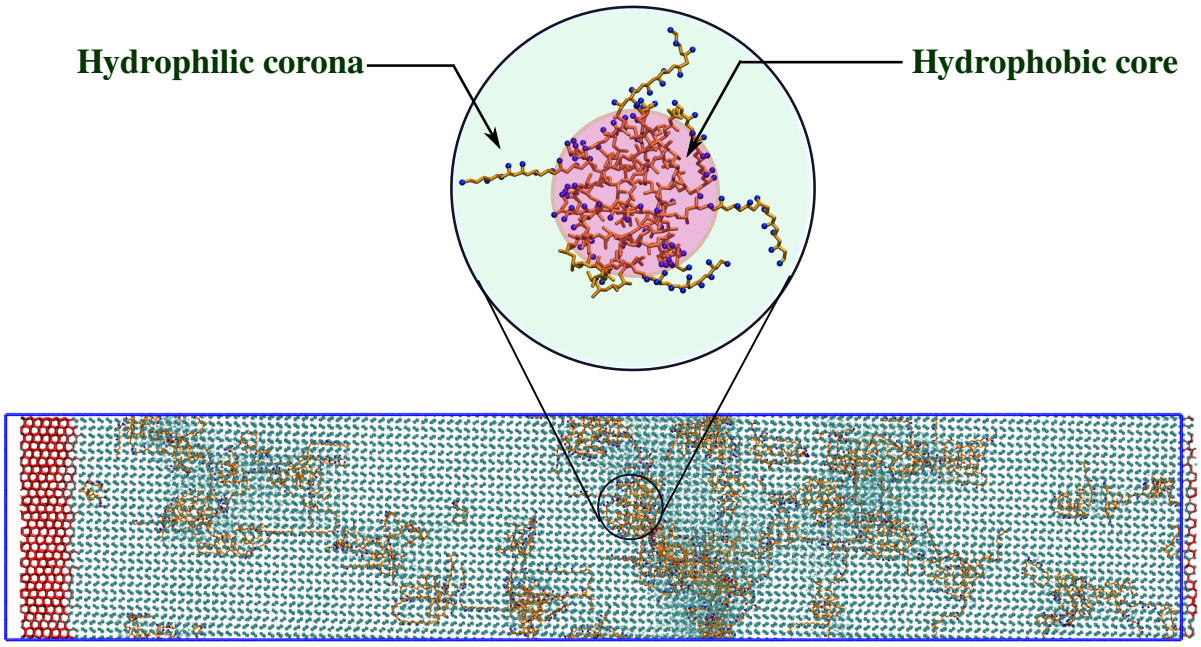

Figure S5: The snapshot of the simulation box after a production run of 100 ns at 5wt% concentration of 20-mer amphiphilic polymer chain with twice the box size in lateral direction (x-axis). The image in the inset shows the structure of the self-assembled aggregate with hydrophobic core and hydrophilic corona.

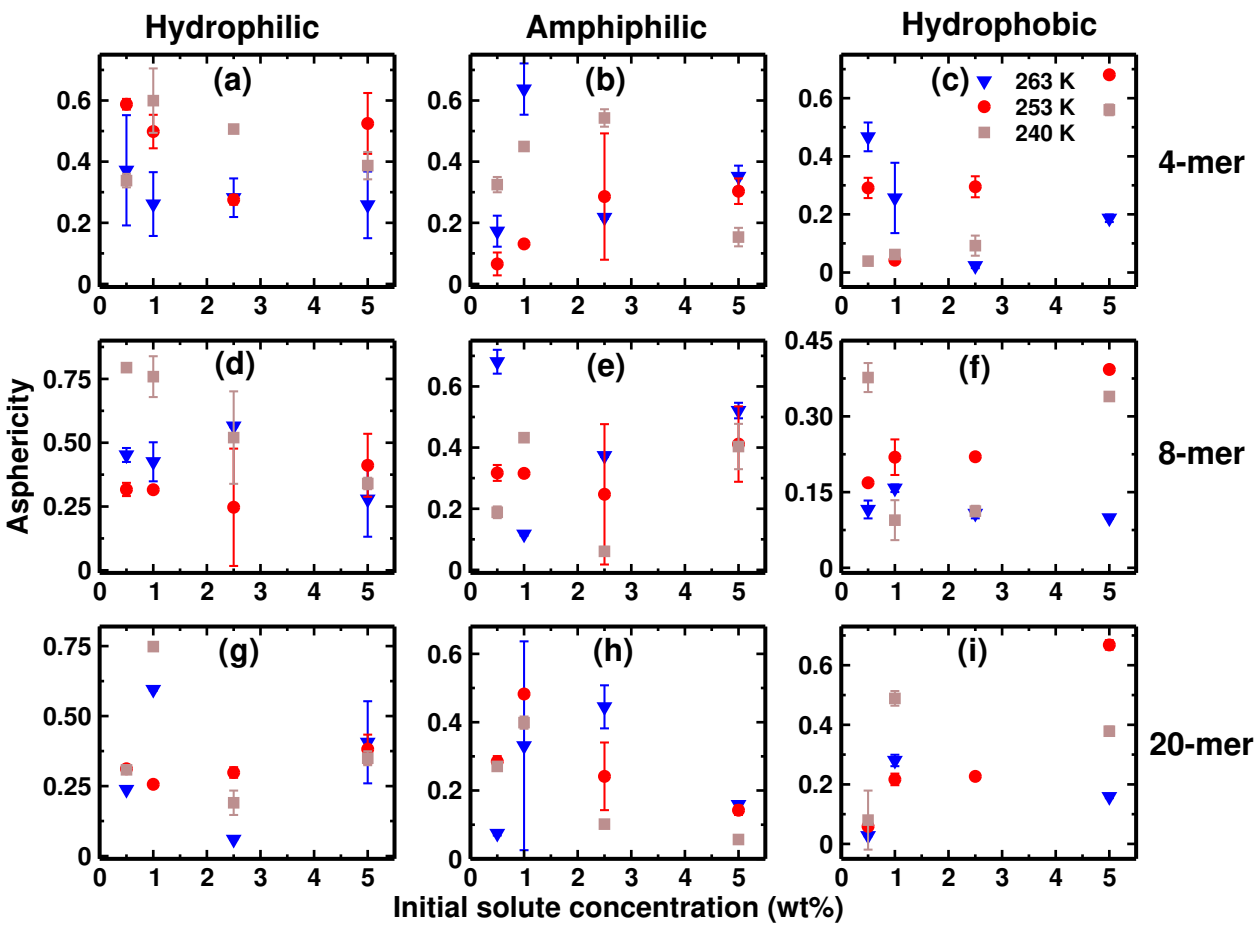

Figure S6: The asphericity of the polymeric aggregates at different DoS, DP, and polymer type.

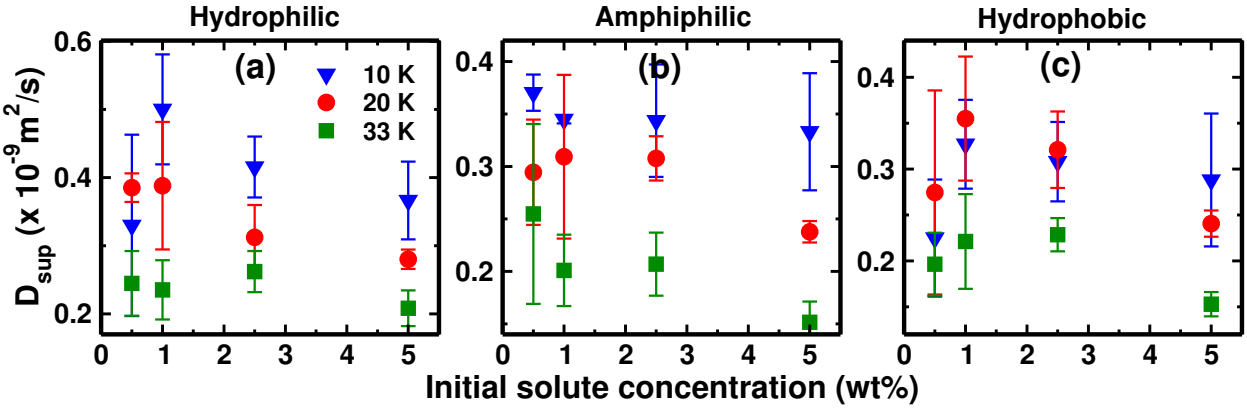

Figure S7: The diffusivity (D_{sup}) of the 20-mer polymers in the supercooled solution as a function of the DoS with different initial concentrations. The diffusivity of (a) hydrophilic, (b) amphiphilic, and (c) hydrophobic 20-mer polymer chains at different DoS. The blue, red, and green colors correspond to the DoS of 10 K, 20 K, and 33 K, respectively.

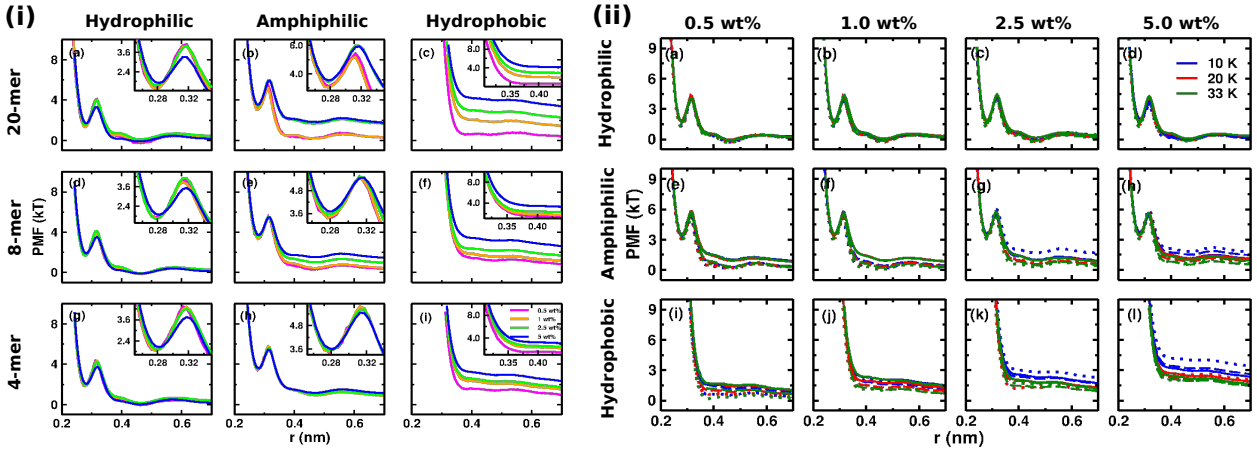

Figure S8: The PMF of the polymer-water interactions at different DoS, DP, and initial polymer concentrations. (i) The PMF of the polymer-water interactions at DoS = 10 K with varying initial concentrations as a function of the DP (horizontal rows) and polymer types (vertical columns), respectively. (ii) The PMF of the polymer-water interactions with varying DoS as a function of the polymer type (horizontal rows) and the initial polymer concentration (vertical columns), respectively. The solid lines, dashed lines, and dotted lines represent the data for polymers with DP 20, 8, and 4 respectively.