

Supporting Information

Explainable Point-Cloud Deep Learning for 3D Conformation Recognition of Temperature-Sensitive Bottlebrush Polymers

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ADDITIONAL FIGURES AND DISCUSSION FOR CG MD SIMULATIONS AND ANALYSES.

S1. Conventional analysis of CG MD trajectories – Methodology

Structural properties of the BBPs from CG MD trajectories were quantified using multiple conventional analyses. The radius of gyration (R_g) (Joshi et al., 2021) was calculated for both, the complete architectures and their backbones using CPPTRAJ (Roe and Cheatham III, 2013 and 2018) to evaluate overall compactness and backbone flexibility. Radial distribution functions (RDFs) (Joshi et al., 2021) were computed to characterize solvent organization around different polymer bead types and to probe temperature-dependent hydration behavior. Solvent accessible surface area (SASA) (Weiser et al., 1999; Roe and Cheatham III, 2013) was determined using a rolling-ball algorithm implemented in CPPTRAJ to estimate the extent of polymer exposure to

surrounding solvent. Free volume (Brassey and Gardiner, 2015; Brassey et al., 2018; Kapoor and Jayaraman, 2020) was estimated by constructing a convex hull around each BBP structure to obtain the occupied volume and subtracting the theoretical bead volume (Joshi et al., 2022), providing a measure of structural compactness. Intra-polymer contacts were defined as bead pairs separated by less than 12 Å, consistent with the coarse-grained van der Waals cutoff, and normalized per monomer to assess aggregation and chain association (Joshi et al., 2022). Finally, asphericity (Yethiraj, 2006; Joshi et al., 2022) was calculated using an in-house code, where values range from 0 for perfectly spherical conformations to 1 for highly elongated cylindrical structures, enabling quantitative comparison of shape transitions across architectures and temperatures.

S2. Conventional analysis of CG MD trajectories – Results

Unfunctionalized TS-BBPs

Visual inspection of the simulation trajectories, akin to our previous work (Joshi et al., 2022), generally showed that TS-BBPs at 320 K exhibited more compact and bent structures than at 300 K, when simulated for 500 ns. Figures S1, S2, and S3 present the final snapshots for the cake-like, dumbbell-like and plus-like TS-BBPs after 500 ns of simulations. Clearly, PNIPAM side chains at 300 K appear more stretched and favorably interacting with surrounding water as compared to at 320 K. This can be attributed to the thermosensitive nature of PNIPAM side chains which makes them hydrophobic above LCST as shown in our prior work, resulting in enhanced interactions between side chains as compared to with the surrounding water. Conventional analyses such as R_g , SASA, asphericity, free volume etc., shown in Table S1 help validate these.

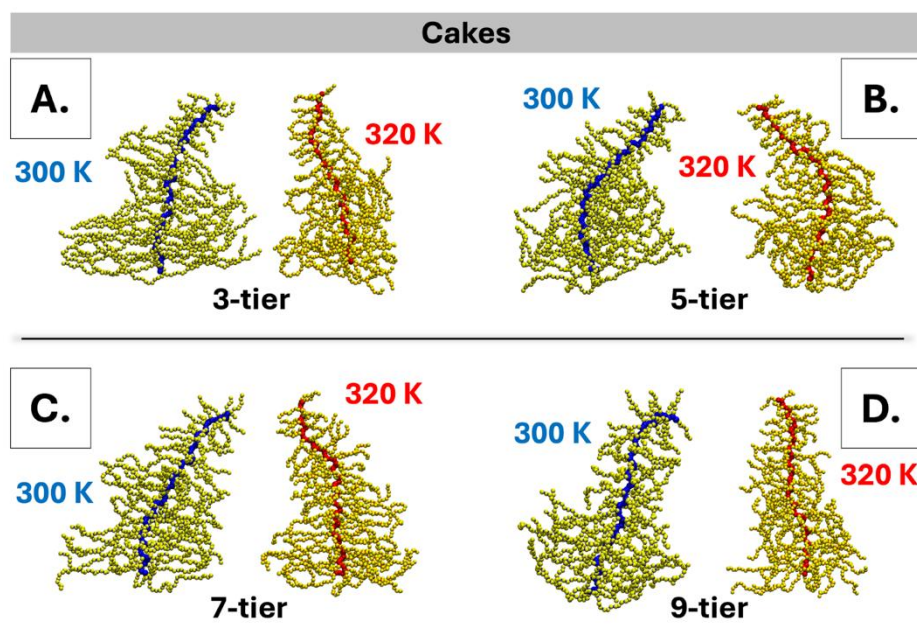


Figure S1: Final snapshots showcasing equilibrated A. 3-tiered, B. 5-tiered, C. 7-tiered, and D. 9-tiered cake-like TS-BBPs after 500 ns simulations. Snapshots at 300 K are presented with a blue BBP backbone and those at 320 K are presented with a red BBP backbone. PNIPAM side chains are presented as yellow spheres.

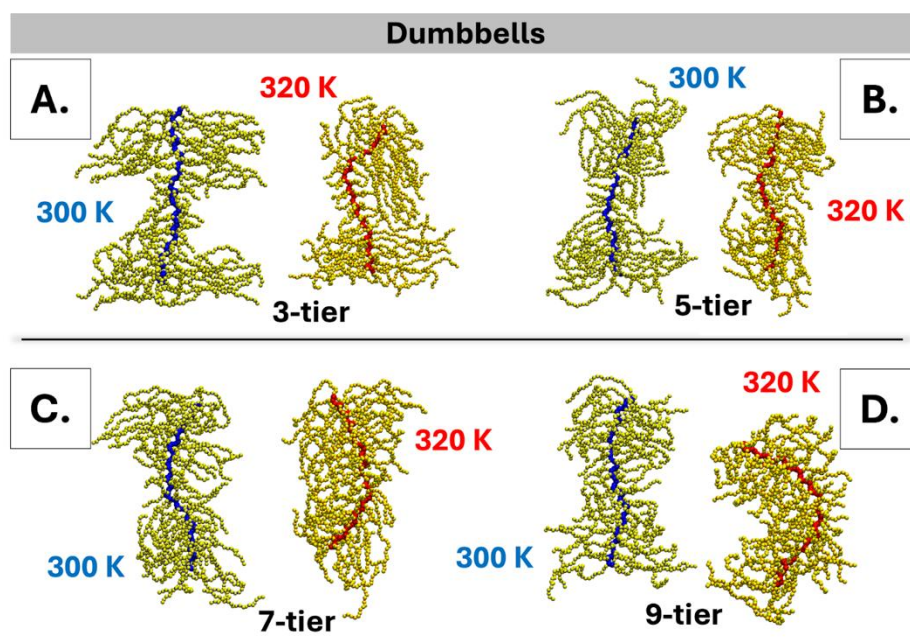


Figure S2: Final snapshots showcasing equilibrated A. 3-tiered, B. 5-tiered, C. 7-tiered, and D. 9-tiered dumbbell-like TS-BBPs after 500 ns simulations. Snapshots at 300 K are presented with a blue BBP backbone and those at 320 K are presented with a red BBP backbone. PNIPAM side chains are presented as yellow spheres.

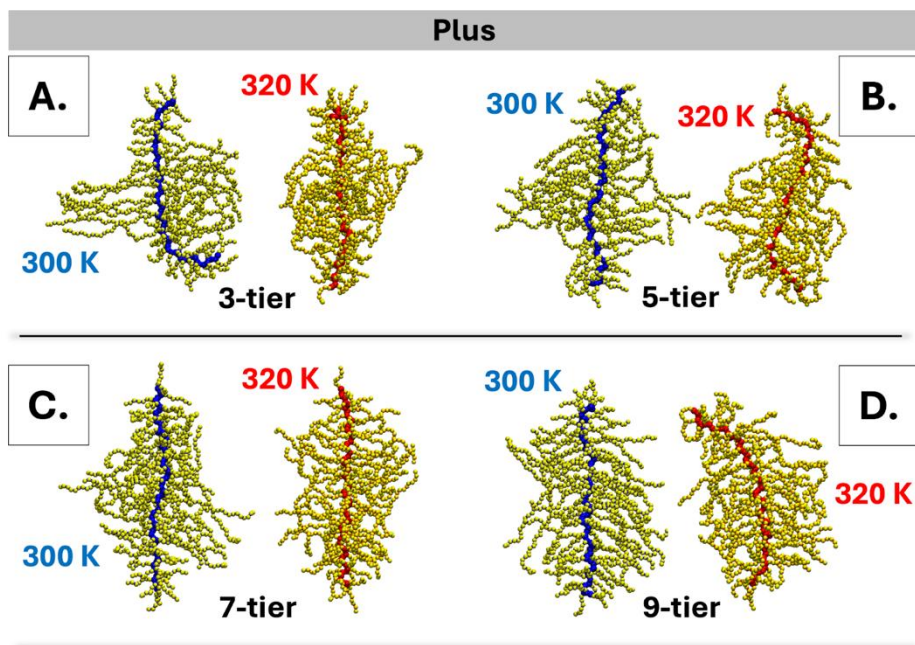


Figure S3: Final snapshots showcasing equilibrated A. 3-tiered, B. 5-tiered, C. 7-tiered, and D. 9-tiered plus-like TS-BBPs after 500 ns simulations. Snapshots at 300 K are presented with a blue BBP backbone and those at 320 K are presented with a red BBP backbone. PNIPAM side chains are presented as yellow spheres.

Table S1: Conventional analysis data for the unfunctionalized TS-BBPs

	Cakes							
	3-tier		5-tier		7-tier		9-tier	
	300K	320K	300K	320K	300K	320K	300K	320K
R_g - BB (Å)	34.95 ± 0.3	35.07 ± 0.3	33.22 ± 0.5	34.65 ± 0.5	35.13 ± 0.3	35.11 ± 0.3	36.54 ± 0.2	36.13 ± 0.3
R_g - Full (Å)	42.43 ± 0.5	40.02 ± 0.3	37.97 ± 0.3	39.78 ± 1.1	40.12 ± 0.4	41.82 ± 0.5	40.96 ± 0.6	42.20 ± 0.4
SASA (Å²)	146018 ± 530	146320 ± 627	144047 ± 560	145423 ± 630	144447 ± 588	144319 ± 487	144245 ± 735	144975 ± 648
Asphericity	0.37 ± 0.01	0.42 ± 0.02	0.37 ± 0.02	0.41 ± 0.01	0.42 ± 0.02	0.49 ± 0.02	0.44 ± 0.01	0.55 ± 0.02
Free Volume	350489 ± 30227	328156 ± 25675	306012 ± 12686	330398 ± 42777	342605 ± 23405	322895 ± 31373	345467 ± 26121	345217 ± 37211
No. of Contacts	104.30 ± 1.3	105.09 ± 1.7	107.56 ± 1.4	104.85 ± 1.6	105.02 ± 1.5	106.17 ± 1.2	104.85 ± 1.5	104.01 ± 1.7
	Dumbbells							
	3-tier		5-tier		7-tier		9-tier	
	300K	320K	300K	320K	300K	320K	300K	320K
R_g - BB (Å)	34.98 ± 0.3	33.67 ± 0.5	35.08 ± 0.6	34.02 ± 0.4	34.47 ± 0.3	32.84 ± 0.6	34.37 ± 0.4	31.86 ± 0.7
R_g - Full (Å)	51.27 ± 0.9	48.87 ± 1.9	51.95 ± 0.8	46.16 ± 0.4	48.39 ± 0.5	43.17 ± 0.9	46.14 ± 1.0	41.54 ± 1.9
SASA (Å²)	178981 ± 855	178674 ± 904	167767 ± 439	166563 ± 707	159545 ± 448	160234 ± 949	154594 ± 462	155158 ± 823
Asphericity	0.45 ± 0.02	0.51 ± 0.01	0.60 ± 0.01	0.58 ± 0.02	0.65 ± 0.01	0.56 ± 0.02	0.57 ± 0.03	0.47 ± 0.03
Free Volume	832649 ± 52590	566916 ± 83621	705959 ± 69055	479842 ± 51466	472104 ± 37697	374335 ± 42220	467445 ± 25578	369802 ± 58684

No. of Contacts	98.74 ± 1.8	102.20 ± 2.2	99.53 ± 0.7	103.99 ± 1.6	104.91 ± 1.0	105.48 ± 2.3	104.62 ± 0.9	104.91 ± 2.3
	Plus							
	3-tier		5-tier		7-tier		9-tier	
	300K	320K	300K	320K	300K	320K	300K	320K
R _g - BB (Å)	34.32 ± 0.3	34.44 ± 0.4	35.16 ± 0.3	34.24 ± 0.3	35.23 ± 0.4	34.65 ± 0.3	35.46 ± 0.4	33.54 ± 0.4
R _g - Full (Å)	38.94 ± 0.5	36.04 ± 0.5	38.11 ± 0.2	36.11 ± 0.2	37.98 ± 0.4	37.31 ± 0.3	38.37 ± 0.2	36.94 ± 0.3
SASA (Å ²)	117722 ± 544	116812 ± 460	125659 ± 499	125260 ± 534	130420 ± 400	129494 ± 529	134540 ± 574	134247 ± 508
Asphericity	0.17 ± 0.02	0.29 ± 0.02	0.34 ± 0.01	0.38 ± 0.04	0.36 ± 0.01	0.47 ± 0.01	0.41 ± 0.03	0.39 ± 0.01
Free Volume	386207 ± 24869	262422 ± 23224	330725 ± 19692	254400 ± 28193	344883 ± 20459	274884 ± 21329	336352 ± 29755	251693 ± 15094
No. of Contacts	102.32 ± 1.6	106.94 ± 1.3	104.45 ± 1.3	107.11 ± 1.6	103.36 ± 1.1	107.81 ± 1.2	104.58 ± 1.8	107.42 ± 1.2

Cakes: For the cake-shaped BBPs, the data in **Table S1** reveal nuanced structural variations across different tiers and temperatures. The backbone R_g values remain largely consistent across all configurations, with only minor differences between 300 K and 320 K, indicating relatively stable and consistent backbone conformations. However, the full R_g tends to decrease at 320 K compared to 300 K for the 3-tier and 5-tier systems, suggesting an overall compaction of the side chain structure at elevated temperature, consistent with the LCST behavior of PNIPAM. Interestingly, in the 7-tier and 9-tier configurations, the full R_g increases at 320 K. SASA values stay relatively stable across all tiers and temperatures, indicating that surface exposure does not drastically change with temperature. Asphericity consistently increases with temperature and more finely tiered structures, suggesting a trend toward more elongated or cylindrical shapes. Free volume decreases notably from 300 K to 320 K in the 3-tier and 7-tier configurations but remains comparable in the 9-tier systems. The number of contacts is largely consistent across tiers and temperatures, with only small fluctuations, implying a balance between chain collapse and structural resistance. Overall, these observations suggest that architectural granularity and temperature interplay to modulate the conformational landscape of cake-like BBPs.

Dumbbells: The dumbbell-shaped BBPs display the most significant temperature-dependent structural changes among the three architectures. A pronounced decrease in both backbone and full R_g values is observed from 300 K to 320 K across all tiers, especially in the higher-tiered

systems (7-tier and 9-tier), indicating extensive compaction at elevated temperature. The SASA values corroborate this compaction, showing a consistent reduction from 300 K to 320 K, particularly in the 5-tier through 9-tier systems. Asphericity values demonstrate diverse behaviors: they increase with temperature in lower-tier systems (3-tier and 5-tier), indicating a transition to more elongated shapes, but decrease in higher-tier configurations, which reflects a shift toward spherical conformations as the system collapses. Notably, the free volume exhibits a dramatic decrease at 320 K compared to 300 K, further affirming the compact and collapsed nature of dumbbell-like BBPs at higher temperatures. The number of contacts increases with temperature across all configurations, reflecting stronger intra-chain interactions under thermoresponsive collapse. These trends collectively show that dumbbell-like BBPs undergo significant LCST-driven restructuring, becoming compact and aggregated as temperature rises.

Plus: Plus-like BBPs exhibit a moderate response to temperature changes compared to cakes and dumbbells. The backbone R_g shows minimal variation with temperature, although a slight decrease is evident in the 7-tier and 9-tier systems at 320 K. The full R_g values, however, consistently drop from 300 K to 320 K across all tiers, indicating temperature-induced global compaction. The SASA increases progressively with finer tiering (from 3-tier to 9-tier), but its temperature dependence is weak, suggesting that while the shape's segmentation affects surface exposure, temperature alone does not drastically alter hydration. Asphericity rises notably with tier complexity and temperature, implying a structural bias toward more cylindrical shapes, particularly at 320 K. Free volume drops significantly at higher temperatures, again consistent with PNIPAM collapse behavior, but the overall compaction appears more regulated compared to dumbbell systems. The number of contacts increases with temperature, reflecting stronger intra-chain aggregation at 320 K. Notably, the changes in contacts and R_g are less extreme than in dumbbells, indicating that the plus-like BBPs strike a balance between structural robustness and thermoresponsive behavior.

Figures S4-S6 present the RDFs of different bead types in unfunctionalized TS-BBPs with respect to water beads, providing insight into the hydration environments of distinct polymer

segments across temperatures and architectures. Specifically, these figures show RDFs at 300 K (blue) and 320 K (red) for the BBP backbone (BB), as well as the CG1, CG2, and CG3 bead types in PNIPAM side chains (panels A-D) in cake-like (Figure S4), dumbbell-like (Figure S5), and plus-like (Figure S6) architectures, each displayed across increasing BBP tiers (3-tier to 9-tier). Across all architectures and bead types, the first hydration peak consistently diminishes in magnitude at 320 K compared to 300 K, indicating reduced solvation due to the hydrophobic collapse of PNIPAM chains above the LCST. This reduction in hydration is most pronounced for the CG2 and CG3 beads - corresponding to longer, more hydrophobic side chains - highlighting their greater contribution to thermoresponsive behavior. Among different architectures, dumbbell-like TS-BBPs exhibit the largest decrease in hydration, cakes show an intermediate response, and plus-like BBPs retain the most hydration, suggesting a hierarchy in structural sensitivity to temperature-induced dehydration.

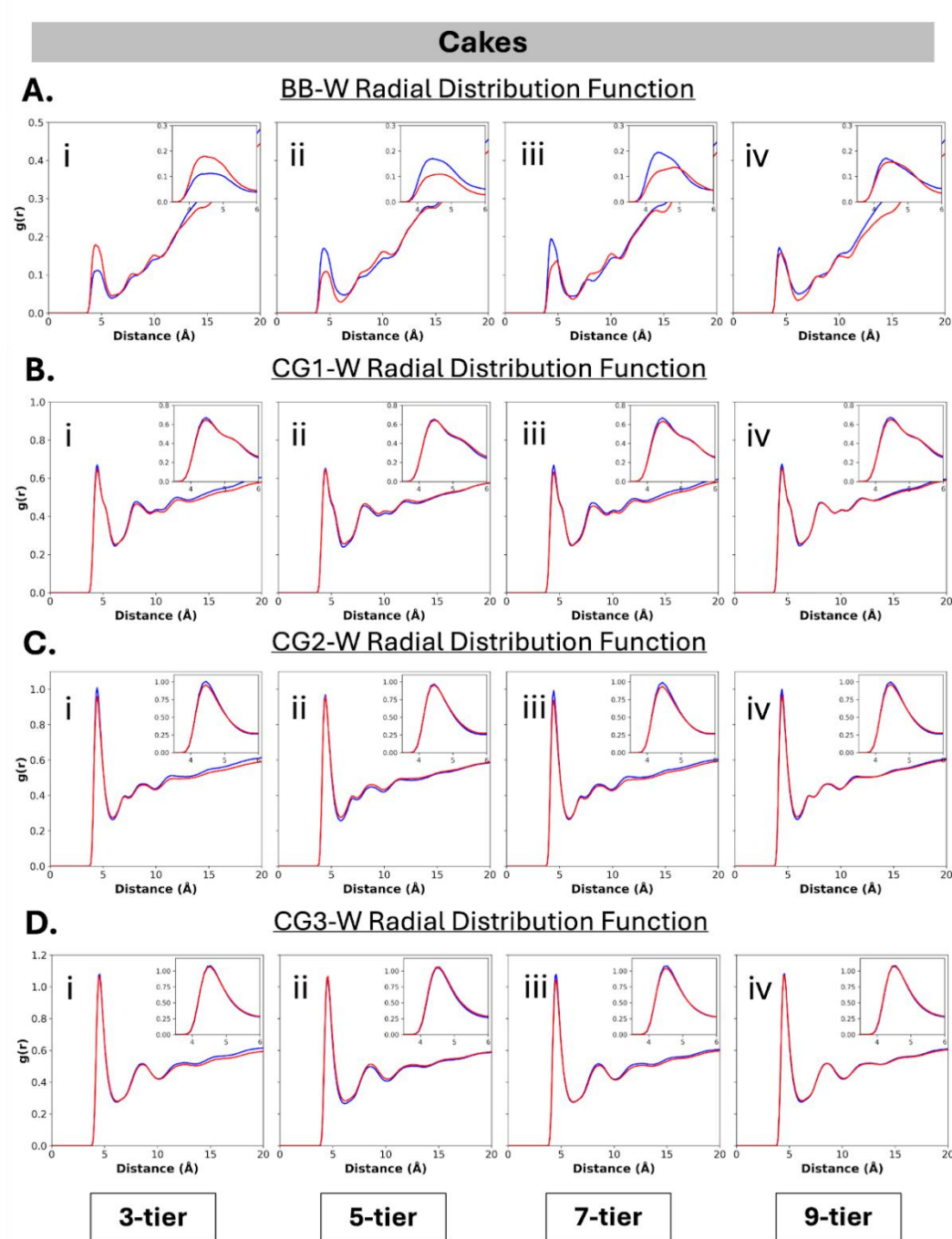


Figure S4: Radial distribution functions (RDFs) of different bead types in cake-like TS-BBPs with respect to water beads, at 300 K (blue) and 320 K (red). Panels A-D correspond to BB-W, CG1-W, CG2-W, and CG3-W RDFs, respectively. Each panel shows four subplots (i-iv), representing four unfunctionalized TS-BBP architectures: 3-tier, 5-tier, 7-tier, and 9-tier, respectively. Inset plots in each subplot magnify the first peak region for clarity.

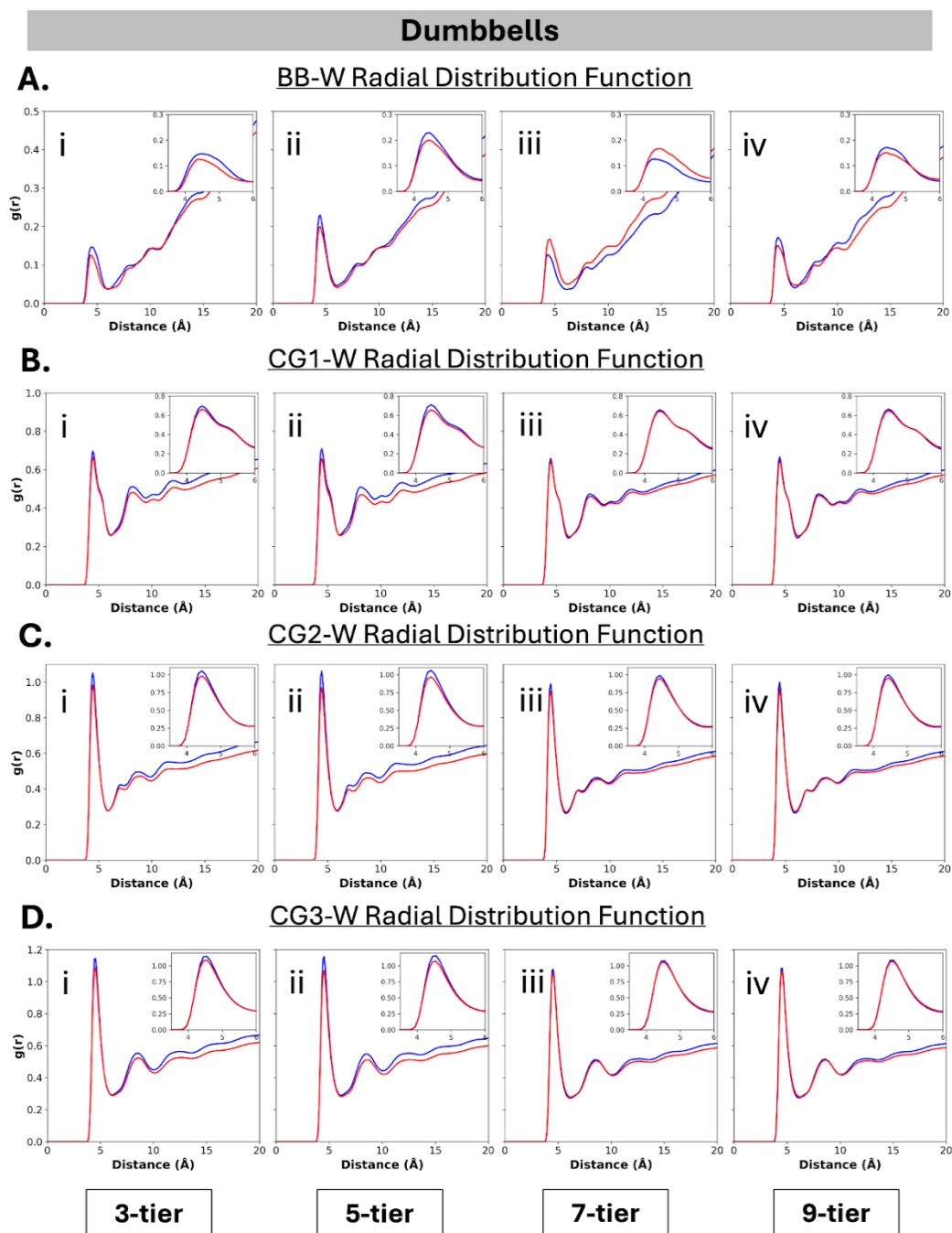


Figure S5: Radial distribution functions (RDFs) of different bead types in dumbbell-like TS-BBPs with respect to water beads, at 300 K (blue) and 320 K (red). Panels A-D correspond to BB-W, CG1-W, CG2-W, and CG3-W RDFs, respectively. Each panel shows four subplots (i-iv), representing four unfunctionalized TS-BBP architectures: 3-tier, 5-tier, 7-tier, and 9-tier, respectively. Inset plots in each subplot magnify the first peak region for clarity.

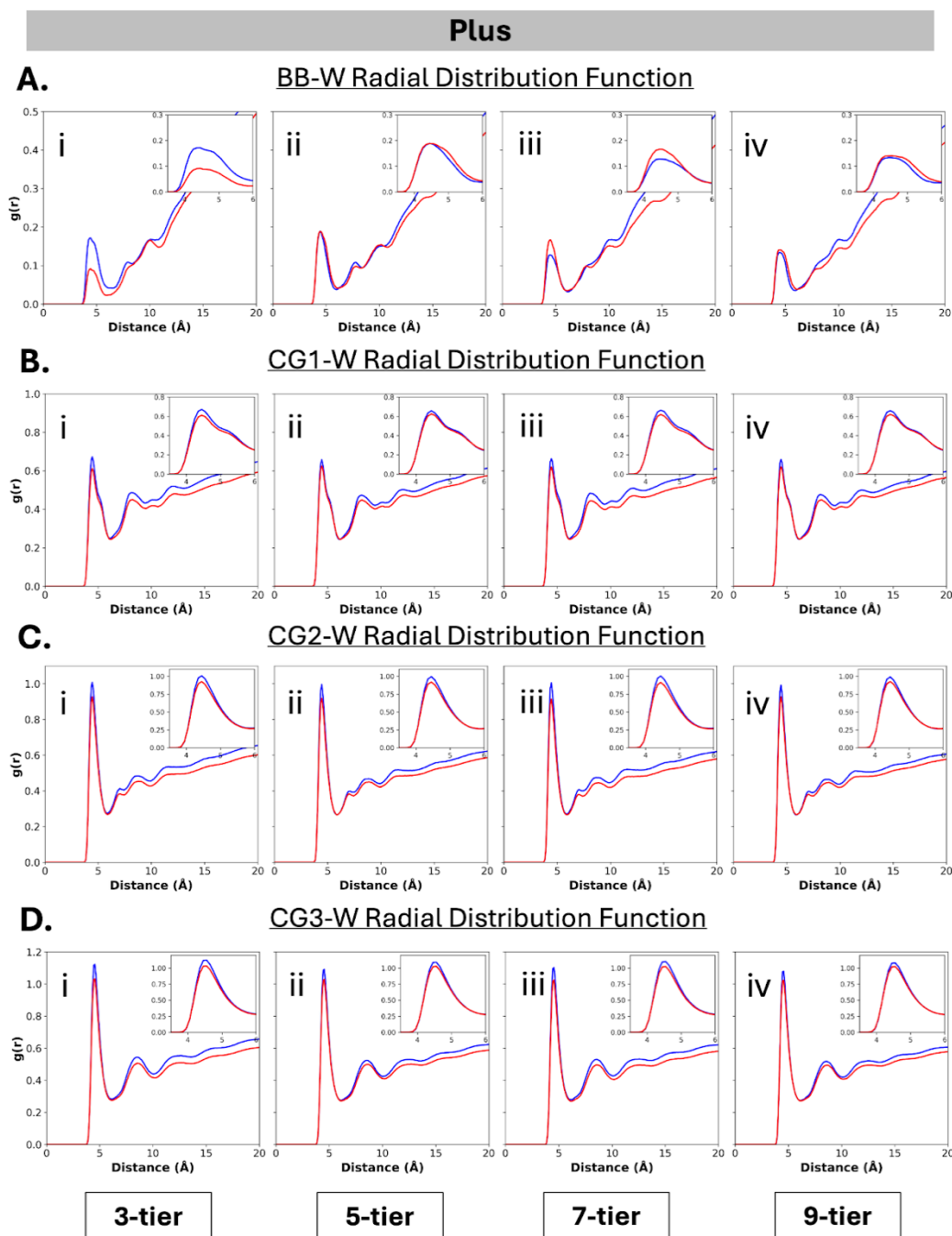


Figure S6: Radial distribution functions (RDFs) of different bead types in plus-like TS-BBPs with respect to water beads, at 300 K (blue) and 320 K (red). Panels A-D correspond to BB-W, CG1-W, CG2-W, and CG3-W RDFs, respectively. Each panel shows four subplots (i-iv), representing four unfunctionalized TS-BBP architectures: 3-tier, 5-tier, 7-tier, and 9-tier, respectively. Inset plots in each subplot magnify the first peak region for clarity.

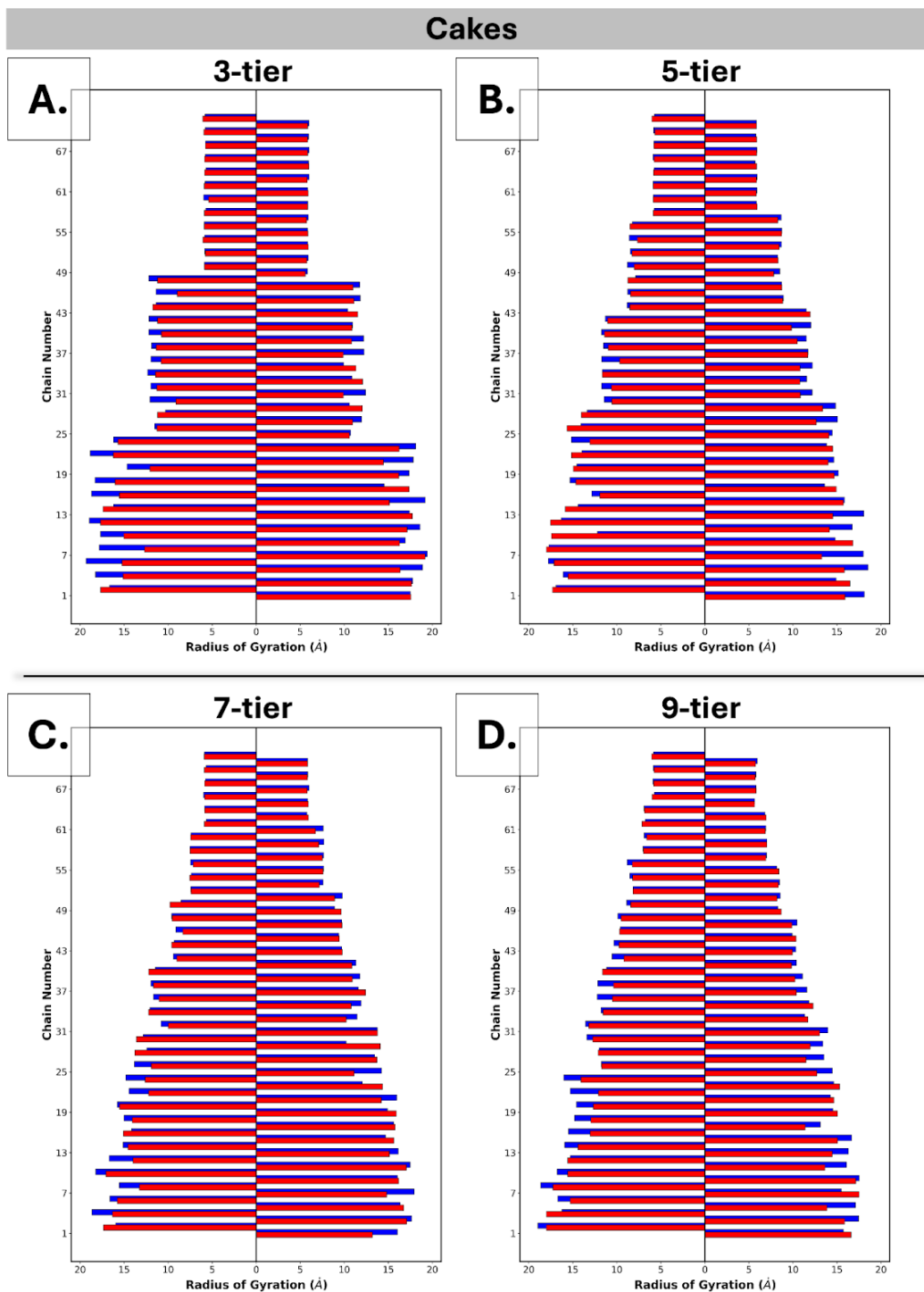


Figure S7: Mean R_g values for each PNIPAM side chain of the unfunctionalized cake-like TS-BBPs with A. 3-tiers, B. 5-tiers, C. 7-tiers, and D. 9-tiers. Data at 300K is presented in blue whereas that at 320K is presented in red.

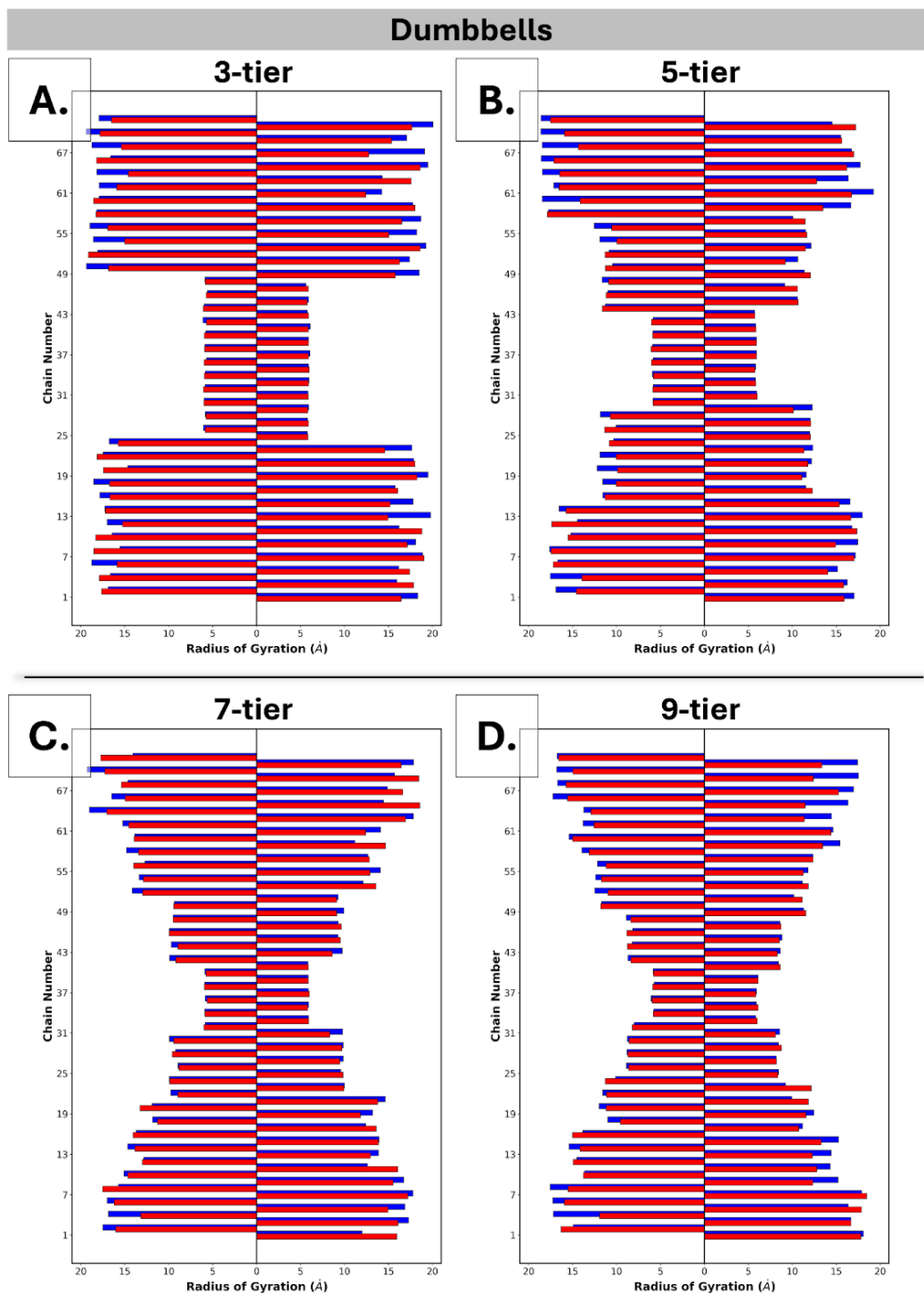


Figure S8: Mean R_g values for each PNIPAM side chain of the unfunctionalized dumbbell-like TS-BBPs with A. 3-tiers, B. 5-tiers, C. 7-tiers, and D. 9-tiers. Data at 300K is presented in blue whereas that at 320K is presented in red.

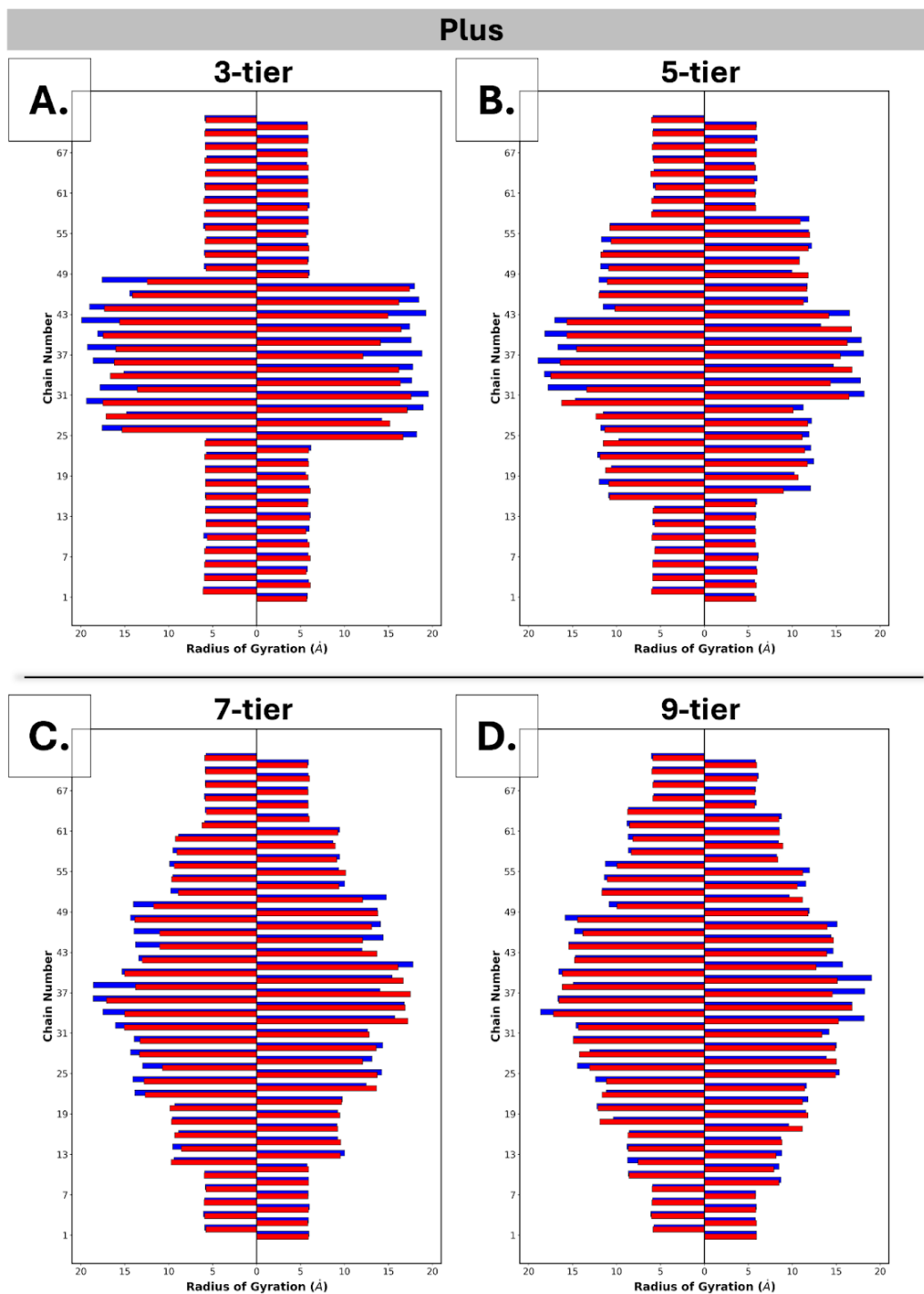


Figure S9: Mean R_g values for each PNIPAM side chain of the unfunctionalized plus-like TS-BBPs with A. 3-tiers, B. 5-tiers, C. 7-tiers, and D. 9-tiers. Data at 300K is presented in blue whereas that at 320K is presented in red.

Figures S7-S9 display the mean R_g profiles of individual PNIPAM side chains along the backbone of unfunctionalized TS-BBPs, capturing the spatial distribution of side chain conformations across architectures and tiers. These figures show R_g values at 300 K (blue) and 320 K (red) for cake-like (Figure S7), dumbbell-like (Figure S8), and plus-like (Figure S9) TS-BBPs. At higher temperature (320 K), side chains generally adopt more compact conformations, reflected by lower R_g values compared to 300 K, consistent with the LCST-driven coil-to-globule transition of PNIPAM. The dumbbell-like TS-BBPs exhibit the most significant decrease in side chain R_g across tiers, indicating their higher thermosensitivity, while plus-like TS-BBPs show more modest changes, indicative of their structural stability.

Functionalized TS-BBPs

Figures S10-S12 illustrate the consequences of dextran 10-mer functionalization on 5-tiered TS-BBPs across the three architectures. Each figure shows representative final simulation snapshots and mean side chain R_g profiles at 300 K (blue) and 320 K (red), for cake-like (Figure S10), dumbbell-like (Figure S11), and plus-like (Figure S12) TS-BBPs functionalized at 33%, 50%, and 100% densities. Visually, increasing dextran density progressively alters the BBPs' global morphology, particularly at high temperature, where dextran's aggregation and hydrophilicity compete with PNIPAM's LCST-driven collapse. Quantitatively, the side chain R_g profiles confirm that dextran functionalization partially mitigates the collapse observed in unfunctionalized BBPs. While side chains still adopt slightly compact conformations at 320 K relative to 300 K, the magnitude of compaction diminishes with higher dextran content. These trends foreshadow the detailed findings in Table S2, where conventional analyses reveal how dextran's steric and hydrophilic effects modulate compactness, hydration, and intra-chain interactions in a shape- and density-dependent manner, ultimately demonstrating the delicate balance between thermoresponsiveness and functionalization-induced stabilization in TS-BBPs.

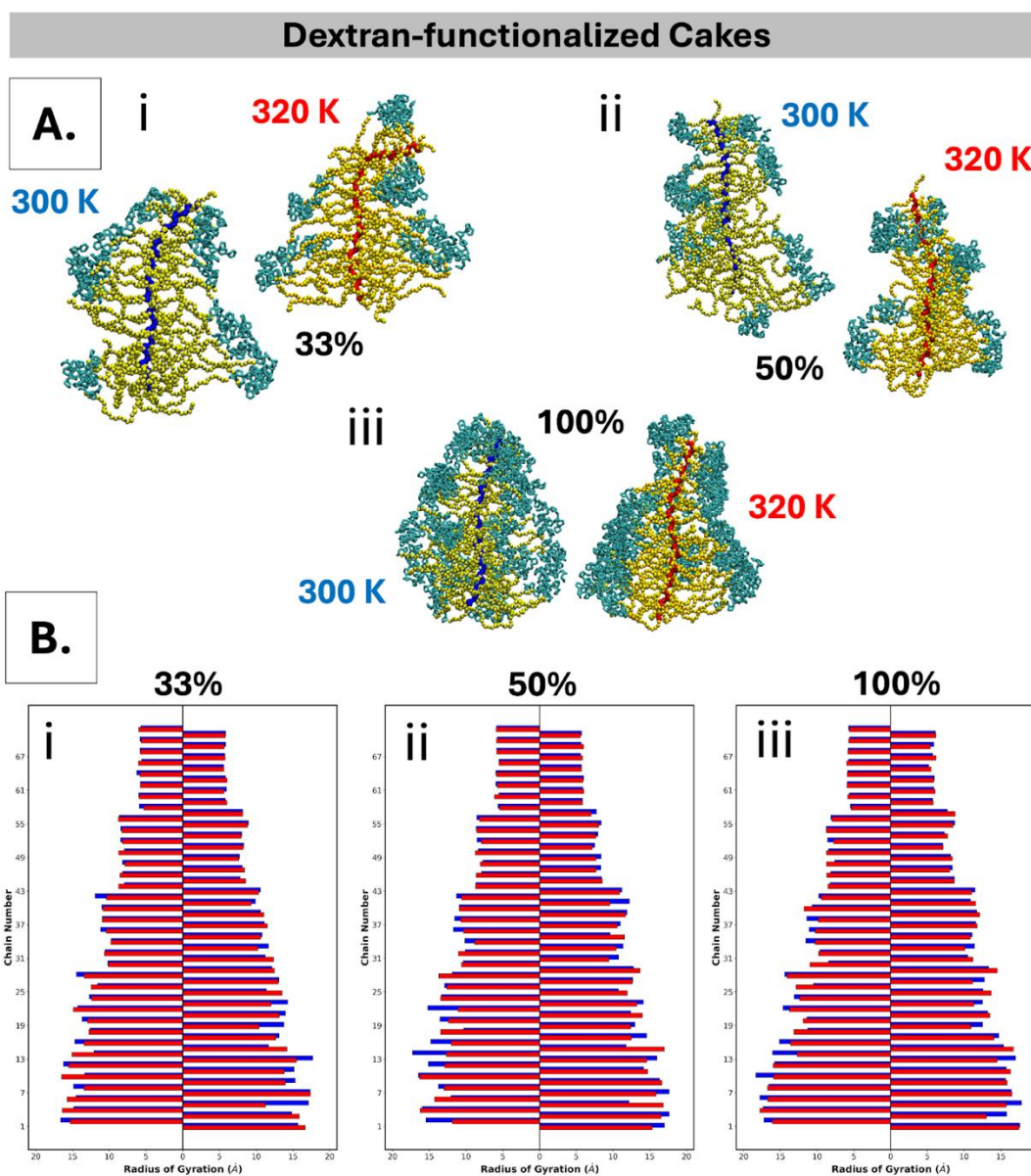


Figure S10: A. Final snapshots showcasing equilibrated i. 33%, ii. 50%, and iii. 100% dextran-functionalized 5-tiered cake-like TS-BBPs after 500 ns simulations. Snapshots at 300 K are presented with a blue BBP backbone and those at 320 K are presented with a red BBP backbone. PNIPAM side chains are presented as yellow spheres. Dextran chains are shown in cyan. B. Mean R_g values for each PNIPAM side chain. Data at 300K is presented in blue whereas that at 320K is presented in red.

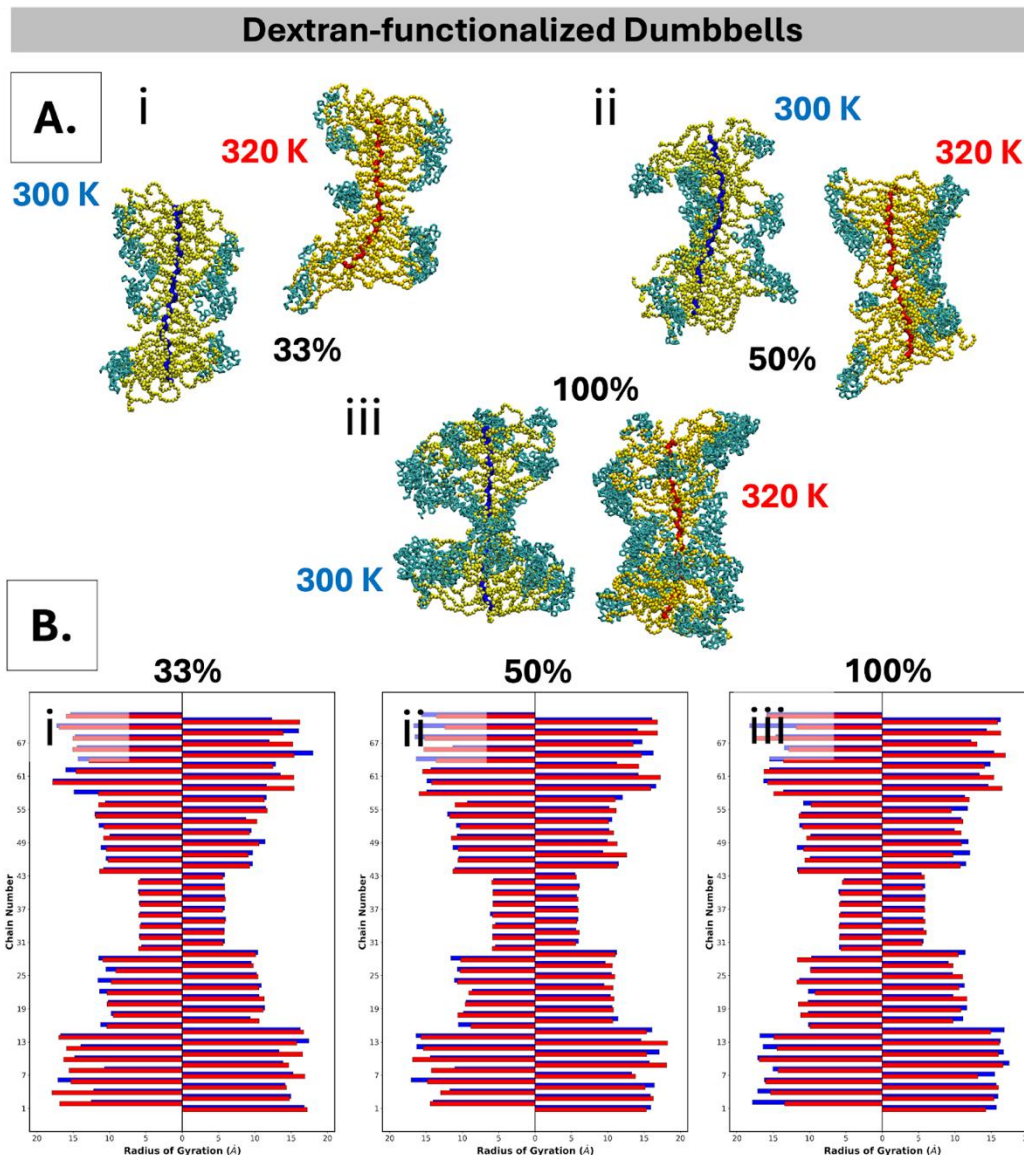


Figure S11: A. Final snapshots showcasing equilibrated i. 33%, ii. 50%, and iii. 100% dextran-functionalized 5-tiered dumbbell-like TS-BBPs after 500 ns simulations. Snapshots at 300 K are presented with a blue BBP backbone and those at 320 K are presented with a red BBP backbone. PNIPAM side chains are presented as yellow spheres. Dextran chains are shown in cyan. B. Mean R_g values for each PNIPAM side chain. Data at 300K is presented in blue whereas that at 320K is presented in red.

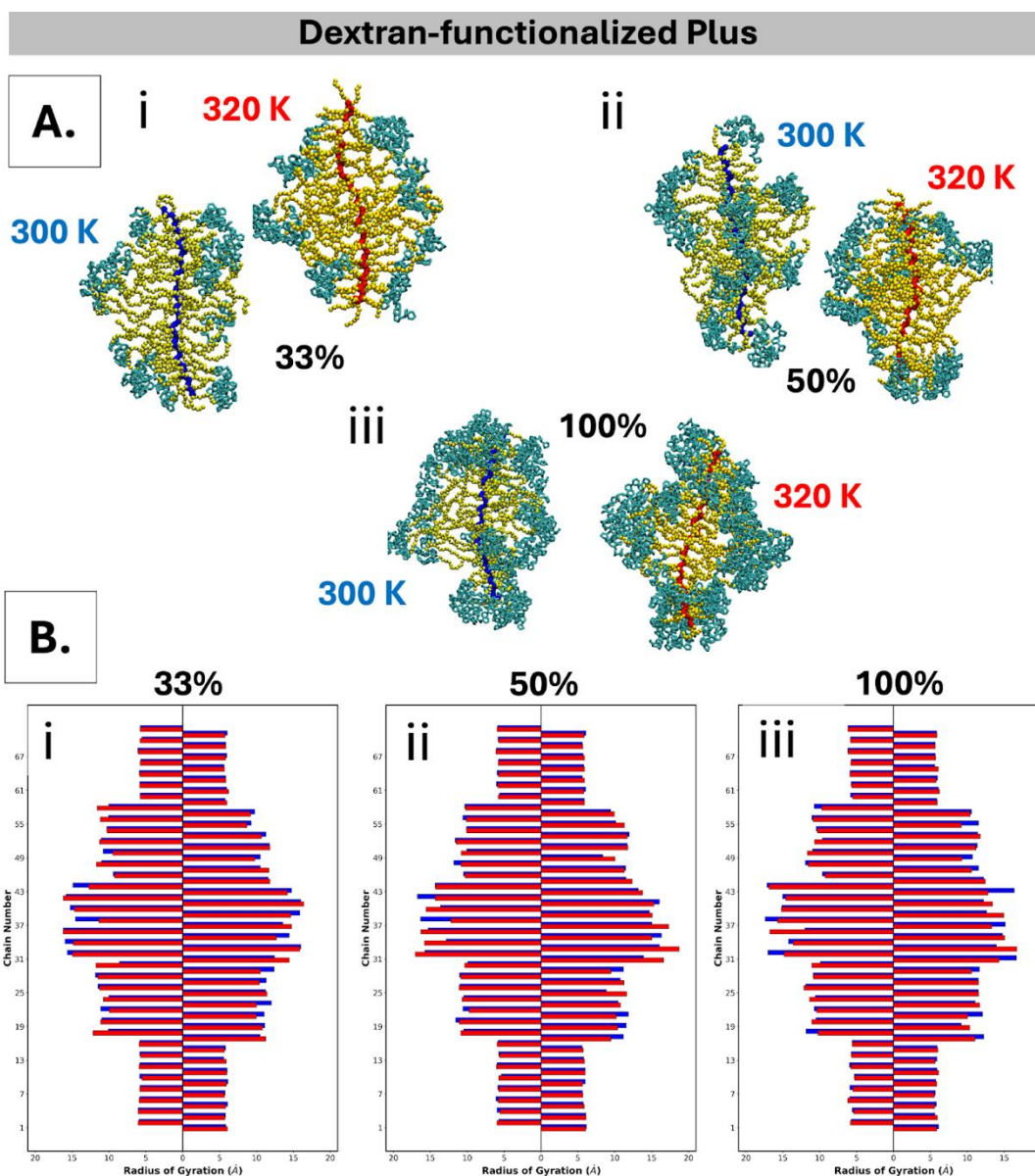


Figure S12: A. Final snapshots showcasing equilibrated i. 33%, ii. 50%, and iii. 100% dextran-functionalized 5-tiered plus-like TS-BBPs after 500 ns simulations. Snapshots at 300 K are presented with a blue BBP backbone and those at 320 K are presented with a red BBP backbone. PNIPAM side chains are presented as yellow spheres. Dextran chains are shown in cyan. B. Mean R_g values for each PNIPAM side chain. Data at 300K is presented in blue whereas that at 320K is presented in red.

Table S2: Conventional analysis data for the functionalized TS-BBPs

	Cakes							
	Dex-0		Dex-33		Dex-50		Dex-100	
	300K	320K	300K	320K	300K	320K	300K	320K
R_g - BB (Å)	33.22 ± 0.5	34.65 ± 0.5	34.94 ± 0.3	33.30 ± 0.3	36.98 ± 0.3	36.15 ± 0.3	36.63 ± 0.2	37.06 ± 0.3
R_g - Full (Å)	37.97 ± 0.3	39.78 ± 1.1	41.27 ± 0.6	39.92 ± 0.2	43.43 ± 0.3	40.54 ± 0.2	42.75 ± 0.2	41.28 ± 0.2
SASA (Å²)	144047 ± 560	145423 ± 630	141534 ± 562	140780 ± 638	139530 ± 522	139440 ± 629	137702 ± 457	136925 ± 568
Asphericity	0.37 ± 0.02	0.41 ± 0.01	0.50 ± 0.01	0.42 ± 0.02	0.54 ± 0.01	0.50 ± 0.02	0.45 ± 0.01	0.44 ± 0.01
Free Volume	306012 ± 12686	330398 ± 42777	359546 ± 20572	324595 ± 25682	370977 ± 19732	295816 ± 15513	432012 ± 11086	365444 ± 15209
No. of Contacts	107.56 ± 1.4	104.85 ± 1.6	104.22 ± 1.4	106.00 ± 1.2	103.69 ± 0.9	106.58 ± 1.1	101.09 ± 0.6	101.70 ± 1.2
	Dumbbells							
	Dex-0		Dex-33		Dex-50		Dex-100	
	300K	320K	300K	320K	300K	320K	300K	320K
R_g - BB (Å)	35.08 ± 0.6	34.02 ± 0.4	37.53 ± 0.2	35.23 ± 0.2	36.64 ± 0.2	36.39 ± 0.2	37.39 ± 0.5	36.97 ± 0.2
R_g - Full (Å)	51.95 ± 0.8	46.16 ± 0.4	50.49 ± 0.3	49.85 ± 0.5	50.16 ± 0.5	49.23 ± 0.3	51.73 ± 0.8	52.33 ± 0.4
SASA (Å²)	167767 ± 439	166563 ± 707	160784 ± 856	161906 ± 573	161732 ± 499	160684 ± 627	157660 ± 574	156339 ± 555
Asphericity	0.60 ± 0.01	0.58 ± 0.02	0.65 ± 0.01	0.62 ± 0.02	0.61 ± 0.01	0.60 ± 0.01	0.60 ± 0.01	0.66 ± 0.01
Free Volume	705959 ± 69055	479842 ± 51466	554346 ± 40451	559168 ± 24652	610352 ± 30643	591235 ± 30528	711643 ± 40860	626344 ± 18028
No. of Contacts	99.53 ± 0.7	103.99 ± 1.6	103.9 ± 1.4	101.20 ± 1.1	100.00 ± 0.7	101.50 ± 0.9	95.67 ± 0.8	97.63 ± 0.7
	Plus							
	Dex-0		Dex-33		Dex-50		Dex-100	
	300K	320K	300K	320K	300K	320K	300K	320K
R_g - BB (Å)	35.16 ± 0.3	34.24 ± 0.3	35.31 ± 0.2	35.97 ± 0.4	36.80 ± 0.3	34.9 ± 0.3	36.64 ± 0.2	36.10 ± 0.3
R_g - Full (Å)	38.11 ± 0.2	36.11 ± 0.2	37.55 ± 0.2	36.69 ± 0.3	37.68 ± 0.2	36.61 ± 0.3	38.39 ± 0.2	37.59 ± 0.2
SASA (Å²)	125659 ± 499	125260 ± 534	120559 ± 423	120720 ± 469	120259 ± 310	119702 ± 651	117379 ± 586	115376 ± 349
Asphericity	0.34 ± 0.01	0.38 ± 0.04	0.44 ± 0.01	0.40 ± 0.02	0.45 ± 0.01	0.40 ± 0.01	0.43 ± 0.01	0.42 ± 0.01
Free Volume	330725 ± 19692	254400 ± 28193	272687 ± 11358	239882 ± 10834	278702 ± 11927	269628 ± 18341	328861 ± 8533	314868 ± 7148
No. of Contacts	104.45 ± 1.3	107.11 ± 1.6	106.69 ± 0.7	107.36 ± 1.1	104.21 ± 0.7	106.65 ± 1.4	101.26 ± 0.9	102.59 ± 1.0

Cakes: Functionalization of cake-shaped TS-BBPs with dextran side chains introduces a complex interplay between compactness, solvation, and structural anisotropy. As the degree of dextran functionalization increases from 0% to 100%, the full R_g generally increases at 300 K, suggesting expansion due to the bulky, hydrophilic dextran groups. Interestingly, the backbone R_g values

show moderate increases with functionalization at 300 K but become more stable or even slightly increase at 320 K, particularly in the 100% dextran system. SASA trends suggest reduced solvent accessibility with higher dextran content, particularly at 100%, where the values drop significantly compared to the unfunctionalized case, possibly due to the shielding of PNIPAM regions by dextran chains. Asphericity increases with dextran content at 300 K, indicating more anisotropic, perhaps elongated conformations, but remains relatively stable at 320 K. Free volume, while initially high in the 33% functionalized system at 320 K (indicating transient structural openness), stabilizes and decreases at higher functionalization levels, pointing to increased compactness as systems equilibrate. Notably, the number of contacts decreases with 33% functionalization, then recovers or slightly increases at higher functionalization levels, suggesting that moderate dextran grafting disrupts intra-BBP interactions while dense grafting may stabilize new compact conformations.

Dumbbells: Dumbbell-shaped BBPs exhibit a distinct structural response to dextran functionalization compared to cakes. At 300 K, increasing dextran content results in higher backbone R_g , suggesting elongation of the backbone due to steric effects of dextran. However, the full R_g remains relatively stable across all functionalization levels, particularly at 320 K, which could imply that dextran's bulk stabilizes the overall polymer size despite chain rearrangements. The SASA steadily decreases with increasing dextran content, especially at 100% functionalization, indicating reduced exposure to solvent and greater shielding of PNIPAM chains. Asphericity remains high and consistent (~ 0.60 - 0.66) across functionalization degrees and temperatures, reflecting the dumbbell's inherent anisotropic structure. Free volume shows a complex, non-linear response: it initially decreases at 33% functionalization, slightly increases at 50%, and peaks again at 100%, indicating dynamic rearrangements in internal packing. Intriguingly, the number of contacts decreases consistently with increasing dextran density, especially at 100% functionalization, pointing to reduced PNIPAM-PNIPAM interactions due to steric hindrance and hydration of dextran. Overall, dumbbell BBPs display a progressive reduction in interchain contacts and solvent exposure with dextran addition, but the overall shape and size

remain relatively consistent, underscoring a robust structural scaffold that tolerates functionalization without drastic collapse.

Plus: Plus-shaped BBPs show a comparatively muted response to dextran functionalization, maintaining structural integrity across a broad range of grafting densities. Backbone R_g increases slightly with functionalization at 300 K but remains stable or shows minimal variation at 320 K. Similarly, full R_g exhibits only modest fluctuations, with values slightly decreasing at intermediate dextran densities but recovering at 100%, especially at 300 K. SASA shows a clear decreasing trend with increasing dextran content, indicating enhanced shielding and decreased polymer-solvent interface, likely due to the outward extension of hydrophilic dextran groups. Asphericity increases slightly at 300 K with functionalization but stabilizes around ~ 0.40 - 0.42 at 320 K, suggesting that the polymers maintain moderately isotropic shapes despite side chain modifications. Free volume follows an initial drop with dextran addition and then increases again at higher functionalization levels, particularly at 100%, possibly due to rearrangement or packing frustration introduced by the uniform grafting of dextran. Interestingly, the number of contacts decreases gradually with functionalization, implying reduced PNIPAM-PNIPAM interactions, though the drop is not as steep as in dumbbells. Collectively, plus-like BBPs exhibit structural resilience to dextran grafting, with subtle modulation of shape and solvation but no drastic conformational changes, making them potentially ideal candidates for functionalized architectures with retained structural consistency.

A comparative analysis of unfunctionalized and functionalized BBPs across the three architectures reveals both universal trends and architecture-specific behaviors. A consistent observation across all shapes is that functionalization with dextran, particularly at 50-100%, generally results in reduced SASA and a lower number of PNIPAM-PNIPAM contacts, indicating shielding effects and disruption of intra-chain interactions due to the bulky, hydrophilic nature of dextran. However, the degree to which these effects manifest varies by shape. Dumbbell BBPs, with their inherently anisotropic and extended morphology, are most sensitive to functionalization, showing substantial reductions in contacts and clear deviations in free volume and R_g trends. In

contrast, plus-shaped BBPs appear structurally robust and display only moderate conformational shifts even at 100% functionalization, highlighting a shape-induced resistance to collapse or distortion. Cake BBPs exhibit intermediate behavior, with a non-monotonic response to dextran density suggesting architectural tuning points where functionalization either stabilizes or disrupts native conformations. Notably, while unfunctionalized BBPs generally become more compact at 320 K due to LCST-driven collapse, highly functionalized systems sometimes display an opposing trend, particularly in dumbbells and cakes, where dextran's aggregation potential or steric hindrance seems to override typical PNIPAM collapse. These nuanced differences underscore the intricate interplay between architecture and functionalization, suggesting that both shape and grafting density must be co-optimized for designing BBPs with tailored responsiveness and structural properties. Viewed across families, these descriptors form a consistent geometric fingerprint. SASA separates the three architectures without overlap across every tier, temperature, and functionalization state in Tables S1 and S2 (Plus $1.15\text{--}1.35 \times 10^5$, Cake $1.37\text{--}1.46 \times 10^5$, and Dumbbell $1.56\text{--}1.79 \times 10^5 \text{ \AA}^2$). Asphericity sets the extended dumbbell architecture apart from the more compact cake and plus architectures but do not reliably resolve cake from plus, whose ranges overlap.

Dextran-functionalized Cakes

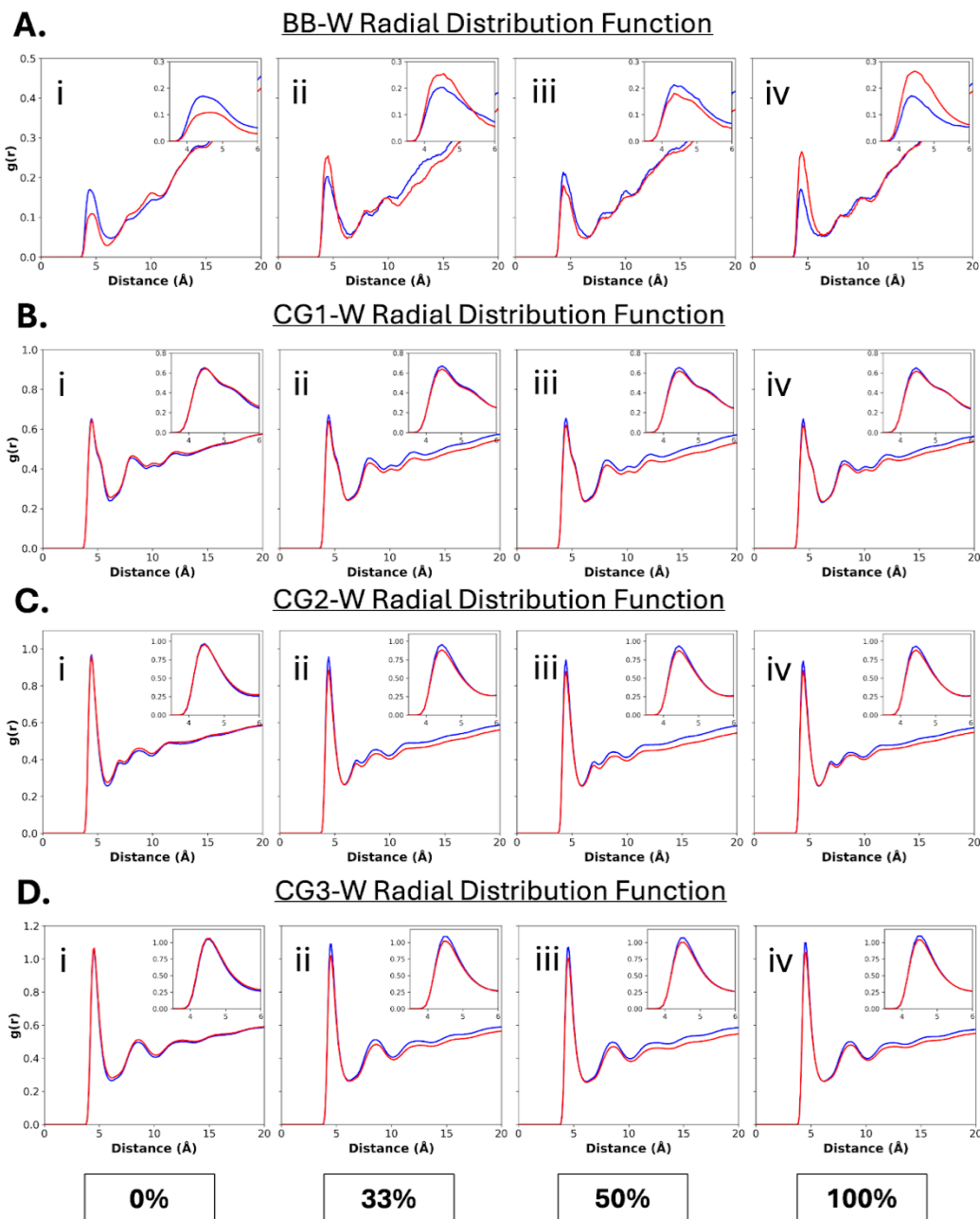


Figure S13: Radial distribution functions (RDFs) of different bead types in dextran functionalized cake-like TS-BBPs with respect to water beads, at 300 K (blue) and 320 K (red). Panels A-D correspond to BB-W, CG1-W, CG2-W, and CG3-W RDFs, respectively. Each panel shows four subplots (i-iv), representing four degrees of functionalization: 0%, 33%, 50%, and 100%, respectively. Inset plots in each subplot magnify the first peak region for clarity.

Dextran-functionalized Dumbbells

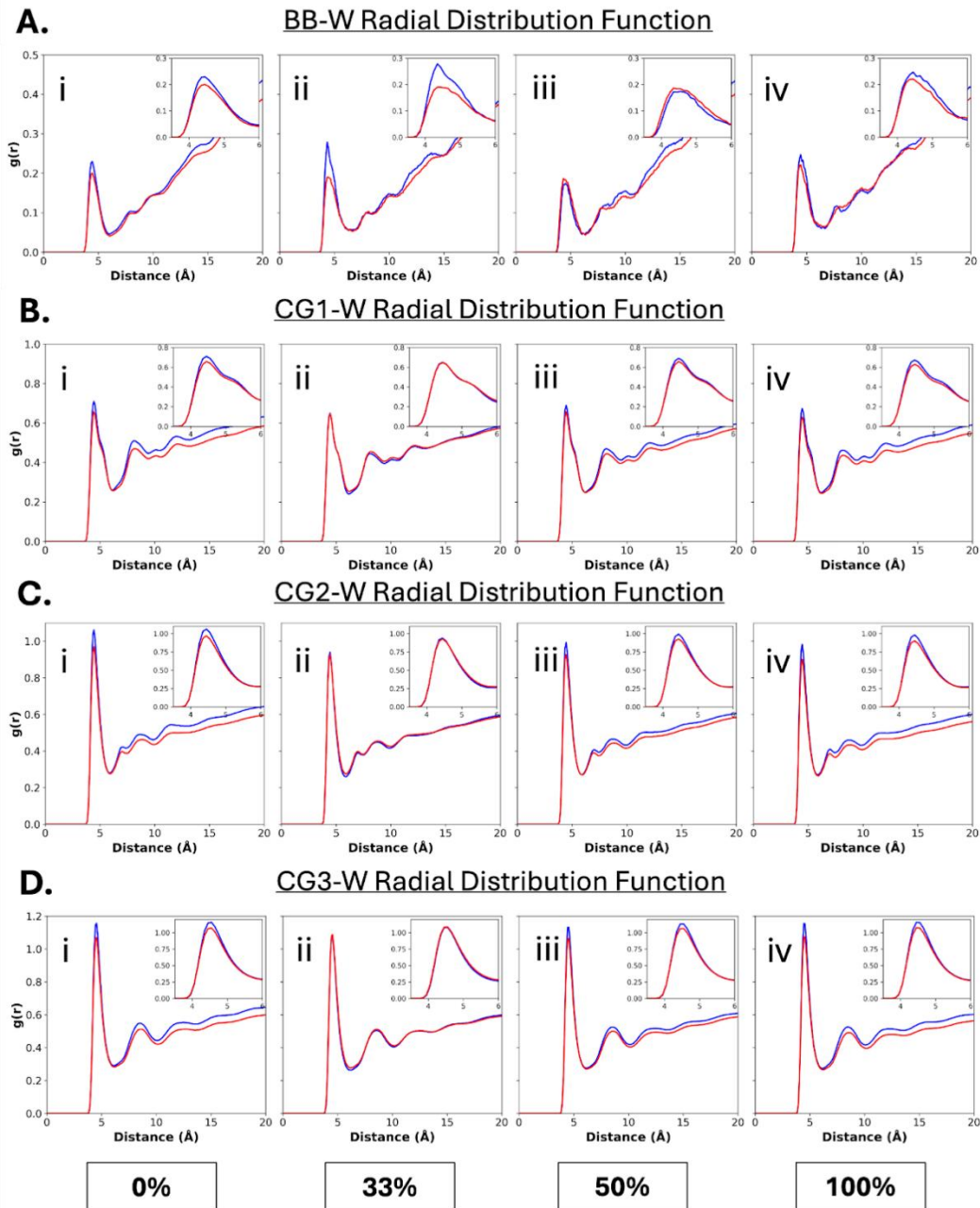


Figure S14: Radial distribution functions (RDFs) of different bead types in dextran functionalized dumbbell-like TS-BBPs with respect to water beads, at 300 K (blue) and 320 K (red). Panels A-D correspond to BB-W, CG1-W, CG2-W, and CG3-W RDFs, respectively. Each panel shows four subplots (i-iv), representing four degrees of functionalization: 0%, 33%, 50%, and 100%, respectively. Inset plots in each subplot magnify the first peak region for clarity.

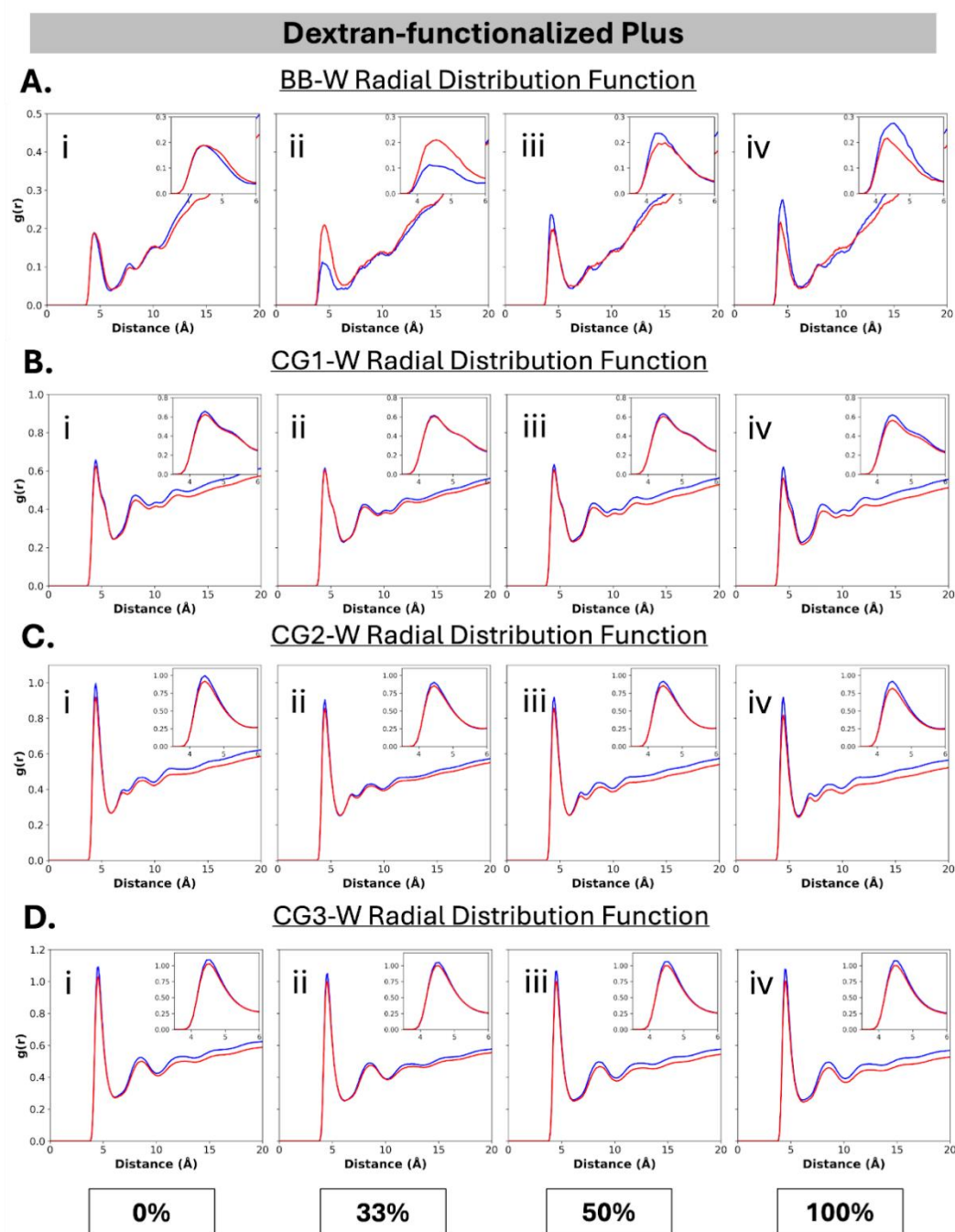


Figure S15: Radial distribution functions (RDFs) of different bead types in dextran functionalized plus-like TS-BBPs with respect to water beads, at 300 K (blue) and 320 K (red). Panels A-D correspond to BB-W, CG1-W, CG2-W, and CG3-W RDFs, respectively. Each panel shows four subplots (i-iv), representing four degrees of functionalization: 0%, 33%, 50%, and 100%, respectively. Inset plots in each subplot magnify the first peak region for clarity.

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