Supporting Information

(Dated: May 29, 2020)

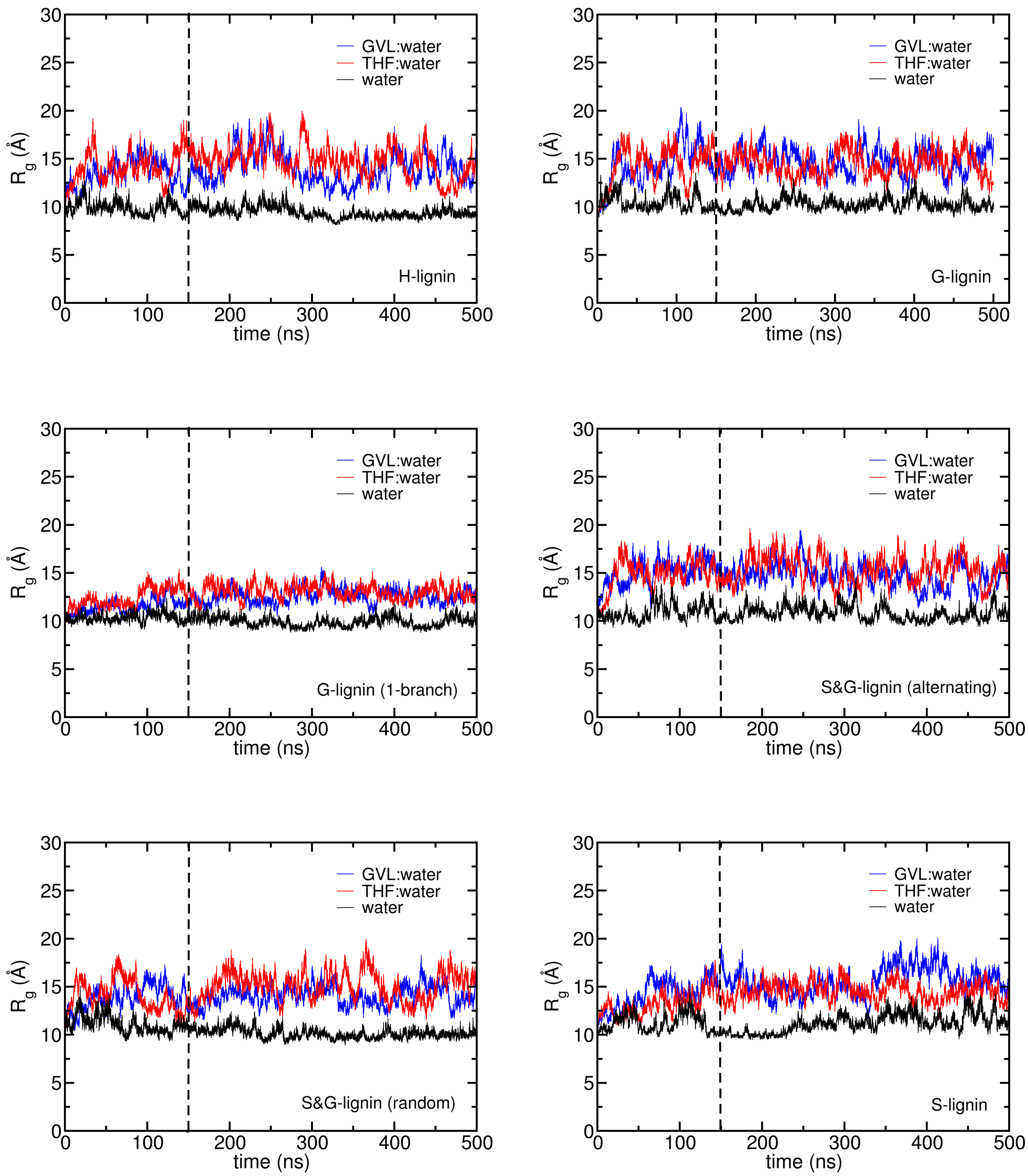


FIG. S-1: The radius of gyration of lignin for each lignin model vs. time. Data is averaged over three different run. After these graphs, we decided to use the trajectories between 150-500 ns.

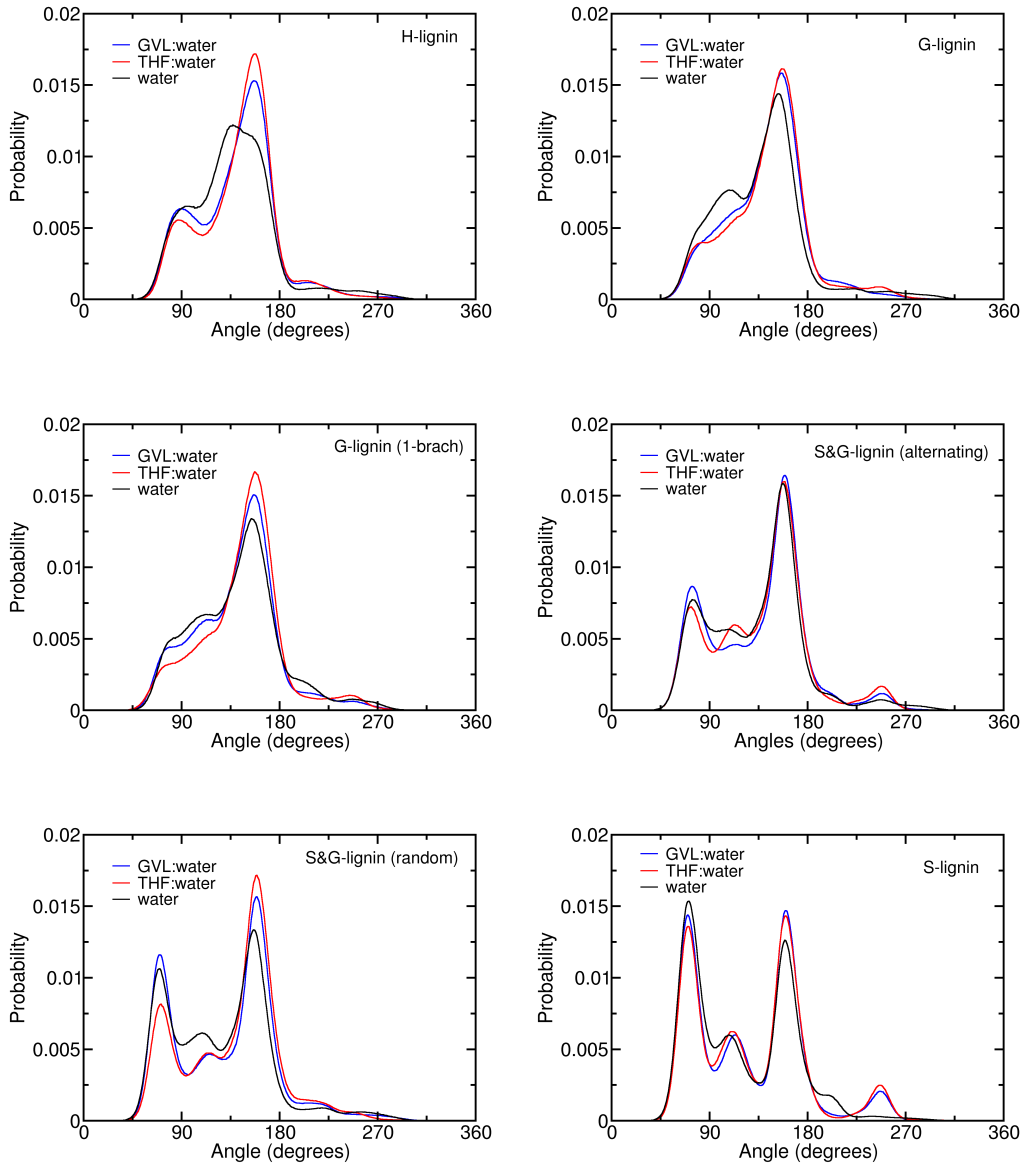
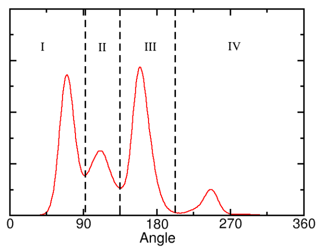


FIG. S-2: The distribution of the $\theta = C_\alpha - C_\beta - O_4 - C_4$ dihedral angles in the $\beta - O - 4$ linkages

TABLE S-1: The populations of Gaussian peaks in the distribution of dihedral angles in Fig. S-2.



		I.region	*II.region*	*III.region*	*IV.region*
		$-0 < \theta < 110$		$110 < \theta < 195$	$195 < \theta < 360$
H-lignin	*water*	0.248		0.695	0.057
	THF:water	0.201		0.747	0.052
	GVL:water	0.234		0.713	0.053
		$0 < \theta < 90$	$90 < \theta < 130$	$130 < \theta < 195$	$195 < \theta < 360$
G-lignin	*water*	0.123	0.291	0.528	0.058
	THF:water	0.098	0.215	0.626	0.061
	GVL:water	0.094	0.239	0.611	0.056
		$0 < \theta < 90$	$90 < \theta < 120$	$120 < \theta < 195$	$195 < \theta < 360$
G-lignin	*water*	0.121	0.189	0.607	0.083
(1-brach)	*THF:water*	0.094	0.137	0.705	0.064
	GVL:water	0.119	0.171	0.648	0.062
		$0 < \theta < 95$	$95 < \theta < 125$	$125 < \theta < 195$	$195 < \theta < 360$
S/G-lignin	*water*	0.238	0.163	0.544	0.055
(alternating)	*THF:water*	0.211	0.16	0.564	0.065
	GVL:water	0.248	0.133	0.56	0.059
		$0 < \theta < 95$	$95 < \theta < 130$	$130 < \theta < 195$	$195 < \theta < 360$
S/G-lignin	*water*	0.305	0.196	0.438	0.061
(random)	*THF:water*	0.222	0.149	0.559	0.07
	GVL:water	0.299	0.145	0.489	0.067
		$0 < \theta < 95$	$95 < \theta < 135$	$135 < \theta < 200$	$200 < \theta < 360$
S-lignin	*water*	0.41	0.184	0.367	0.039
	THF:water	0.34	0.19	0.4	0.07
	GVL:water	0.36	0.18	0.398	0.062

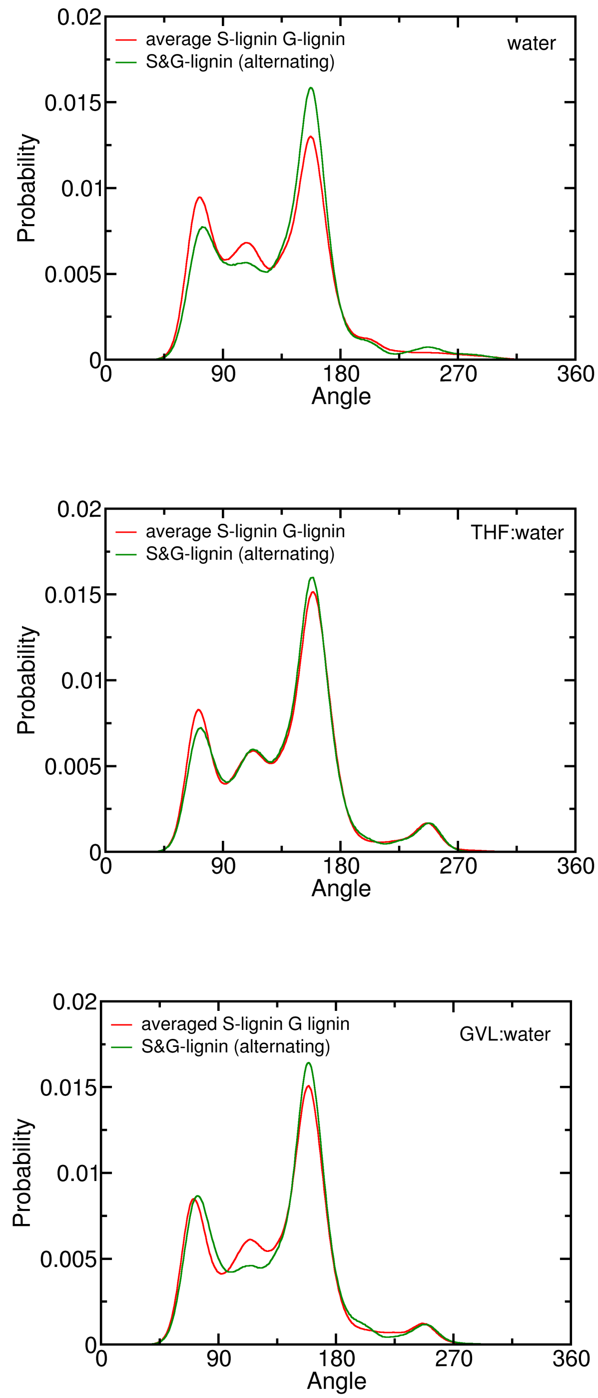


FIG. S-3: The averaged probability of dihedral angles, only β-O-4 linkages, of S and G lignins is compared with the probability of dihedral angles of S&G-lignin (alternating).

TABLE S-2: Fitting parameters obtained from the fits of Eq.(3) to the distribution of the end-to-end distance (see Fig.4)

		L	ν	K
H-lignin	*THF:water*	0.88	0.61	1.07
	GVL:water	0.95	0.564	1.12
G-lignin	*THF:water*	0.96	0.61	1.08
	GVL:water	0.91	0.6	1.09
S-lignin	*THF:water*	0.85	0.61	1.03
	GVL:water	0.86	0.64	1.04

TABLE S-3: Fitting parameters obtained from the fits of $P(R) = A \times (4\pi R^2) \times (\frac{3}{2\pi{<}R{>}^2})^{3/2} \times \exp(-\frac{3R^2}{2{<}R{>}^2})$ to the distribution of the end-to-end distance (see Fig.4)

		A (Å)	$< R >$ (Å)
H-lignin	*THF:water*	10.75	39.84
	GVL:water	10.55	36.24
G-lignin	*THF:water*	10.78	37.17
	GVL:water	10.96	39.71
S-lignin	*THF:water*	10.87	40.49
	GVL:water	11.26	43.57

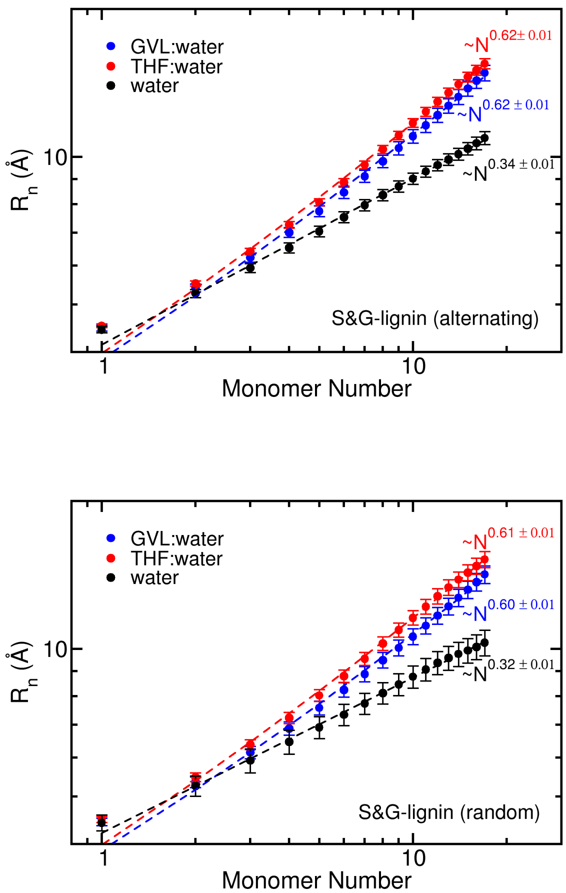


FIG. S-4: The radius of gyration of lignin vs. monomer number.

TABLE S-4: Fitting parameters obtained from the fits of Eq.(4) to the radius of gyration vs. monomer number (see Figs.5 and S-4)

		A	ν	B
H-lignin	*water*	4.329	0.28 ± 0.01	
	THF:water	2.155	0.61 ± 0.01	2.404
	GVL:water	2.175	0.59 ± 0.01	2.37
G-lignin	*water*	4.18	0.32 ± 0.01	
	THF:water	2.218	0.60 ± 0.01	2.35
	GVL:water	2.108	0.61 ± 0.01	2.407
S-lignin	*water*	4.21	0.35 ± 0.01	
	THF:water	2.151	0.60 ± 0.01	2.422
	GVL:water	2.019	0.65 ± 0.01	2.441
S&G-lignin	*water*	4.145	0.34 ± 0.01	
(alternating)	*THF:water*	2.192	0.62 ± 0.01	2.286
	GVL:water	2.079	0.62 ± 0.01	2.456
S&G-lignin	*water*	4.219	0.32 ± 0.01	
(random)	*THF:water*	2.209	0.61 ± 0.01	2.254
	GVL:water	2.084	0.60 ± 0.01	2.474

TABLE S-5: Interaction energies between lignin and the solvent (in kcal/mol) averaged over all the trajectories,

	THF	**GVL**
lignin-cosolvent	-1036 ± 8	-1047 ± 18
lignin-water	-1514 ± 43	-1590 ± 28
Total	-2550 ± 51	-2637 ± 46

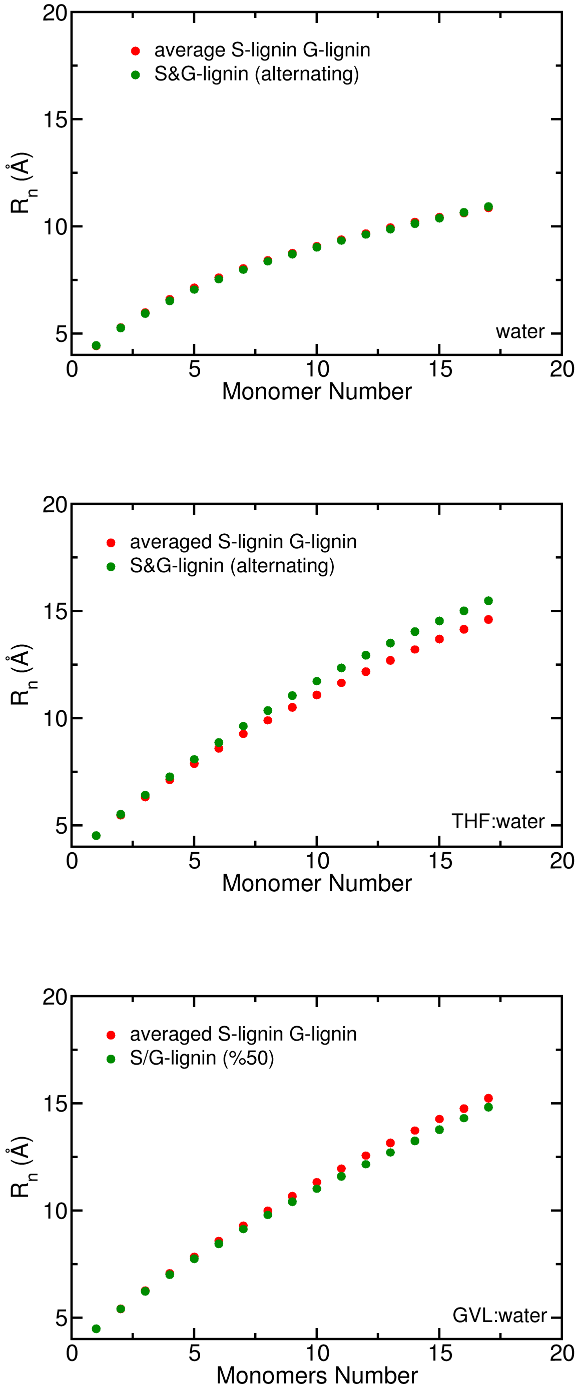


FIG. S-5: The averaged radius of gyration value of S and G lignins vs. monomer number is compared with the radius of gyration of S/G-lignin (alternating).

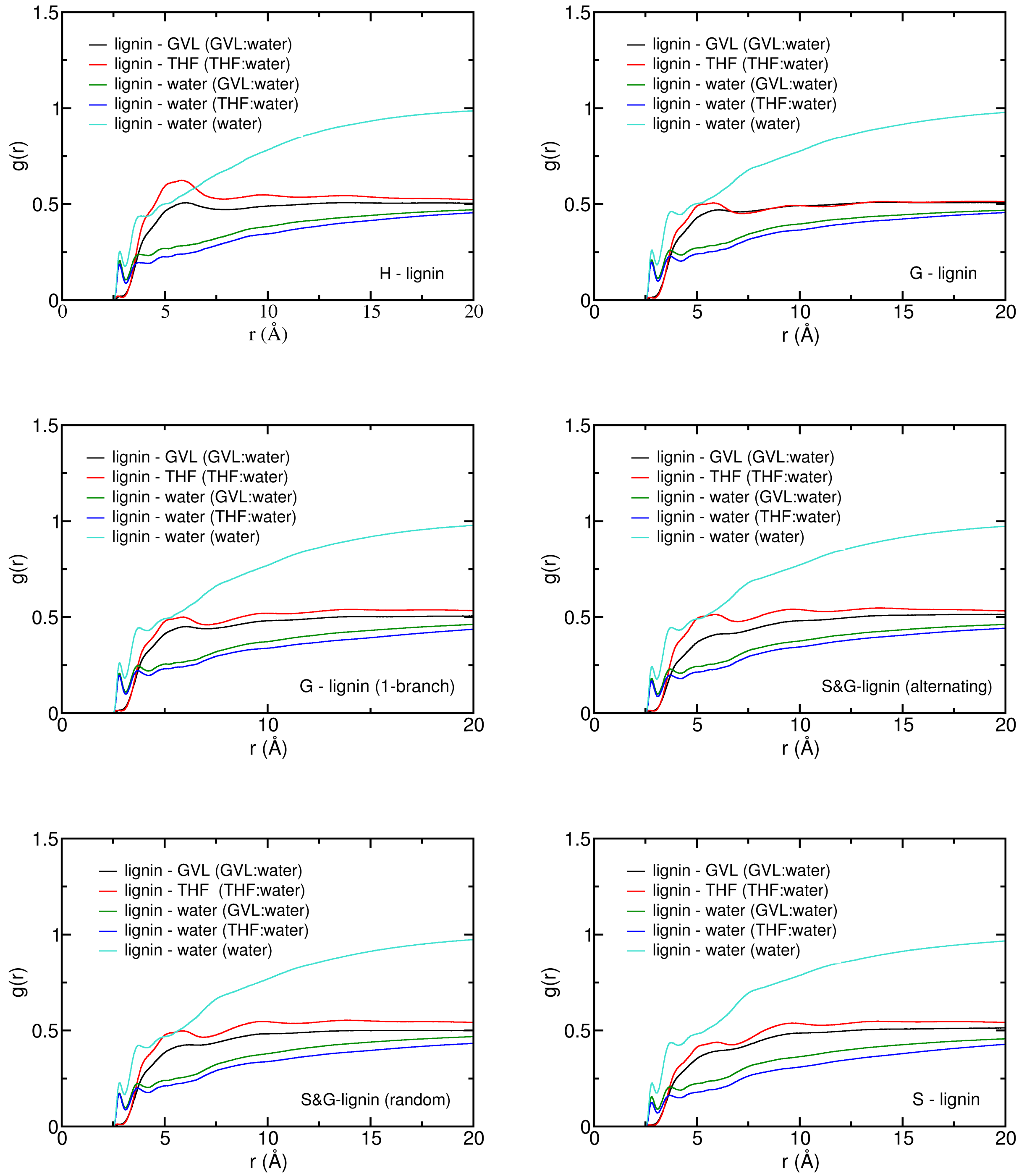


FIG. S-6: The radial distribution of the distance between lignin and water, and between lignin and co-solvents (THF and GVL).

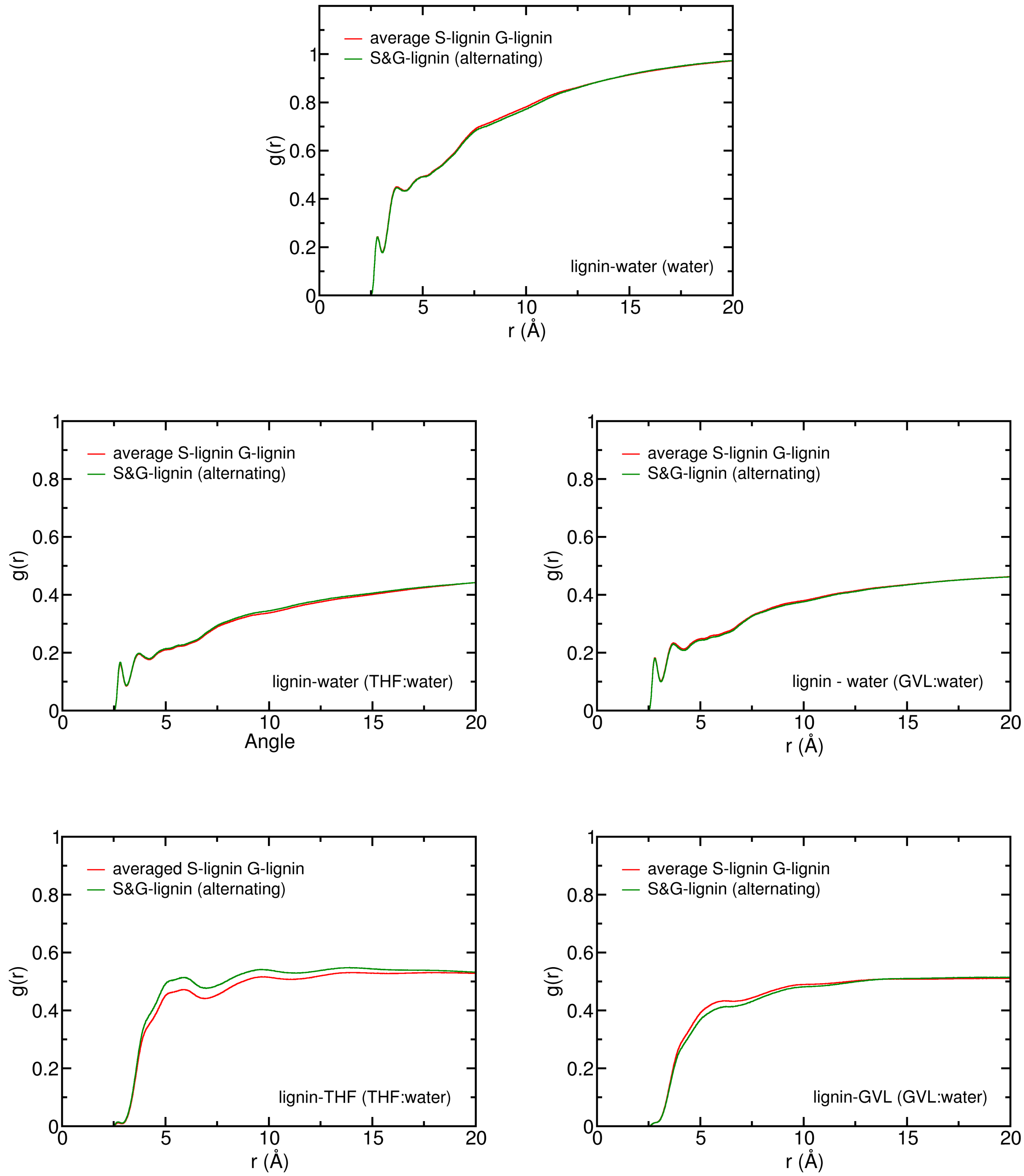


FIG. S-7: The averaged radial distribution function of G- and S-lignin compared to the radial distribution function of S/G-lignin (alternating).

TABLE S-6: H-units with $\beta - O - 4$ linkages

ID	monomers	bond	linkages
1	H		
2	H	1-2	βO4L
3	H	2-3	βO4L
4	H	3-4	βO4L
5	H	4-5	βO4L
6	H	5-6	βO4L
7	H	6-7	βO4R
8	H	7-8	βO4R
9	H	8-9	βO4R
10	H	9-10	βO4R
11	H	10-11	βO4R
12	H	11-12	βO4L
13	H	12-13	βO4R
14	H	13-14	βO4L
15	H	14-15	βO4R
16	H	15-16	βO4L
17	H	16-17	βO4R
18	H	17-18	βO4L

TABLE S-7: G-units with $\beta - O - 4$ linkages (linear)

ID	monomers	bond	linkages
1	G		
2	G	1-2	βO4L
3	G	2-3	βO4L
4	G	3-4	βO4L
5	G	4-5	βO4L
6	G	5-6	βO4L
7	G	6-7	βO4R
8	G	7-8	βO4R
9	G	8-9	βO4R
10	G	9-10	βO4R
11	G	10-11	βO4R
12	G	11-12	βO4L
13	G	12-13	βO4L
14	G	13-14	βO4L
15	G	14-15	βO4L
16	G	15-16	βO4R
17	G	16-17	βO4R
18	G	17-18	βO4R

TABLE S-8: G-units with 16 $\beta - O - 4$ and 1 $5 - 5$ linkages (one branch)

ID	monomers	bond	linkages
1	G		
2	G	1-2	βO4L
3	G	2-3	βO4L
4	G	3-4	βO4L
5	G	4-5	βO4L
6	G	5-6	βO4L
7	G	6-7	βO4R
8	G	7-8	5-5
9	G	8-9	βO4R
10	G	9-10	βO4R
11	G	10-11	βO4R
12	G	11-12	βO4R
13	G	7-13	βO4L
14	G	13-14	βO4L
15	G	14-15	βO4L
16	G	15-16	βO4R
17	G	16-17	βO4R
18	G	17-18	βO4R

TABLE S-9: 50% S and 50% G with $\beta - O - 4$ linkages (alternating)

ID	monomers	bond	linkages
1	G		
2	S	1-2	βO4L
3	G	2-3	βO4L
4	S	3-4	βO4L
5	G	4-5	βO4L
6	S	5-6	βO4L
7	G	6-7	βO4R
8	S	7-8	βO4L
9	G	8-9	βO4L
10	S	9-10	βO4R
11	G	10-11	βO4R
12	S	11-12	βO4R
13	G	12-13	βO4R
14	S	13-14	βO4R
15	G	14-15	βO4R
16	S	15-16	βO4L
17	G	16-17	βO4R
18	S	17-18	βO4R

TABLE S-10: 50% S and 50% G with 15 $\beta - O - 4$ (88%) and 2 $\beta - 5$ (12%) linkages (random)

ID	monomers	bond	linkages
1	G		
2	G	1-2	βO4L
3	G	2-3	βO4L
4	S	3-4	βO4L
5	S	4-5	βO4L
6	S	5-6	βO4L
7	S	6-7	βO4R
8	G	7-8	β5R
9	G	8-9	βO4R
10	S	9-10	βO4R
11	S	10-11	βO4R
12	G	11-12	β5L
13	G	12-13	βO4L
14	S	13-14	βO4L
15	G	14-15	βO4L
16	S	15-16	βO4R
17	G	16-17	βO4R
18	S	17-18	βO4R

TABLE S-11: S-units with $\beta - O - 4$ linkages

ID	monomers	bond	linkages
1	S		
2	S	1-2	βO4L
3	S	2-3	βO4R
4	S	3-4	βO4R
5	S	4-5	βO4L
6	S	5-6	βO4L
7	S	6-7	βO4R
8	S	7-8	βO4R
9	S	8-9	βO4R
10	S	9-10	βO4R
11	S	10-11	βO4L
12	S	11-12	βO4L
13	S	12-13	βO4R
14	S	13-14	βO4L
15	S	14-15	βO4R
16	S	15-16	βO4L
17	S	16-17	βO4L
18	S	17-18	βO4L