Supplementary Material

Table 1 Mean values of the Cremer–Pople puckering parameters for each pyranose ring at the reducing and non-reducing ends of each disaccharide (CH, C4S, C6S, and HA). The mean value of the third puckering parameter, ϕ_{CP}, is not included because it was uniformly distributed in each case. $\theta_{CP} = 0^{o}$ indicates a $^{4}C_{1}$ chair conformation (Cremer and Pople, 1975) and the absence of error estimates indicates that the estimated error was less than the smallest significant figure shown.

		At Reducing Terminus		**At Non-reducing Terminus**	
		$\langle Q_{CP} \rangle$ (Å)	$\langle \theta_{CP} \rangle$ (˚)	$\langle Q_{CP} \rangle$ (Å)	$\langle \theta_{CP} \rangle$ (˚)
CH	**GlcUA**	0.58	8.6 ± 0.3	0.57	8.8 ± 0.2
	GalNAc	0.57	8.7 ± 0.4	0.58	8.2 ± 0.4
C4S	**GlcUA**	0.58	8.6 ± 0.2	0.57	8.8 ± 0.3
	GalNac4S	0.58	8.1 ± 0.6	0.58	8.0 ± 0.2
C6S	**GlcUA**	0.58	8.6 ± 0.4	0.57	8.7 ± 0.3
	GalNac6S	0.57	9.1 ± 0.5	0.58	8.2 ± 0.5
HA	**GlcUA**	0.58	8.7 ± 0.4	0.57	8.6 ± 0.3
	GlcNAc	0.58	8.4 ± 0.3	0.57	8.7 ± 0.3

Table 2 Coarse-grained model bond lengths, b, valence angles, θ, and torsion angles, ν. A prime denotes that the atom belongs to the reducing sugar terminus. ϕ and ψ denote the glycosidic torsion angles, the only flexible internal degrees of freedom present in the model. V_Q denotes the center of charge site used to model electrostatic interactions between charged monosaccharide units and V_G denotes the center of geometry (repulsive Lennard-Jones site) used to model steric interactions between non-adjacent monosaccharides.

Internal Coordinate (Å or degrees)	**GlcUA** $J = 4$, $I = 3$	**GlcNAc** $J = 3$, $I = 4$	**GalNAc** $J = 3$, $I = 4$	**GalNAc4S** $J = 3$, $I = 4$	**GalNAc6S** $J = 3$, $I = 4$
b(O1'–CJ')	1.42	1.42	1.42	1.42	1.42
b(CJ'–C1')	2.89	2.52	2.52	2.52	2.53
b(C1'–O1')	1.41	1.41	1.41	1.41	1.41
b(C1'–V_G')	1.69	1.51	1.37	1.72	1.48
b(C1'–V_Q')	3.31	*na*	*na*	5.78	5.90
θ(C1–O1–CJ')	117.5	117.7	117.6	117.2	117.7
θ(O1–CJ'–C1')	147.8	144.0	145.1	144.4	145.0
θ(CJ'–C1'–O1')	148.4	144.6	144.4	144.4	144.2
θ(CJ'–C1'–V_G')	6.1	7.2	10.0	19.4	26.3
θ(CJ'–C1'–V_Q')	42.8	*na*	*na*	53.0	86.3
ϕ(CI–C1–O1–CJ')	–173.2	–110.9	–111.1	–112.2	–111.8
ψ(C1–O1–CJ'–C1')	–179.6	–123.2	–142.6	–137.0	–145.9
ν(O1–CJ'–C1'–O1')	171.4	2.0	–1.7	–0.9	–1.6
ν(O1–CJ'–C1'–V_G')	–76.7	–84.9	–31.8	–74.7	–113.4
ν(O1–CJ'–C1'–V_Q')	93.5	*na*	*na*	–73.9	–116.4

Glycosidic Linkage PMFs

The glycosidic linkage PMFs, $F_{kl}^{B}(\phi,\psi)$, computed from the all-atom disaccharide simulations are provided in tabulated form. The PMFs correspond to the virtual bond definition of the glycosidic linkage torsion angles (see **Topology** section and Table 2). In discretized form, the PMFs are given by, $F_{kl}^{B}(\phi_i,\psi_j)$, where $\phi_i = -180 + \frac{\Delta\phi}{2} + i\Delta\phi$, $\psi_j = -180 + \frac{\Delta\psi}{2} + j\Delta\psi$, and using angle increments of $\Delta\phi = \Delta\psi = 10$ degrees, (i and j = 0, 1, …, 35). Rows and columns in the files correspond to the ϕ and ψ degrees of freedom, respectively.

PMF filenames:

$F_{kl}^{B}(\phi,\psi)$	**Glycosidic Linkage Type**	**Filename**
$F_{AB}^{B}(\phi,\psi)$	CH β1,3	pmf_ch_b13.txt
$F_{BA}^{B}(\phi,\psi)$	CH β1,4	pmf_ch_b14.txt
$F_{AC}^{B}(\phi,\psi)$	C4S β1,3	pmf_c4s_b13.txt
$F_{CA}^{B}(\phi,\psi)$	C4S β1,4	pmf_c4s_b14.txt
$F_{AD}^{B}(\phi,\psi)$	C6S β1,3	pmf_c6s_b13.txt
$F_{DA}^{B}(\phi,\psi)$	C6S β1,4	pmf_c6s_b14.txt
$F_{AE}^{B}(\phi,\psi)$	HA β1,3	pmf_ha_b13.txt
$F_{EA}^{B}(\phi,\psi)$	HA β1,4	pmf_ha_b14.txt