Electronic Supplementary Information

Analyst

Tandem mass spectrometry and ion Mobility mass spectrometry for the analysis of molecular sequence and architecture of hyperbranched glycopolymers

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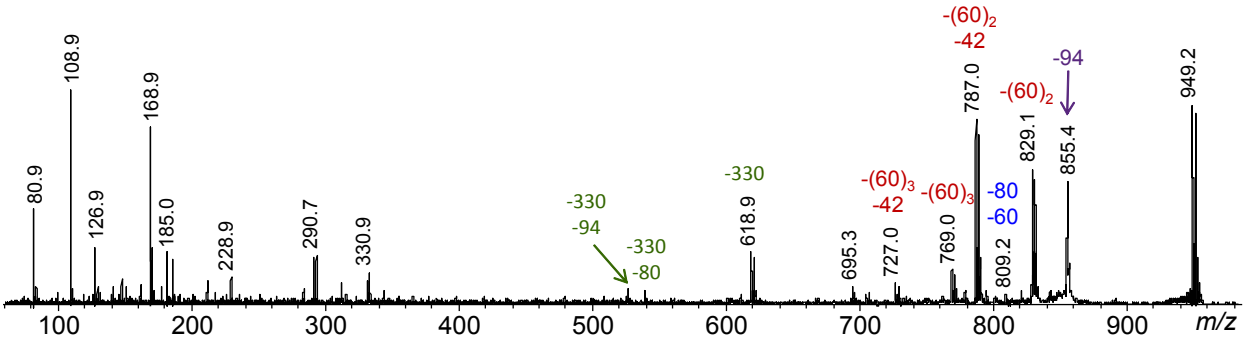

Fig. S1. MALDI-MS^2 mass spectrum of sodiated A_1B_1 (*m/z* 949.2); the numbers on top of the peaks give monoisotopic *m/z* ratios (in black) and the mass of the neutral loss(es) in Da (in color). This spectrum was acquired using MALDI-ToF/ToF instrumentation, with which the entire isotope cluster of the precursor ion is mass-selected. The $[M + Na]^+$ ion of A_1B_1 contains one Br atom; fragments containing the Br atom are clearly discernible from the corresponding isotope pattern.

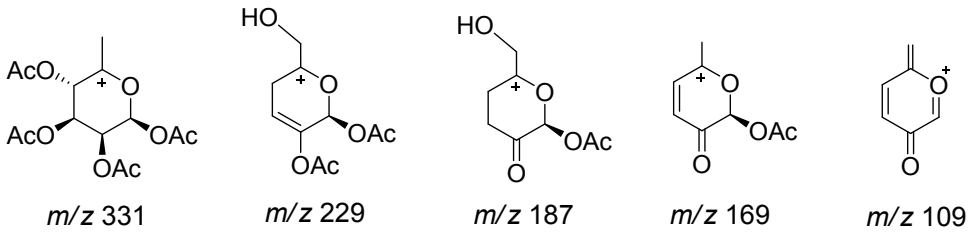

Fig. S2. Plausible fragments from the mannose pendants of sodiated glycopolymer n-mers, which dominate in the low mass region of the MALDI-MS^2 spectra.

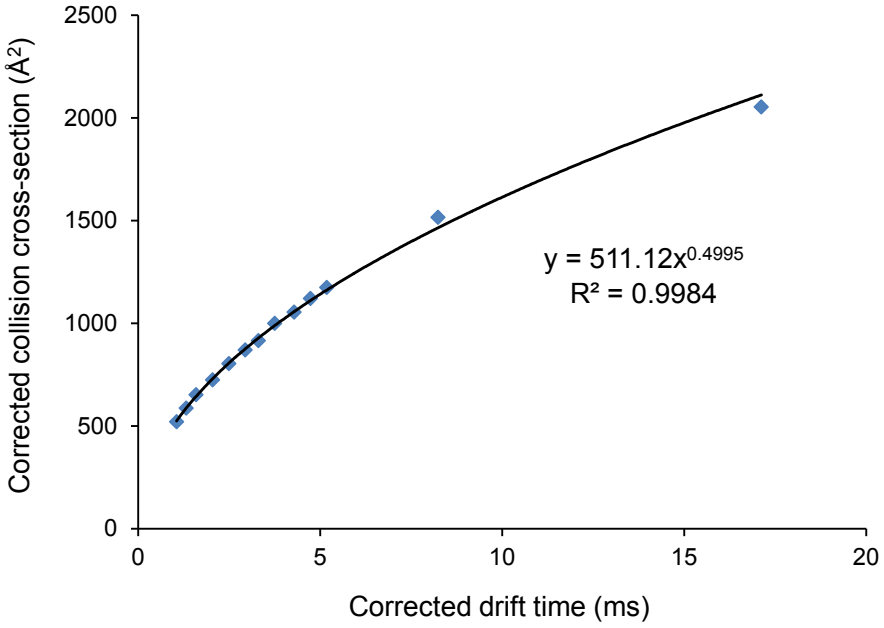

Fig. S3. Plot of corrected collision cross-section (CCS') *vs.* corrected drift time (t'_d) for the calibrant ions. Corrected drift times and corrected collision cross-sections were calculated from the drift times measured for the calibrant ions under the IM-MS conditions used for the glycopolymer (t_d) and from the reported collision cross-sections of the calibrant ions (CCS),[1] respectively (see Table S1).[2-5] The calibration curve renders a corrected collision cross-section of 1716.8 Å^2 for the glycopolymer tetramer A_2B_2 (t_d = 11.37 ms; t'_d = 11.309 ms). The actual CCS obtained from this value *via* the equation CCS = CCS' x ($z/\mu^{0.5}$) is 327 Å^2 (z is the ion charge and μ is the reduced mass of the ion/drift gas complex). The combined error introduced by the calibration procedure, the uncertainty in the calibrant CCS values and the reproducibility of our drift time measurements is ± <4%.[5]

Table S1. Drift times and reported collision cross-sections of the calibrant ions.

Calibrant ion	charge	*m/z*	t_d (ms) [d]	t'_d (ms) [e]	CCS (Å^2) [f]	Reduced mass, μ [g]	CCS' (Å^2) [h]
$(Ala)_4$ [a]	1	303.17	1.08	1.06	102.9	5.06	521.05
$(Ala)_5$ [a]	1	374.20	1.35	1.32	115.0	5.10	587.06
$(Ala)_6$ [a]	1	445.24	1.62	1.59	127.0	5.13	651.95
$(Ala)_7$ [a]	1	516.28	2.08	2.05	140.5	5.15	724.20
$(Ala)_8$ [a]	1	587.32	2.53	2.50	155.5	5.17	804.03
$(Ala)_9$ [a]	1	658.35	2.98	2.94	167.9	5.18	870.28
$(Ala)_{10}$ [a]	1	729.39	3.34	3.30	176.3	5.19	915.64
$(Ala)_{11}$ [a]	1	800.43	3.79	3.75	192.2	5.20	999.86
$(Ala)_{12}$ [a]	1	871.46	4.33	4.29	202.4	5.21	1054.38
$(Ala)_{13}$ [a]	1	942.50	4.78	4.74	214.9	5.22	1120.81
$(Ala)_{14}$ [a]	1	1013.54	5.23	5.19	224.9	5.22	1174.16
Insulin chain A [b]	1	2530.52	17.19	17.12	390.0	5.26	2052.73
Cytochrome C [c]	7	1766.7	8.30	8.24	2007.0	5.29	1515.40

[a] $[M + H]^+$ ions of polyalanine oligomers with the structure $H–[HNCH(CH_3)CO]_n–OH$.

[b] $[M + H]^+$ of insulin chain A oxidized ammonium salt from bovine pancreas (Sigma-Aldrich).

[c] $[M + 7H]^{7+}$ of equine cytochrome C (Sigma-Aldrich).

[d] Using a traveling wave velocity of 350 m/s, a traveling wave height of 10.5 V and a drift gas (N_2) flow rate of 22.7 mL/min.

[e] $t'_d = t_d – [C \times (m/z)^{0.5}/1000]$ (C = 1.41 is a correction factor for instrumental flight time effects.

[f] From ref. 1.

[g] $\mu = [m(ion) \times mass(drift\ gas)] / [mass(ion) + mass(drift\ gas)]$.

[h] $CCS' = CCS \times (\mu^{0.5}/z)$, where z is the ion charge.

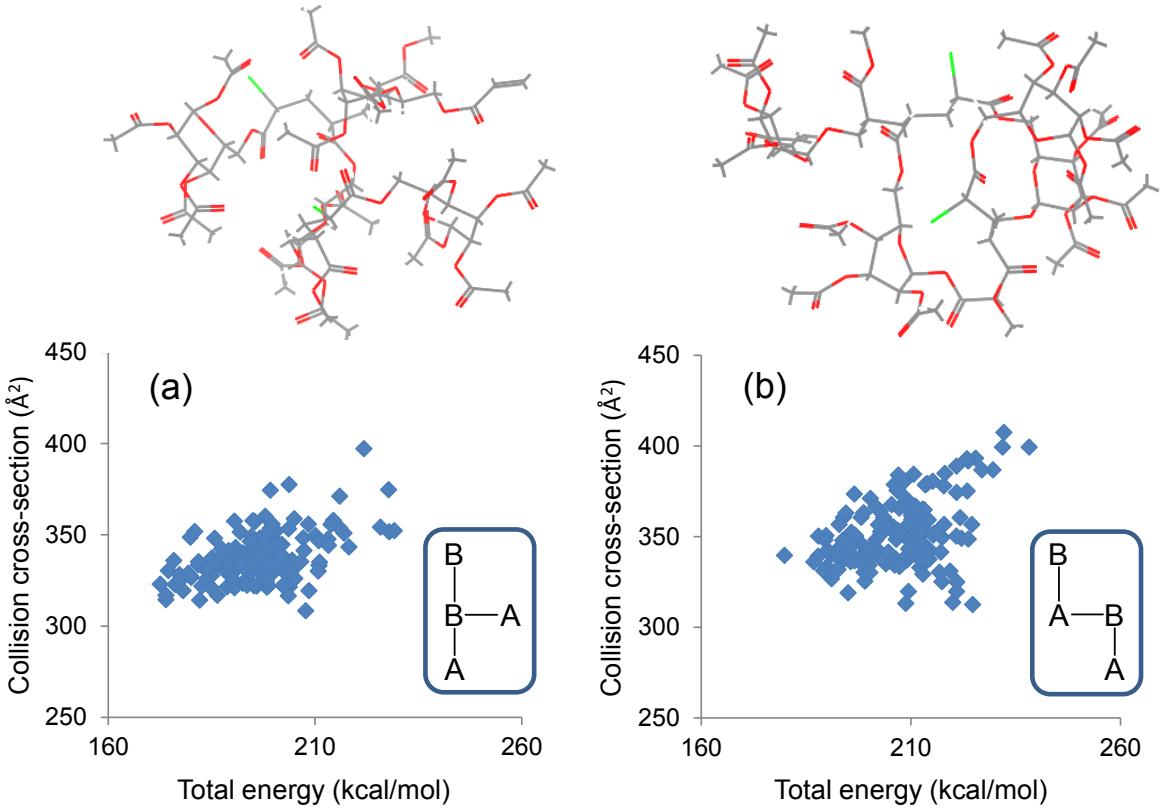

Fig. S4. Plot of collision cross-section (CCS) *vs.* total energy for 150 energy-minimized structures of the glycopolymer 4-mers with the sequence (a) B(B)A_2 and (b) B(A)B(A); representative structures are shown on top of the plots: C is grey, H is white, O is red, and Br is green. The standard deviation of an individual point is (a) 14.1 Å^2 for the B(B)A_2 structures and (b) 18.7 Å^2 for the B(A)B(A) structures. The mean collision cross-section of all 150 structures (and the corresponding mean standard deviation) is (a) 338 (1) Å^2 for B(B)A_2 and (b) 352 (2) Å^2 for B(A)B(A).

References

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