### **Supplementary Materials**

## The first synthesis of periodic and alternating glycopolymers by RAFT polymerization: A novel synthetic pathway for glycosaminoglycan mimics

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1. <sup>1</sup>H and <sup>13</sup>C NMR spectra of vinyl monomers (MalVE, LacVE and MalMI)

**Fig. S1-1**. <sup>1</sup>H NMR spectrum of **MalVE** in D<sub>2</sub>O (x and \*; remaining solvents).



Fig. S1-2. <sup>13</sup>C NMR spectrum of MalVE in D<sub>2</sub>O.



Fig. S1-3. <sup>1</sup>H NMR spectrum of LacVE in D<sub>2</sub>O (x; remaining solvent).



Fig. S1-4. <sup>13</sup>C NMR spectrum of LacVE in D<sub>2</sub>O.



**Fig. S1-5**. <sup>1</sup>H NMR spectrum of **MalMI** in D<sub>2</sub>O (x; remaining solvent).



Fig. S1-6. <sup>13</sup>C NMR spectrum of MalMI in D<sub>2</sub>O.

# 2. Comparison of copolymerization of MalVE and EtMI with and without RAFT agent



**Fig. S2**. SEC curves of poly(MalVE-*co*-EtMI) obtained in the radical copolymerization (a) without and (b) with RAFT agent using  $0.2 \text{ mol } L^{-1} \text{ NaNO}_3$  aq. as the eluent.



Scheme S1. Schematics of radical copolymerization of MalVE (M1) and EtMI (M2).

#### 3. RAFT copolymerization of LacVE and EtMI.



**Fig. S3**. Time-conversion curves for the RAFT copolymerization of LacVE and EtMI with BTSE.



Fig. S4. Experimentally observed  $M_n$  and  $M_w/M_n$  value of poly(LacVE-*co*-EtMI) plotted against theoretical  $M_n$  of poly(LacVE-*co*-EtMI). Filled circles and squares correspond to the  $M_n$  data obtained by <sup>1</sup>H NMR and SEC, respectively.

### 4. RAFT copolymerization of LacVE and MalMI.



**Fig. S5**. Time-conversion curves for the RAFT copolymerization of LacVE and MalMI with BTSE.



**Fig. S6**. SEC curves of poly(LacVE-*co*-MalMI) using 0.2 mol L<sup>-1</sup> NaNO<sub>3</sub> aq. as the eluent.

5. Lectin binding assay



**Fig. S7**. Photography of (a) poly(MalVE-*co*-EtMI) and (b) poly(LacVE-*co*-EtMI) solution before and after the addition of FITC-unlabeled Con A or PNA.