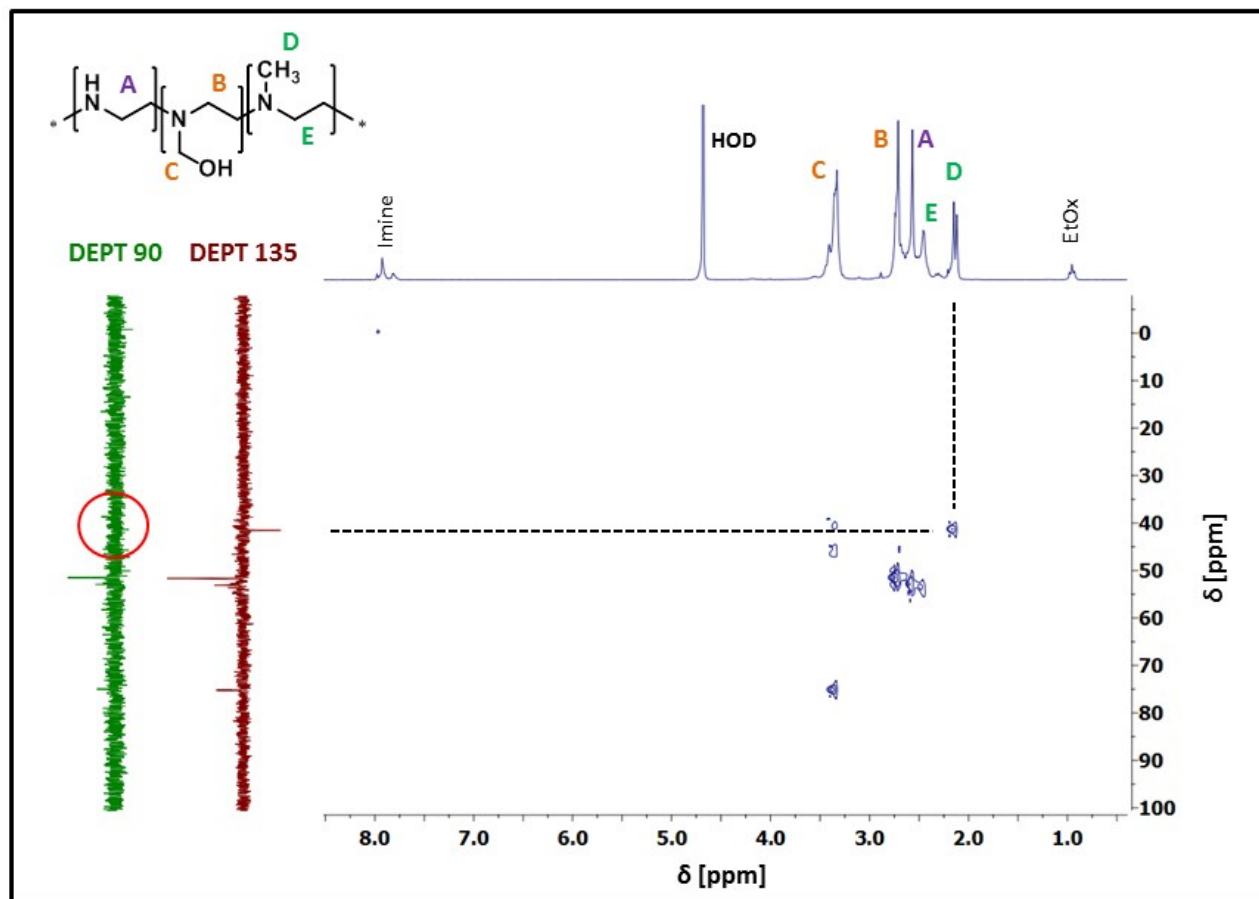


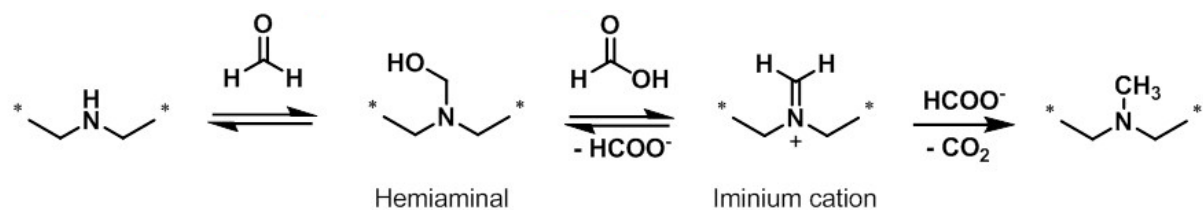
## SUPPORTING INFORMATION

### Facile Carbohydrate-Mimetic Modifications of Poly(ethylene imine) Carriers for Gene Delivery Applications

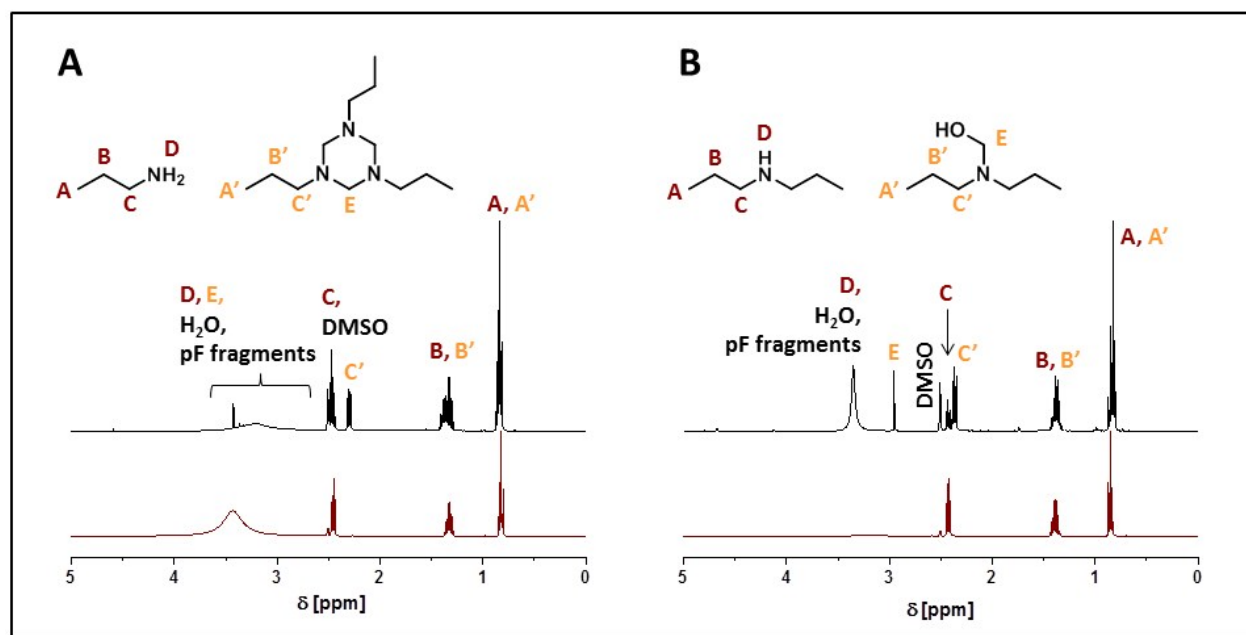
Christoph Englert,<sup>a,b,c</sup> Mareva Fevre,<sup>a</sup> Rudy J. Wojtecki,<sup>a</sup> Wei Cheng,<sup>d</sup> Qingxing Xu,<sup>d</sup> Chuan Yang,<sup>d</sup> Xiyu Ke,<sup>d</sup> Matthias Hartlieb,<sup>b,c,#</sup> Kristian Kempe,<sup>b,c,#</sup> Jeannette M. Garcia,<sup>a</sup> Robert J. Ono,<sup>a</sup> Ulrich S. Schubert,<sup>b,c,\*</sup> Yi Yan Yang,<sup>d,\*</sup> James L. Hedrick<sup>a,\*</sup>



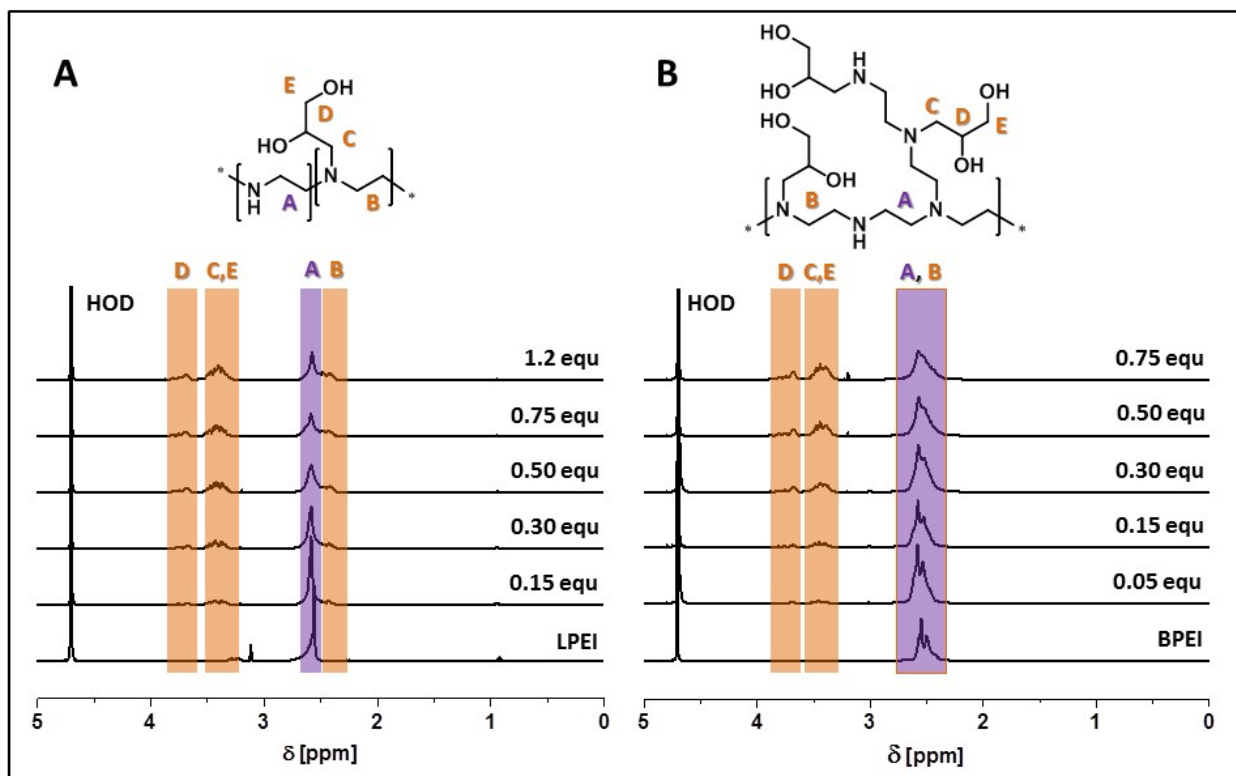
**Figure S1.** HSQC-DEPT-NMR spectra of L4 (0.75 equiv. formaldehyde). The appearance of a negative signal in the DEPT 135 experiment that disappears in DEPT 90 indicated the presence of a N-CH<sub>3</sub> group and, therefore, the methylation of LPEI (D<sub>2</sub>O, 400 MHz).



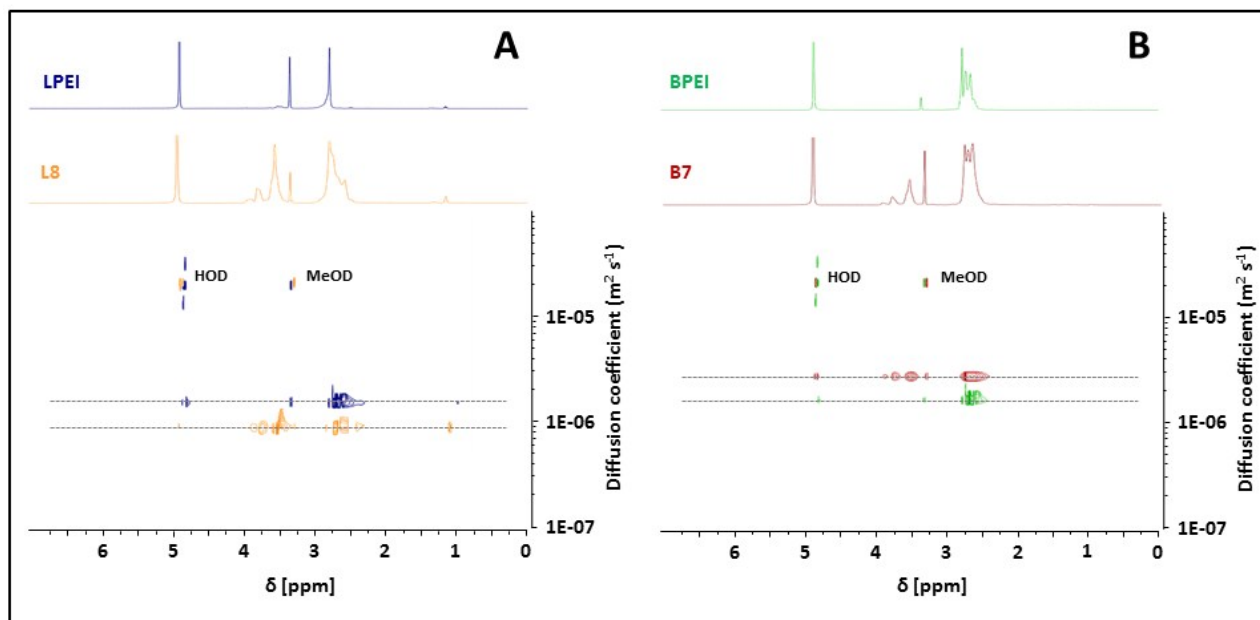
**Scheme S1.** Mechanism for Eschweiler-Clarke rearrangement leading to the methylation of secondary amines.<sup>37,69</sup>



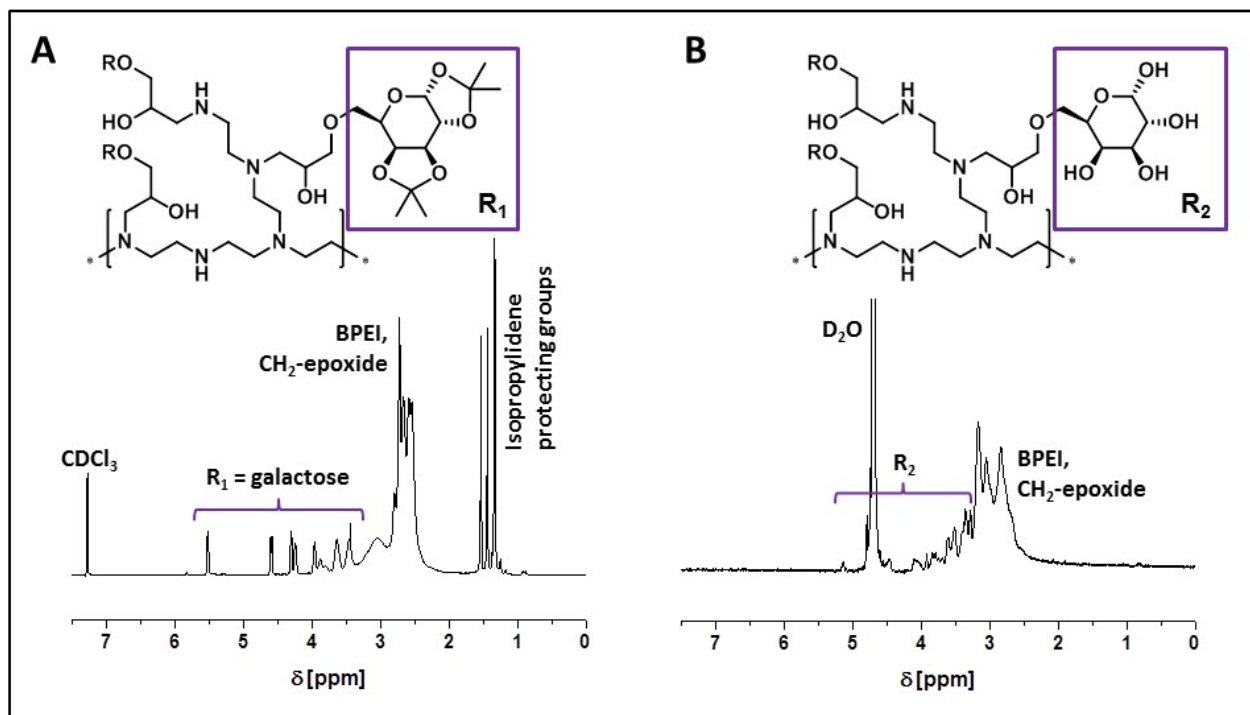
**Figure S2.** <sup>1</sup>H NMR spectra (*d*<sub>6</sub>-DMSO, 400 MHz) of the reaction mixture of A) *n*-propylamine and 0.5 equiv. paraformaldehyde in *d*<sub>6</sub>-DMSO (0.7 mL) after stirring at 90 °C for 2 h, and, B) dipropylamine and 0.5 equiv. paraformaldehyde in *d*<sub>6</sub>-DMSO (0.7 mL) after stirring at 90 °C for 2 h.



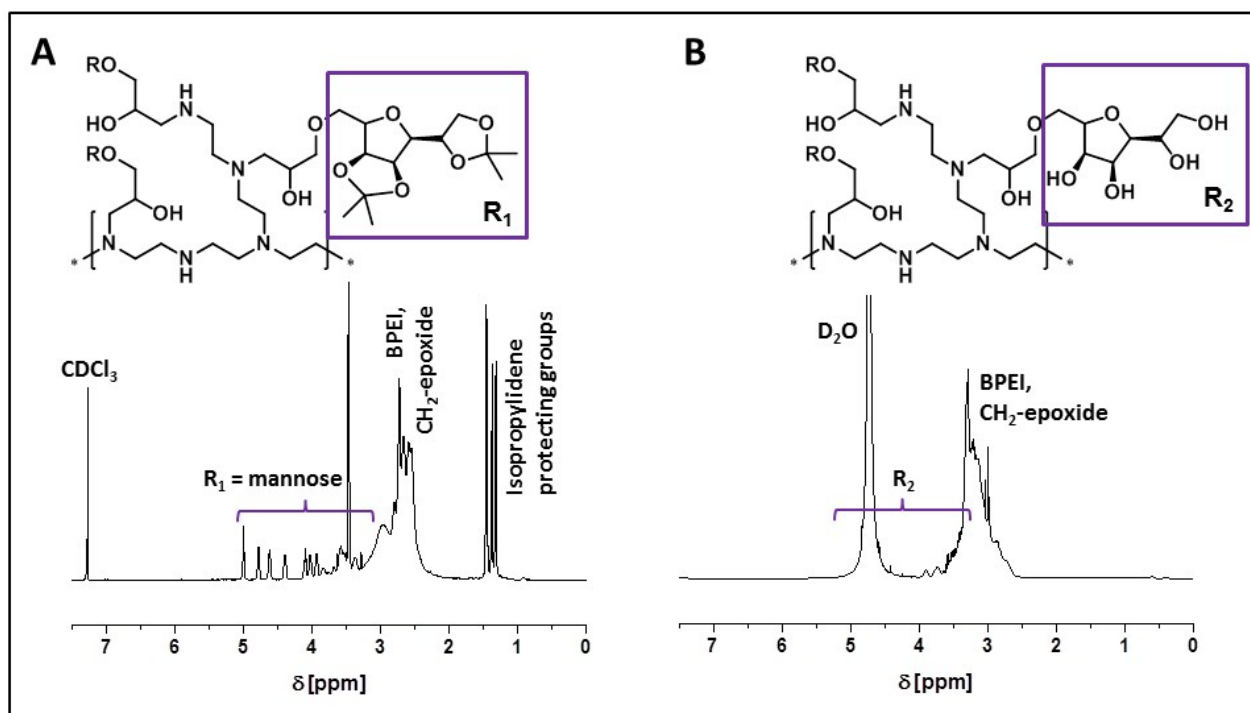
**Figure S3.**  $^1\text{H}$  NMR spectra of (A) linear (L6-L10) and (B) branched PEI, modified with varying contents of glycidol (B5-B9) ( $\text{D}_2\text{O}$ , 400 MHz).



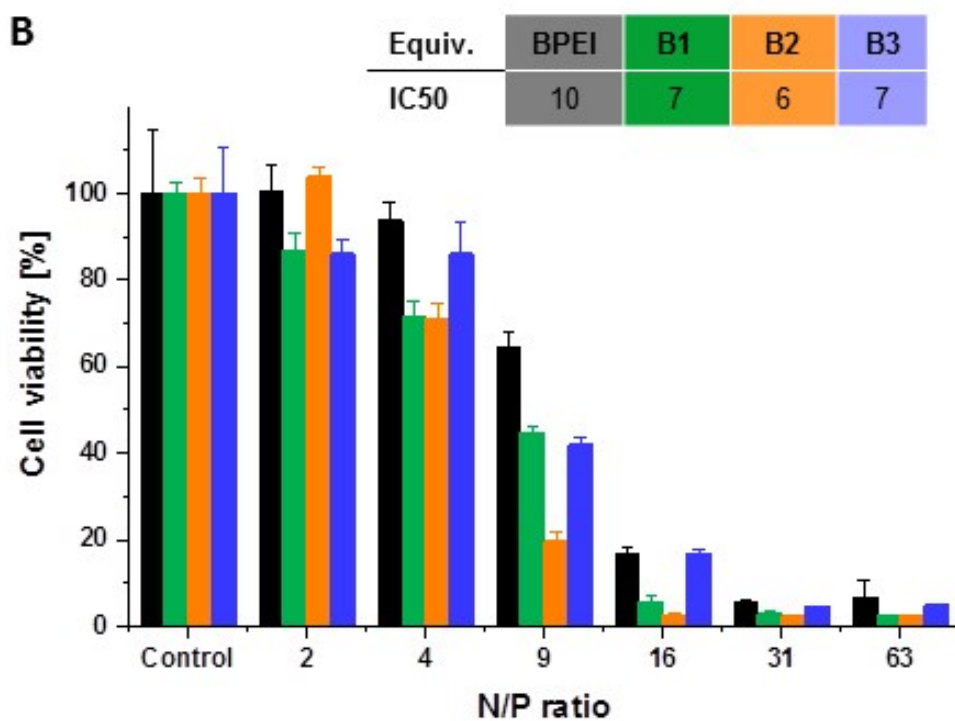
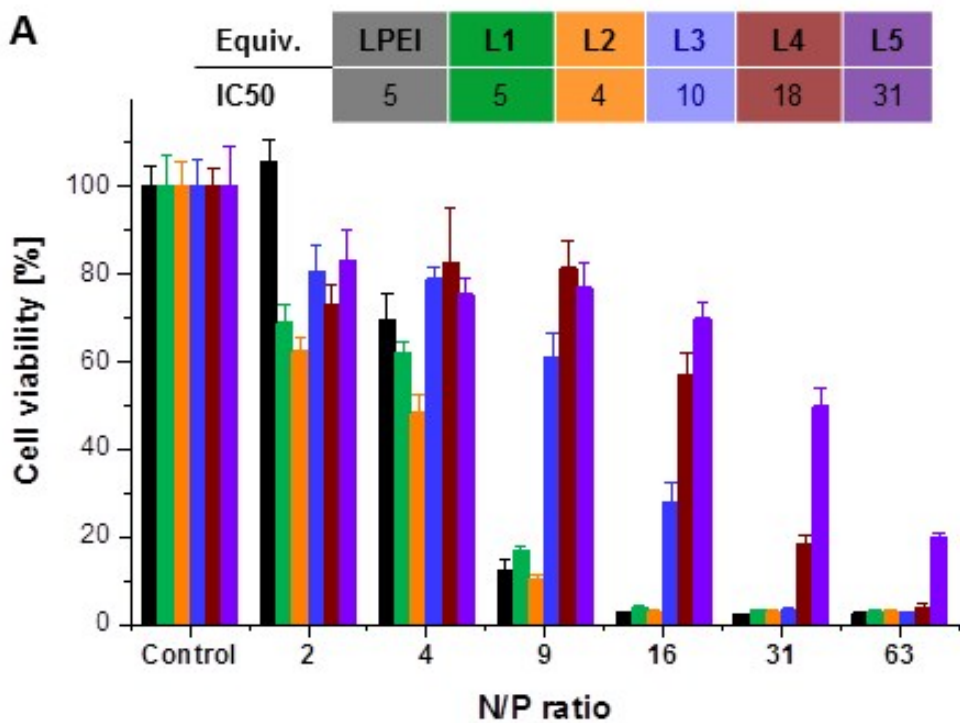
**Figure S4.** Diffusion ordered NMR spectra (MeOD, 400 MHz, 25 °C) of (A) LPEI and corresponding glycidol-functionalized **L8** (0.5 equiv. glycidol vs. -NH), and, (B) BPEI and corresponding glycidol-functionalized species **B7** (0.3 equiv. glycidol per amine functionality, including primary, secondary and tertiary amine groups).



**Figure S5.**  $^1\text{H}$  NMR spectra of A) a dialyzed aliquot of **isoB10** ( $\text{CDCl}_3$ , 400 MHz), and, B) the dialyzed aliquot of **B10** after hydrolysis ( $\text{D}_2\text{O}$ , 400 MHz).

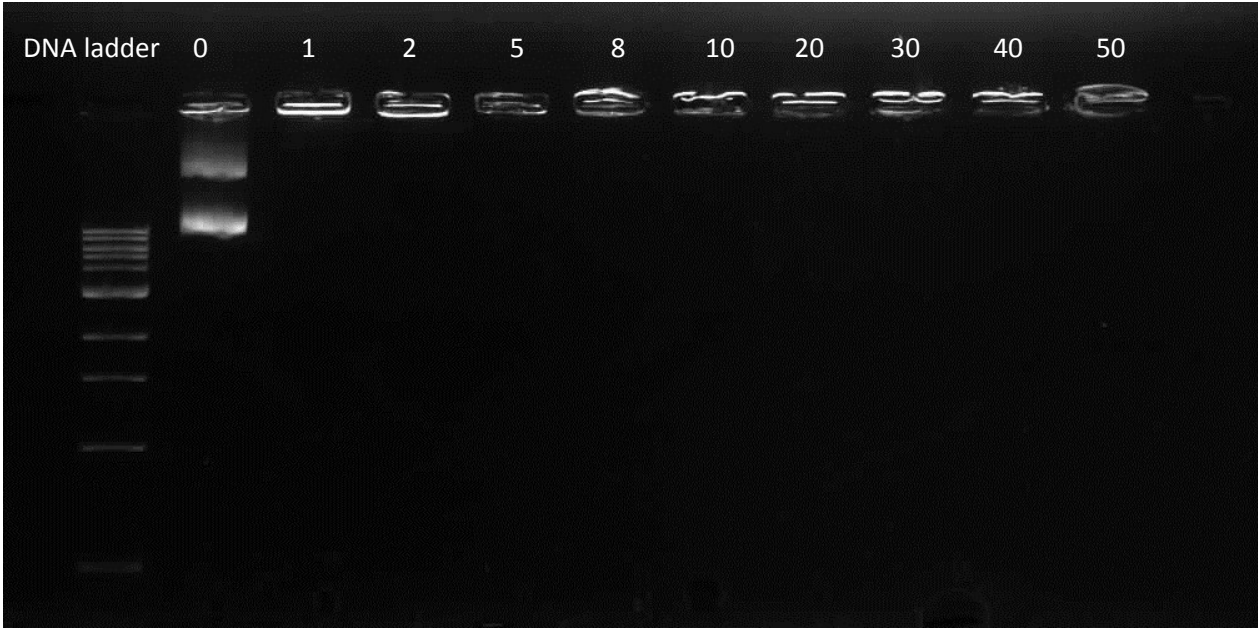


**Figure S6.** <sup>1</sup>H NMR spectra of A) a dialyzed aliquot of *isoB11* (CDCl<sub>3</sub>, 400 MHz), and, B) the dialyzed aliquot of **B11** after hydrolysis (D<sub>2</sub>O, 400 MHz).

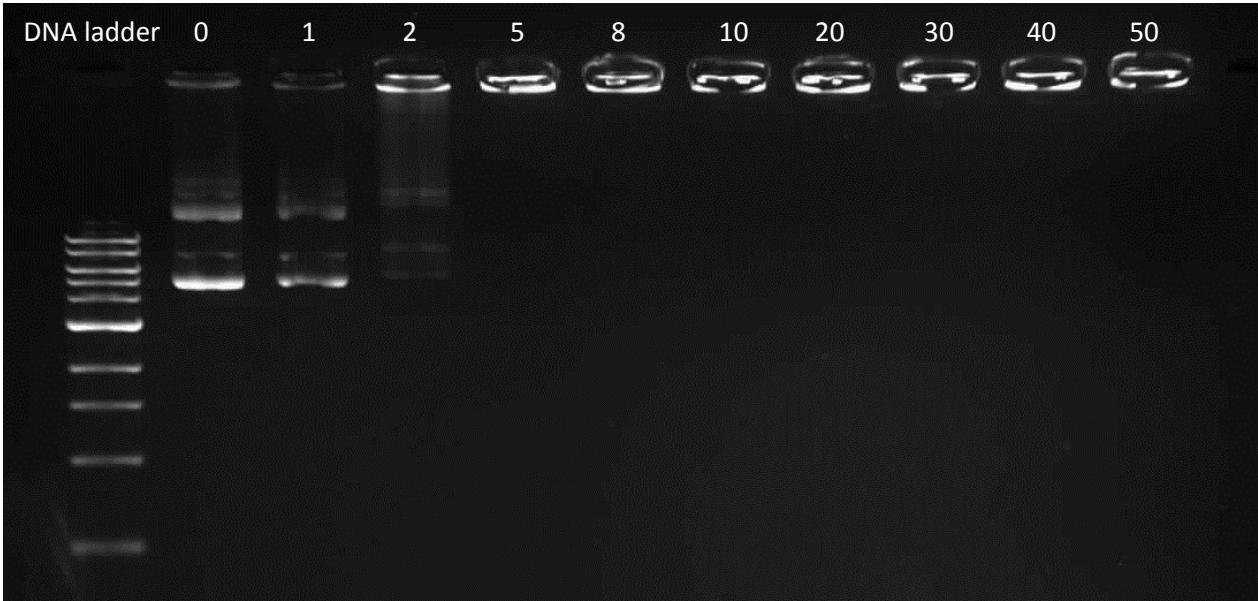


**Figure S7.** Cytotoxicity of formaldehyde functionalized A) LPEI (**L1-L5**) and B) BPEI (**B1-B3**) by MTT assay on HEK 293 cells.

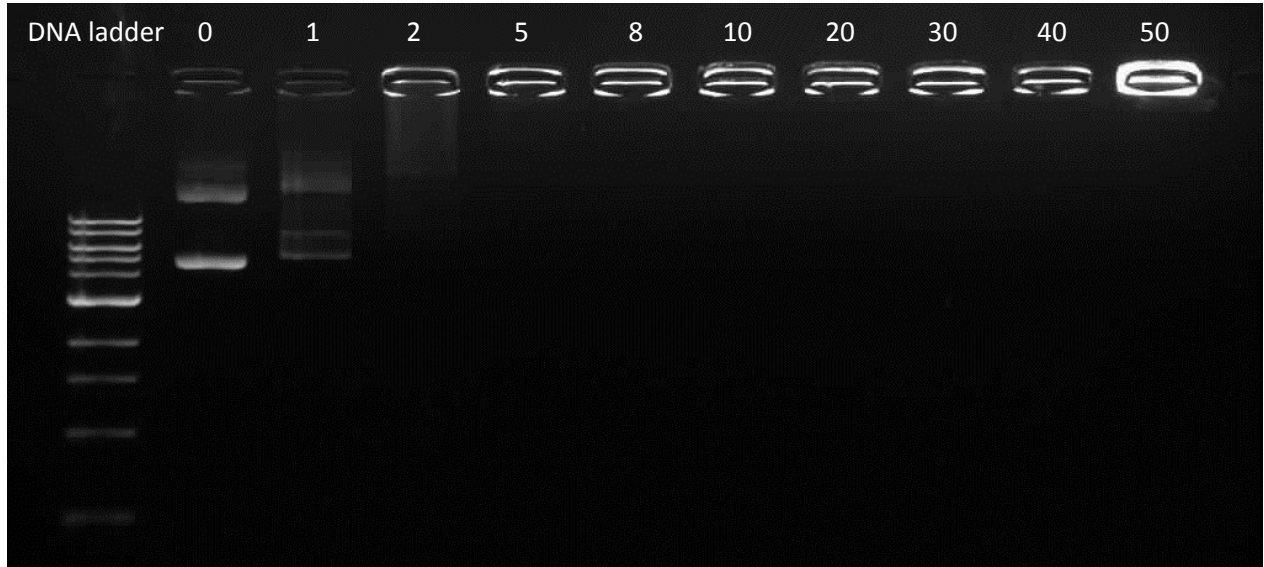
*B6 (0.15 equiv. glycidol)*



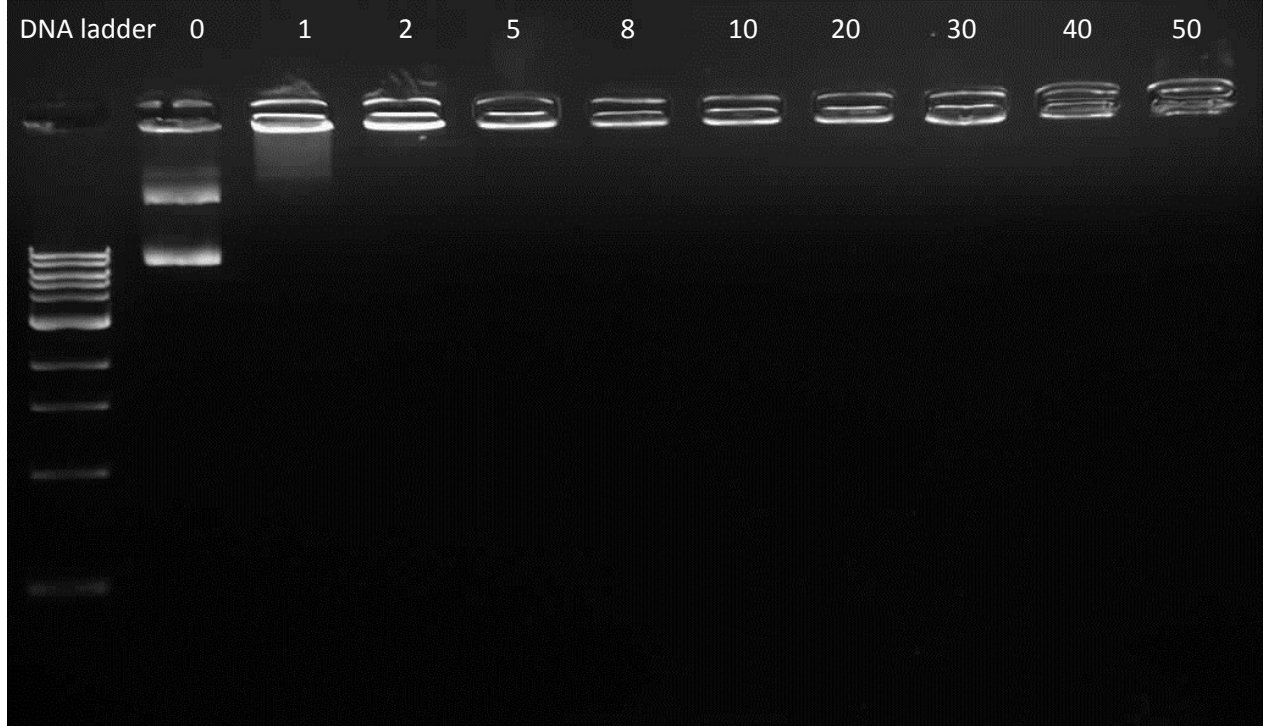
*B9 (0.75 equiv. glycidol)*



*B10 (0.09 equiv. galactose)*

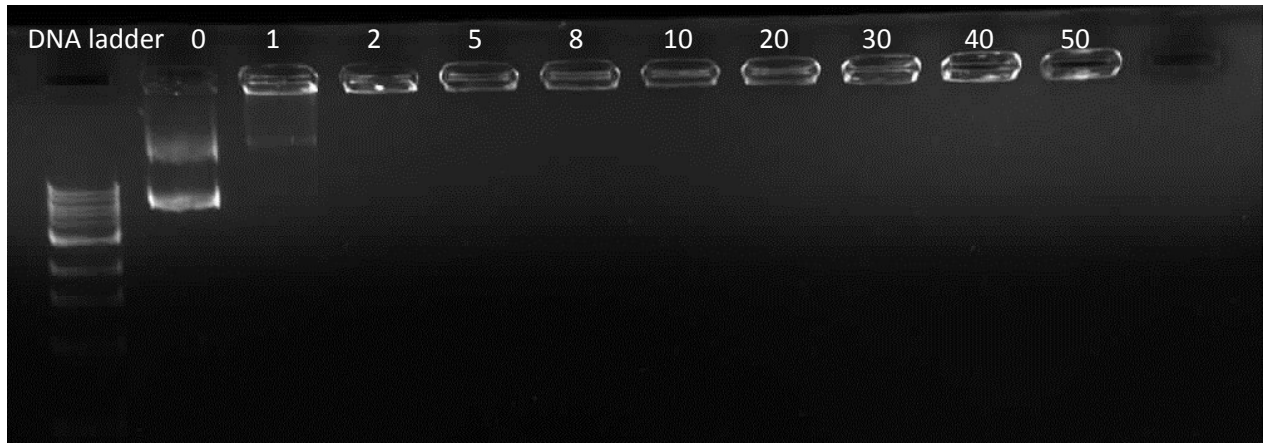


*B11 (0.09 equiv. mannose)*



*BPEI*





**Figure S8.** Electrophoretic mobility of DNA in polymer/DNA complexes.