

## Supplementary Information

# Synthesis of Diblock/Statistical Cationic Glycopolymers with Pendant Galactose and Lysine Moieties: Gene Delivery Application and Intracellular Behaviors

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**Scheme S1.** Synthesis of the glycomonomer 6-O-methacryloyl-1,2,3,4-di-O-isopropylidene-galactopyranose (MAIGal)

**Figure S1.** a) <sup>1</sup>H NMR spectrum of the galactose methylacrylate monomer (MAIGal) in CDCl<sub>3</sub>. b) <sup>13</sup>C NMR spectrum of the galactose methylacrylate monomer (MAIGal) in CDCl<sub>3</sub>

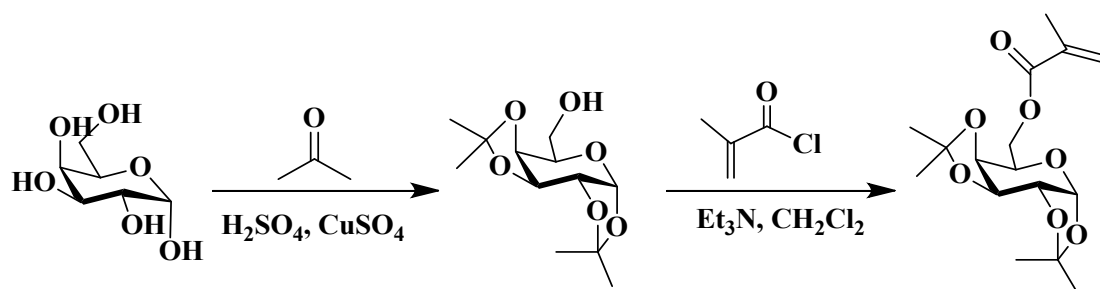
**Figure S2.** <sup>1</sup>H NMR spectra of the statistical copolymer P (HMLBoc<sub>40</sub>-*st*-MAIGal<sub>13</sub>) (a) and BOC-deprotected cationic polymer P (HML<sub>40</sub>-*st*-MAGal<sub>13</sub>) (b) in DMSO-*d*<sub>6</sub>

**Figure S3.** FT-IR spectra of the statistical copolymer P (HMLBoc<sub>40</sub>-*st*-MAIGal<sub>13</sub>) (a) and BOC-deprotected cationic polymer P(HML<sub>40</sub>-*st*-MAGal<sub>13</sub>) (b)

**Figure S4.** TEM images of the PHML<sub>40</sub>, PHML<sub>40</sub>-*b*-PMAGal<sub>3</sub> and P(HML-*st*-MAGal<sub>4</sub>)/pDNA polyplexes (N/P=40)

**Figure S5.** Fluorescence microscopic images (400×) of the localization of Cy3-labeled pDNA in H1299 cells recorded after 6 h gene transfection by P(HML<sub>40</sub>-*st*-MAGal<sub>4</sub>) vector in the presence of 10% FBS (Green: LysoTracker labeled lysosomes; Red: Cy3 labeled pDNA; Blue: DAPI stained cell nuclei)

**S1.** Synthesis of the glycomonomer 6-O-methacryloyl-1, 2, 3, 4-di-O-isopropylidene-galactopyranose (MAIGal)



Firstly, the hydroxy groups of D-galactose were protected by condensation with acetone in the presence of concentrated H<sub>2</sub>SO<sub>4</sub> (98%) and anhydrous CuSO<sub>4</sub>, then the protected D-galactose was further esterified with methacryloyl chloride at 0 °C. The solvent was evaporated to afford crude product, finally, pure product of MAIGal was purified via column chromatography and obtained as white solid. Yield of the two steps: 57 %.

<sup>1</sup>H NMR (CDCl<sub>3</sub>, δ in ppm): 6.13 (m, 1H, =CHH), 5.58 (m, 1H, =CHH), 5.53 (d, 1H, Galactopyranose (Gal)-H at 1 position), 4.61 (m, 1H, Gal-H at 3 position), 4.30 (m, 4H, Gal-H at 2, 4 and 6 position), 4.05 (m, 1H, Gal-H at 5 position), 1.93 (s, 3H, CH<sub>3</sub>CR=CH<sub>2</sub>), 1.53-1.33 (m, 12H, (CH<sub>3</sub>)<sub>2</sub>COO).

<sup>13</sup>C NMR (CDCl<sub>3</sub>, δ in ppm): 167.2, 136.1, 125.8, 109.5, 108.8, 96.3, 72.1, 70.7, 70.5, 66.1, 63.6, 25.9, 25.0, 24.4, 18.3. FTIR (in cm<sup>-1</sup>): 2978, 2927, 1715, 1385, 1258, 1210, 1176, 1164, 1112, 1064, 1006, 936, 901, 865.

ESI-MS [M+H<sup>+</sup>] (in m/z): 329.1 (Cal: 329.2).

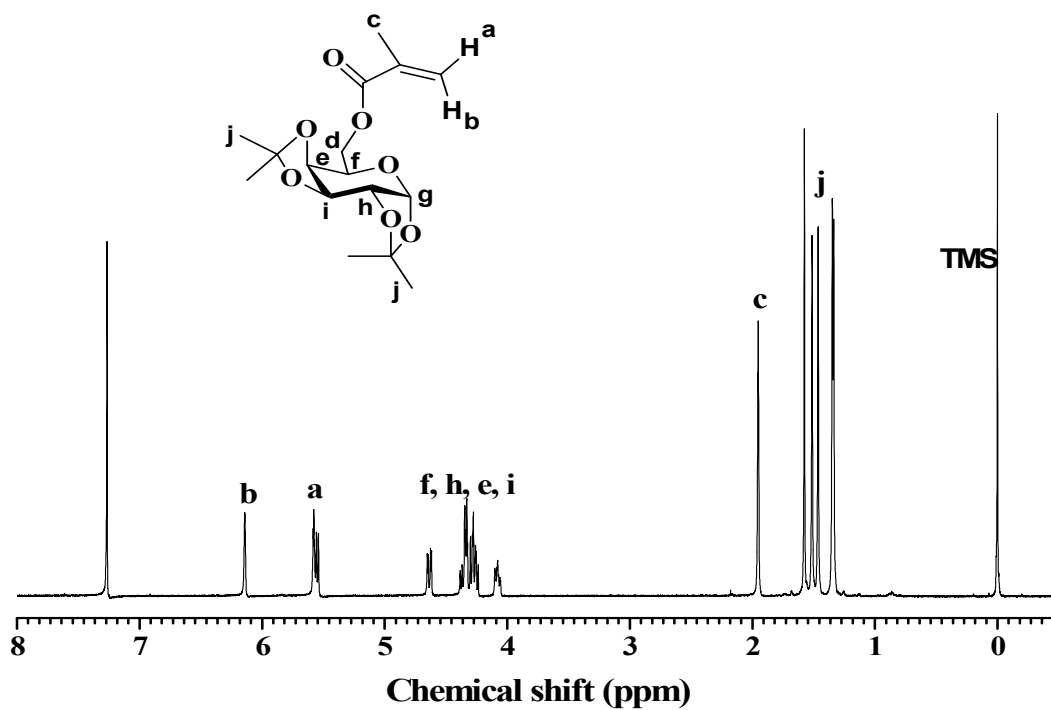


Figure S1 a)  $^1\text{H}$  NMR spectrum of the galactose methylacrylate monomer (MAIGal) in  $\text{CDCl}_3$

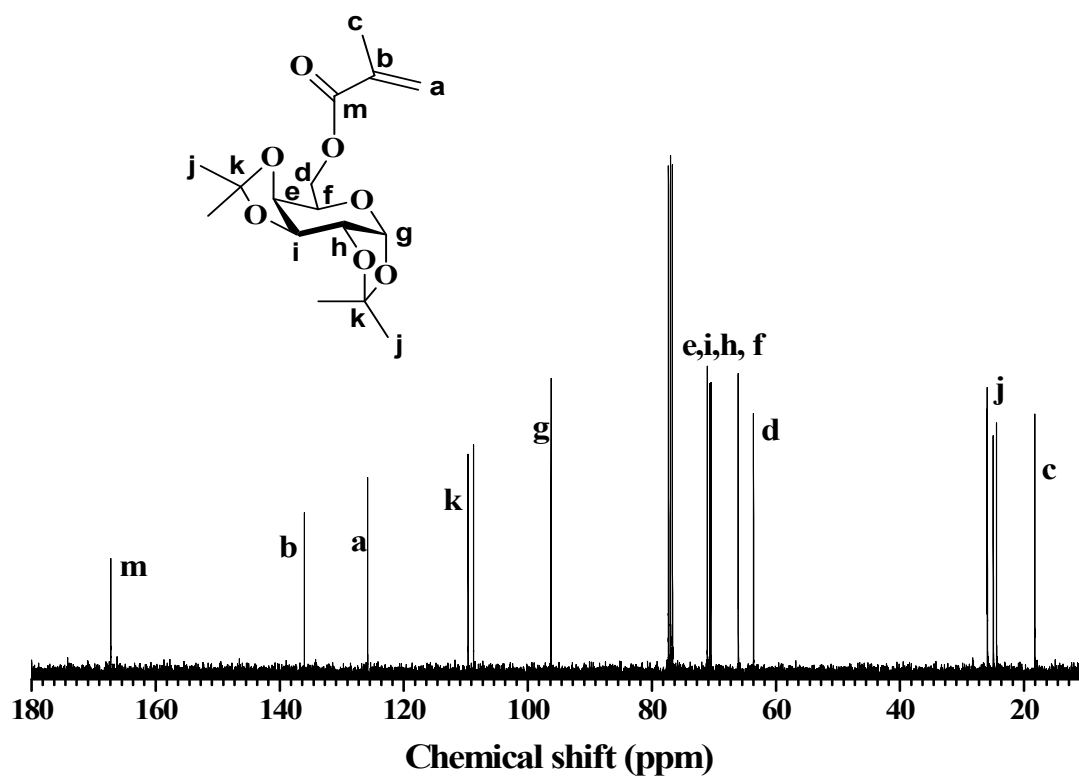
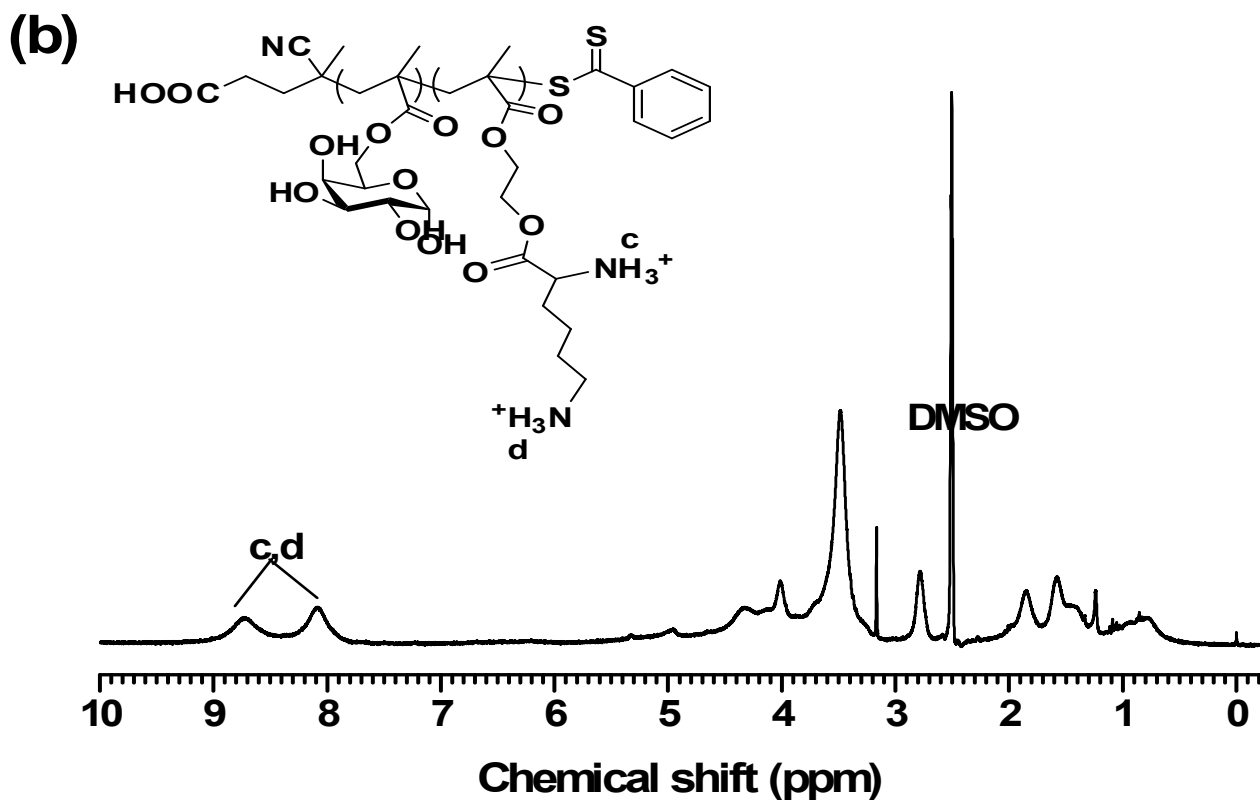
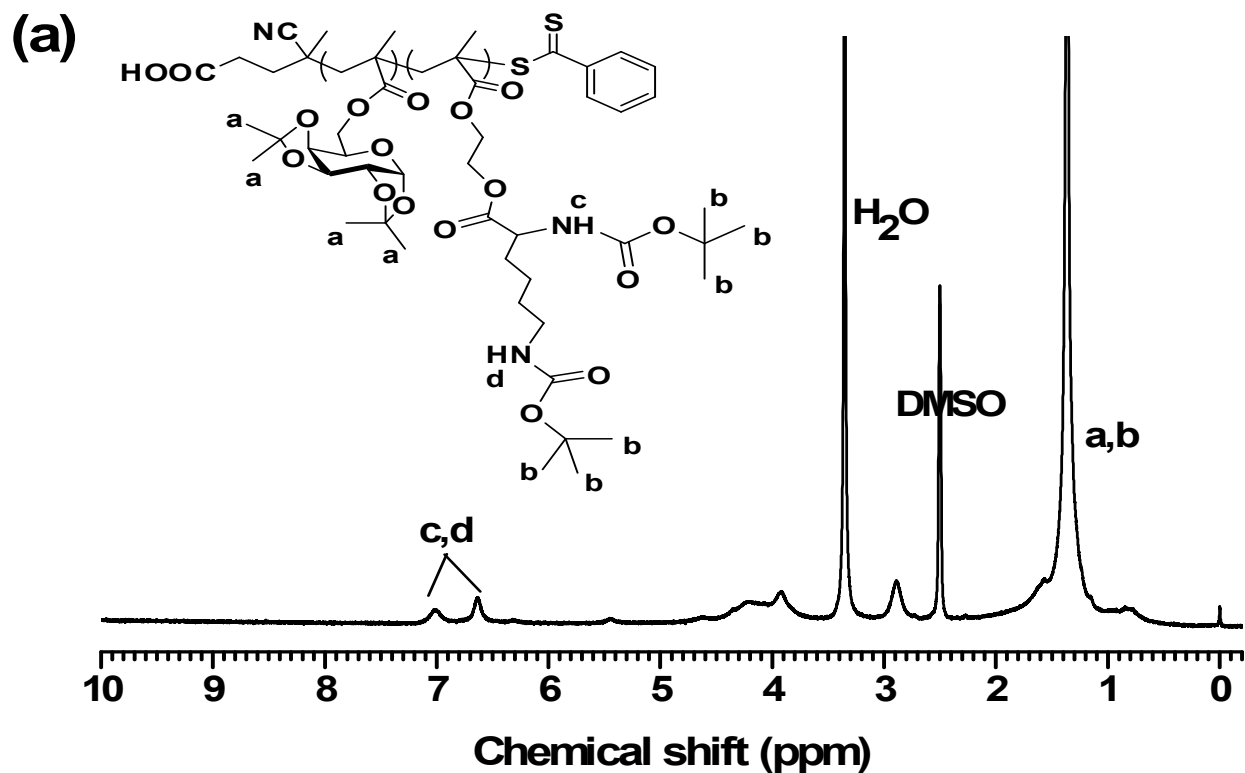
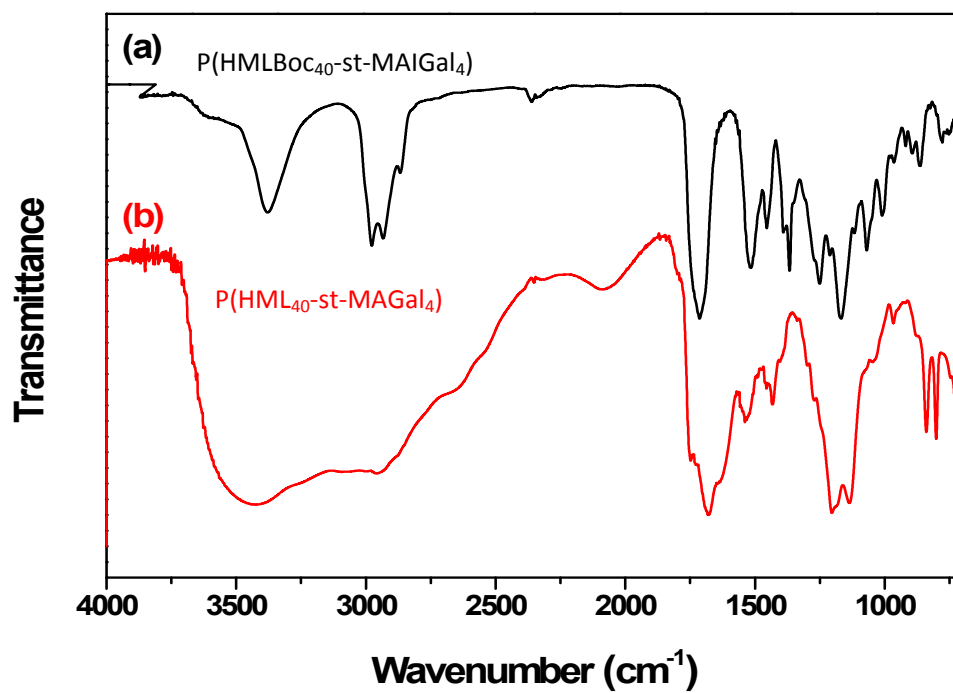


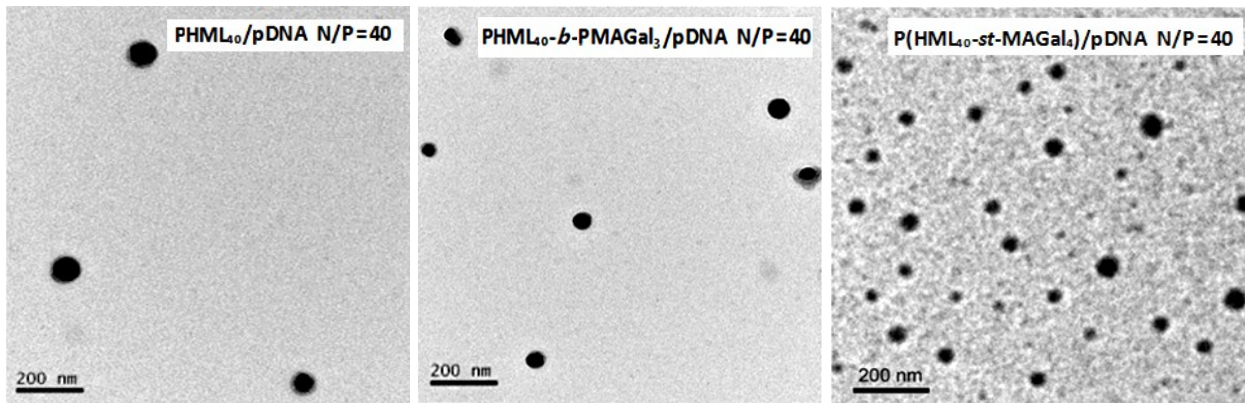
Figure S1 b)  $^{13}\text{C}$  NMR spectrum of the galactose methylacrylate monomer (MAIGal) in  $\text{CDCl}_3$



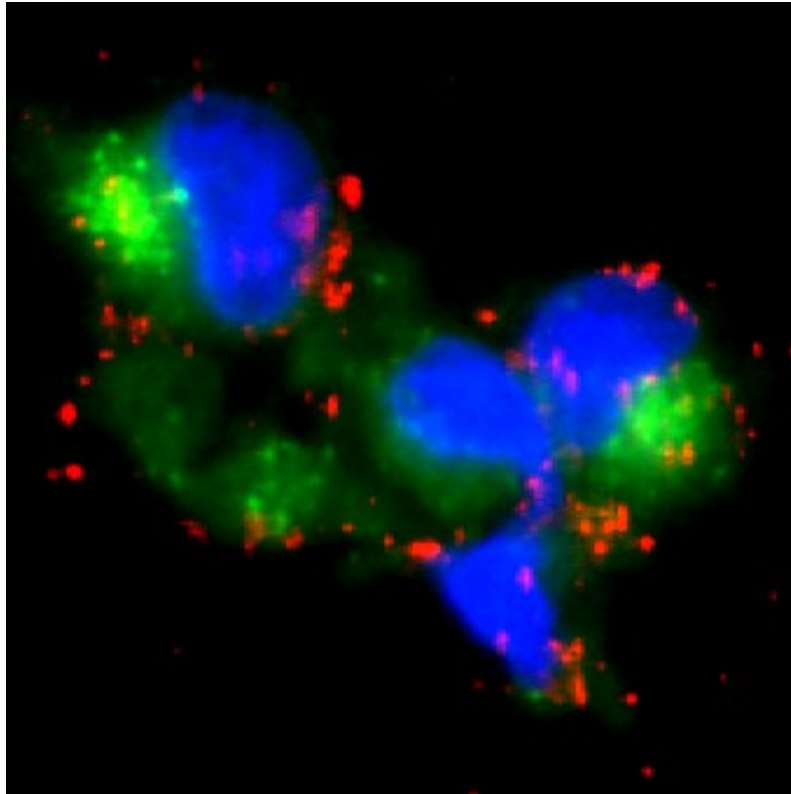
**Figure S2.** <sup>1</sup>H NMR spectra of the statistical copolymer P (HMLBoc<sub>40</sub>-st-MAIGal<sub>13</sub>) (a) and BOC-deprotected cationic polymer P(HML<sub>40</sub>-st-MAGal<sub>13</sub>) (b) in DMSO-*d*<sub>6</sub>



**Figure S3.** FT-IR spectra of the statistical copolymer P(HMLBoc<sub>40</sub>-st-MAIGal<sub>13</sub>) (a) and BOC-deprotected cationic polymer P(HML<sub>40</sub>-st-MAGal<sub>13</sub>) (b).



**Figure S4.** TEM images of the PHML<sub>40</sub>, PHML<sub>40</sub>-b-PMAGal<sub>3</sub> and P(HML<sub>40</sub>-st-MAGal<sub>4</sub>)/pDNA polyplexes (N/P=40)



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