† Electronic Supplementary Information (ESI) available:

A well-defined coil-comb polycationic brush with "star polymer" as side chains for gene delivery

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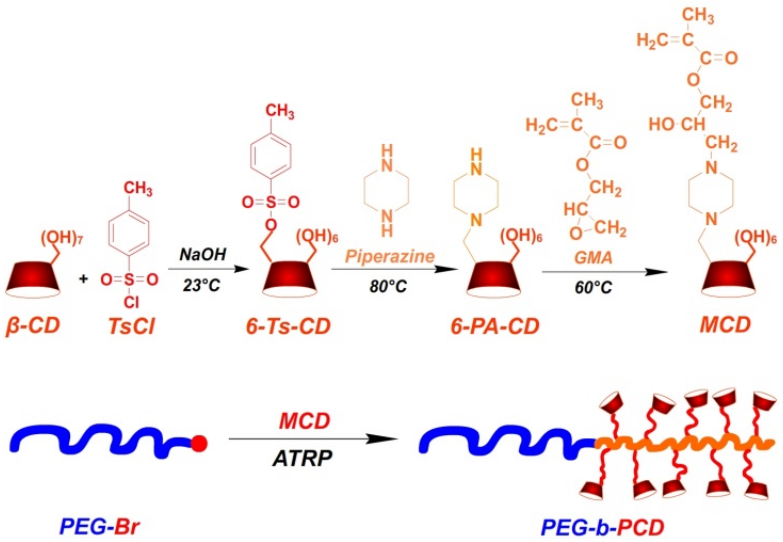
Synthesis of *mono*-methacrylate substituted cyclodextrin (MCD)

Mono-6-(*p*-tolyl sulfonyl)-β-cyclodextrin (6-Ts-CD) was synthesized according to the reference[1]. 6-Ts-CD (9.5 g) was added to 15 g of molten piperazine and reacted at 80˚C for 24 h. After the reaction was completed, the mixture was diluted in water and precipitated into acetone. The product was dissolved in water and poured into acetone several times for the removal of unreacted piperazine and then recrystallized from water. The sample obtained was dried under vacuum to give a white powder (6-PA-CD) (6.5 g, 73%).

6-PA-CD (6.015 g, 5 mmol) was dissolved in 62.5 mL of dry DMF and then excess GMA (2 mL, 15 mmol) was added. After purging with Ar for 30 min, the mixture was stirred at 60°C for 24 h. The product (MCD) was precipitated in excess acetone, recovered by filtration, washed by acetone for several times and dried under vacuum (6.7 g, 99%).

Synthesis of PEG-*b*-PCD diblock copolymer *via* ATRP

Poly(ethylene glycol) macroinitiator (PEG-Br) was synthesized by the esterification of poly(ethylene glycol) monomethyl ether (PEG, M_n=5,000) and BiBB according to the literature[2]. CuCl (0.0025 g, 0.025 mmol), $CuCl_2$ (0.0017 g, 0.0125 mmol) and PMDETA (15.66 μL, 0.075 mmol) were dissolved in dry DMF (0.5 mL) in a 10 mL two-neck flask and degassed with three freeze-pump-thaw cycles. A solution of PEG-Br (0.1376 g, 0.025 mmol) and MCD (1.0088 g, 0.75 mmol) in dry DMF (2.0 mL) was added into the solution through a syringe under Ar atmosphere, and the mixture was degassed with another two freeze-pump-thaw cycles. The reaction mixture was then stirred at 90°C for 48 h. The polymer was further purified by dialysis against deionized water for 48 h and recovered by lyophilization.



Scheme S1† Synthesis of *mono*-methacrylate substituted cyclodextrin (MCD) and atom transfer radical polymerization of MCD from PEG-Br initiator.

Synthesis of CD-Br initiator

β-CD (1 mmol, 1.135 g) was dissolved in 7 mL of dry NMP and cooled to 0°C. BiBB (12 mmol, 1.483 ml) diluted by 1.5 mL NMP was added dropwise. The reaction mixture was stirred at 0°C for 4 h and then at 25°C for an additional 44 h. After completion of stirring, 50 ml of dichloromethane was added into the mixture. The organic solution was washed with aqueous sodium bicarbonate solution and distilled water for three times individually. The organic layers were collected, dried over $MgSO_4$, and most of the solvent was removed by rotary evaporation prior to precipitation into excess *n*-hexane. The purified initiator CD-Br was obtained by drying under vacuum to remove the residual solvent. The ^{1}H NMR and ^{13}C NMR spectra were displayed in Fig. S1†.

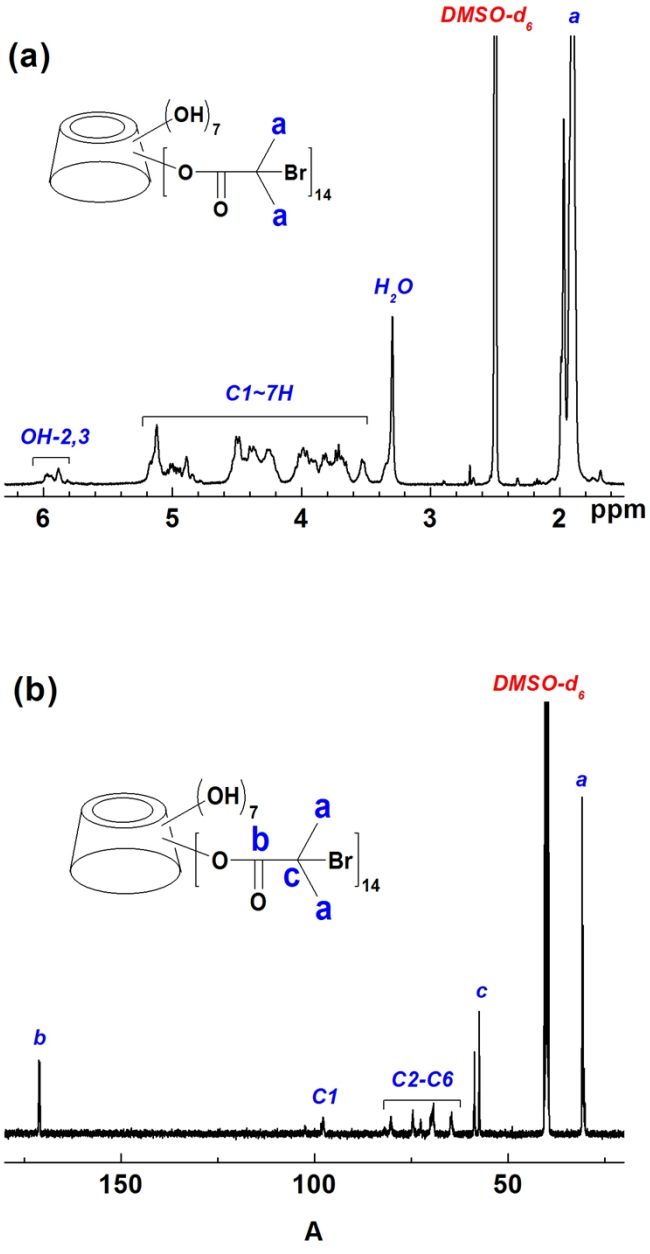


Fig. S1† ^{1}H NMR (a) and ^{13}C NMR (b) spectra of CD-Br in DMSO-d_6.

Synthesis of CD-*g*-PDMA star polymer from CD-Br *via* ATRP

The star polymer was synthesized by ATRP of DMAEMA using CD-Br as the initiator. The molar feed ratio of [DMAEMA(7.2 mmol)]:[Br]:[CuCl]:[$CuCl_2$]:[bpy] was 30:1:0.6:0.3:1.8. CuCl, $CuCl_2$ and bpy were dissolved in 9 mL of acetone/water (v/v=95/5) in a two-neck flask and degassed with three freeze-pump-thaw cycles. A solution of CD-Br and DMAEMA in 9 mL of acetone/water (v/v=95/5) was added into the solution through a syringe under Ar atmosphere, and the mixture was then degassed with another two freeze-pump-thaw cycles. The reaction mixture was stirred at 35°C for 20 h. The polymer was further purified by dialysis against deionized water for 2 days and recovered by lyophilization.

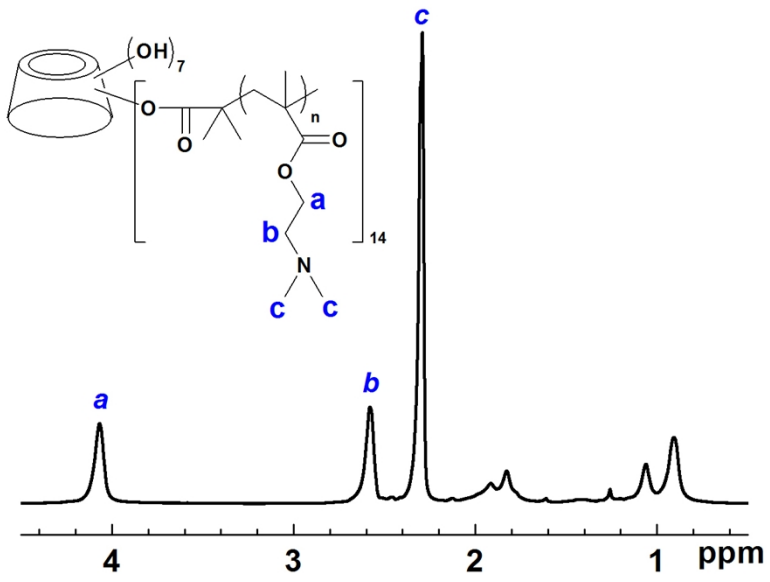


Fig. S2† ^{1}H NMR spectrum of CD-*g*-PDMA in $CDCl_3$.

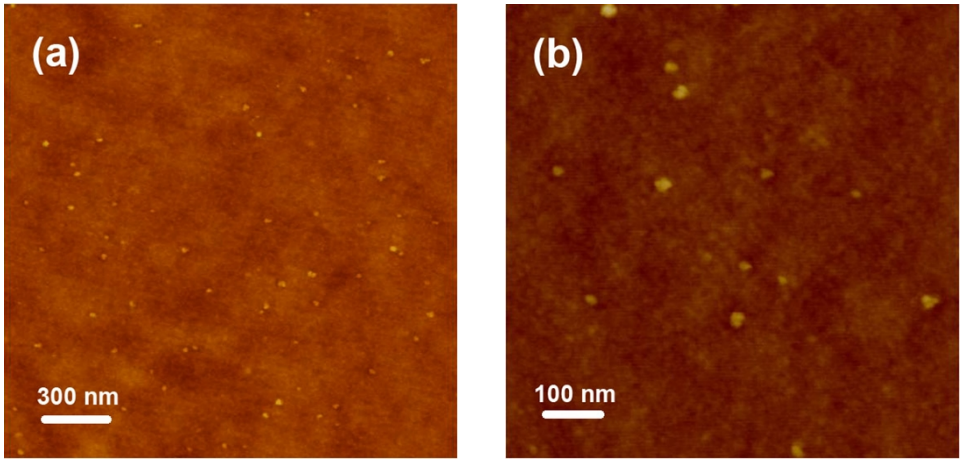
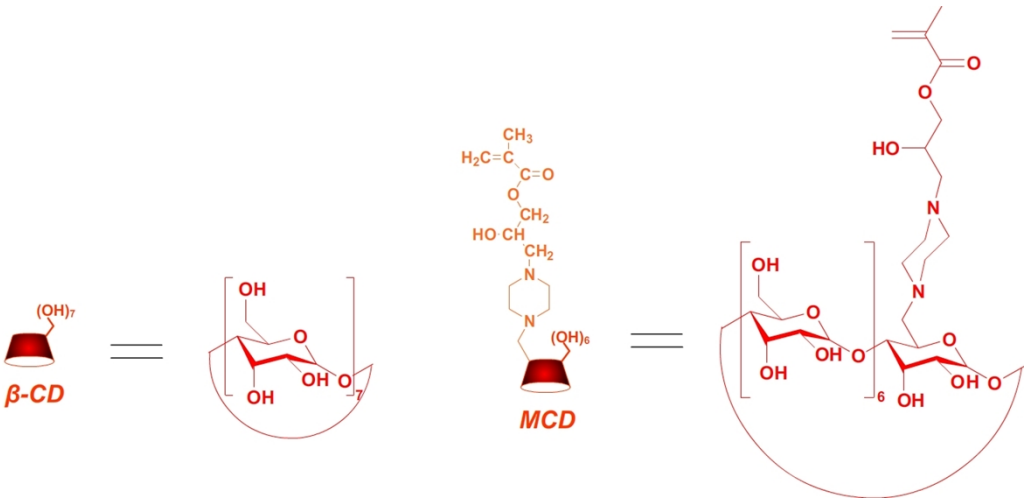
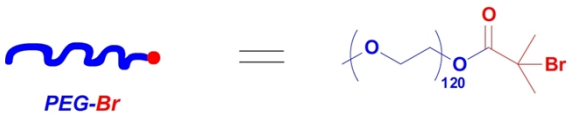
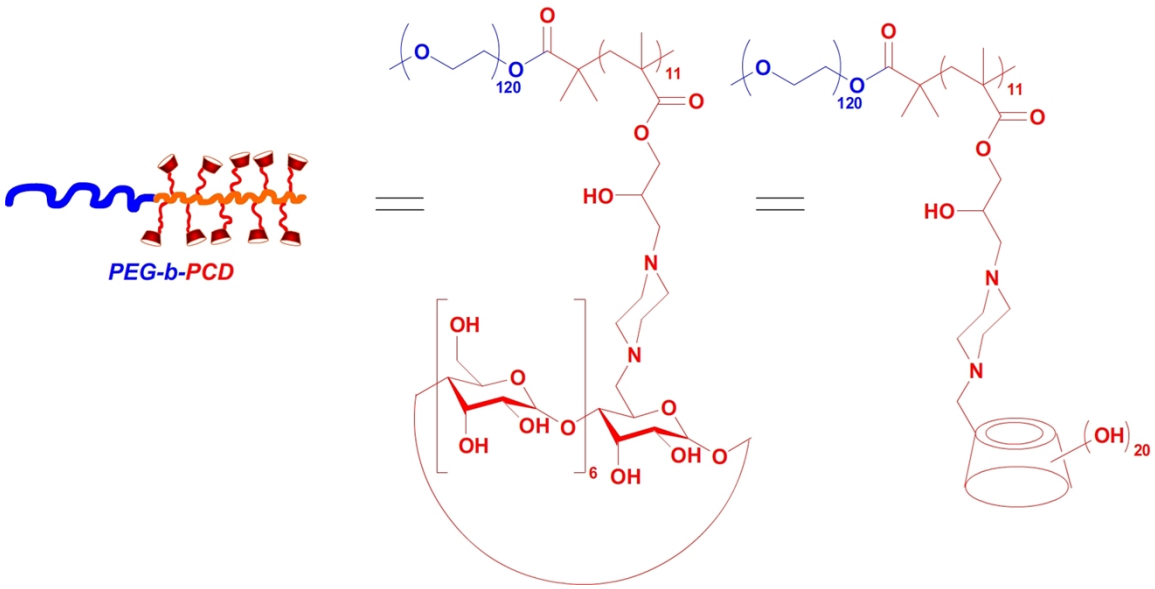
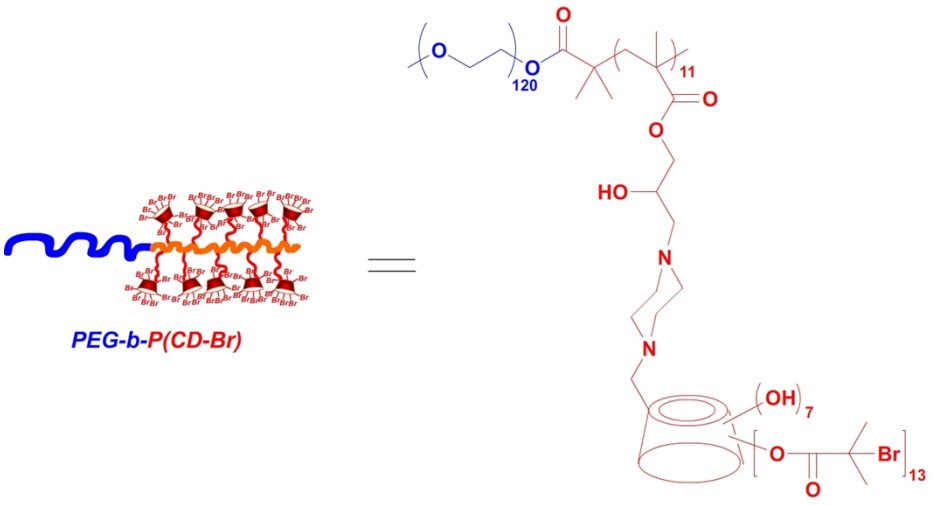


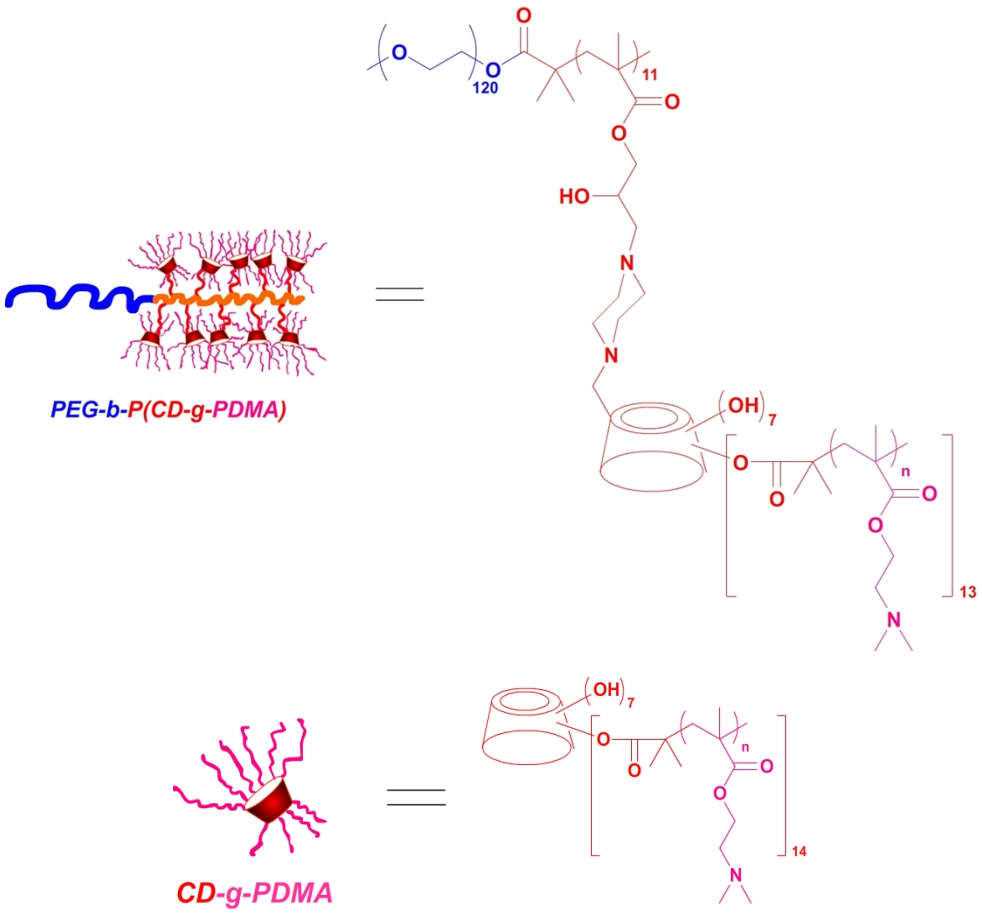
Fig. S3† AFM height images of brush3. The scale bar is 300 nm for (a) and 100 nm for (b).


β-CD
MCD


PEG-Br


PEG-b-PCD


PEG-b-P(CD-Br)



Scheme S2† The molecular structures of main chemicals and polymers.

References

1. R. C. Petter, J. S. Salek, C. T. Sikorski, G. Kumaravel and F. T. Lin, *Journal of the American Chemical Society*, 1990, **112**, 3860-3868.
2. L. Liu, M. Zhang and H. Zhao, *Macromolecular Rapid Communications*, 2007, **28**, 1051-1056.