Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

PGMA-based starlike polycations with flanking phenylboronic acid groups for high-efficient multifunctional gene delivery systems

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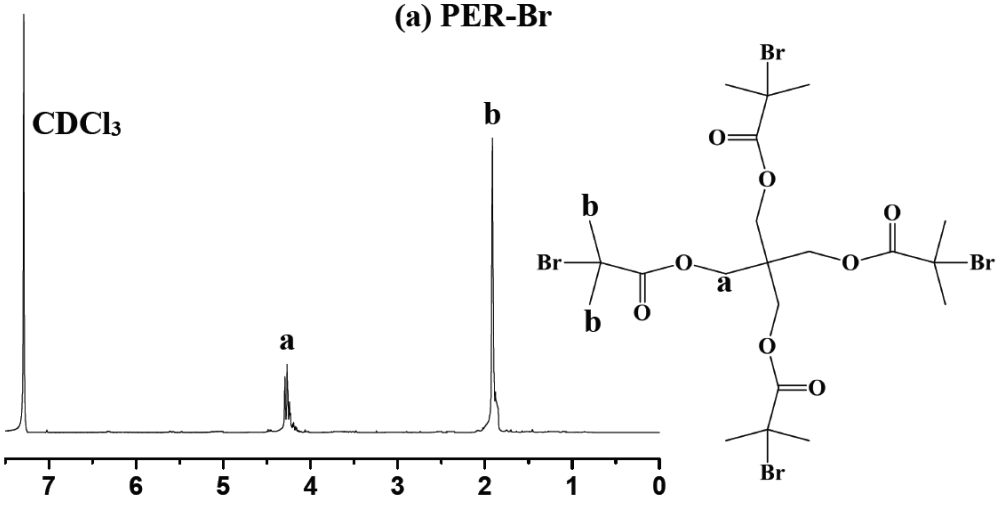
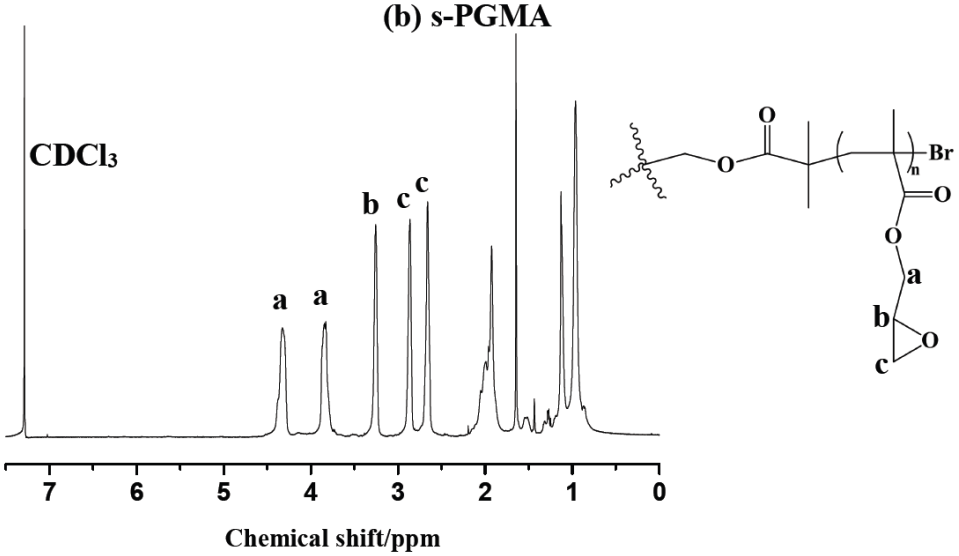
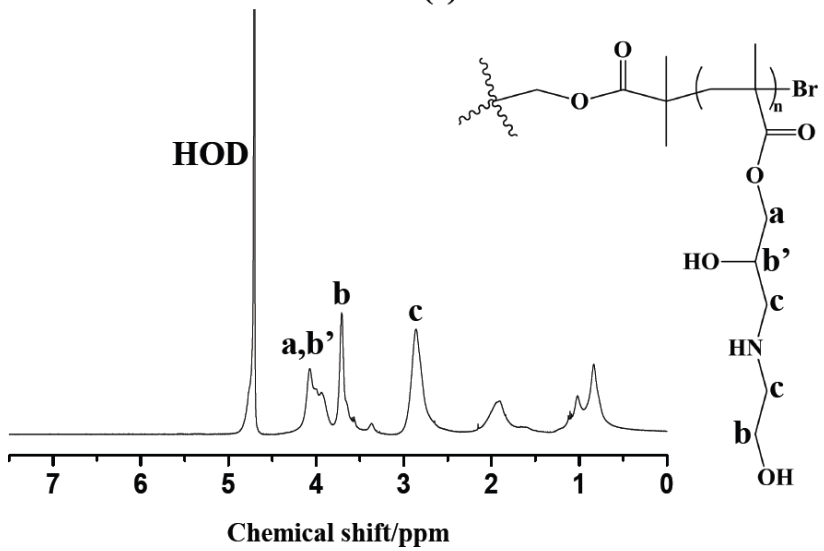
(a) PER-Br



(b) s-PGMA



(c) s-PGEA



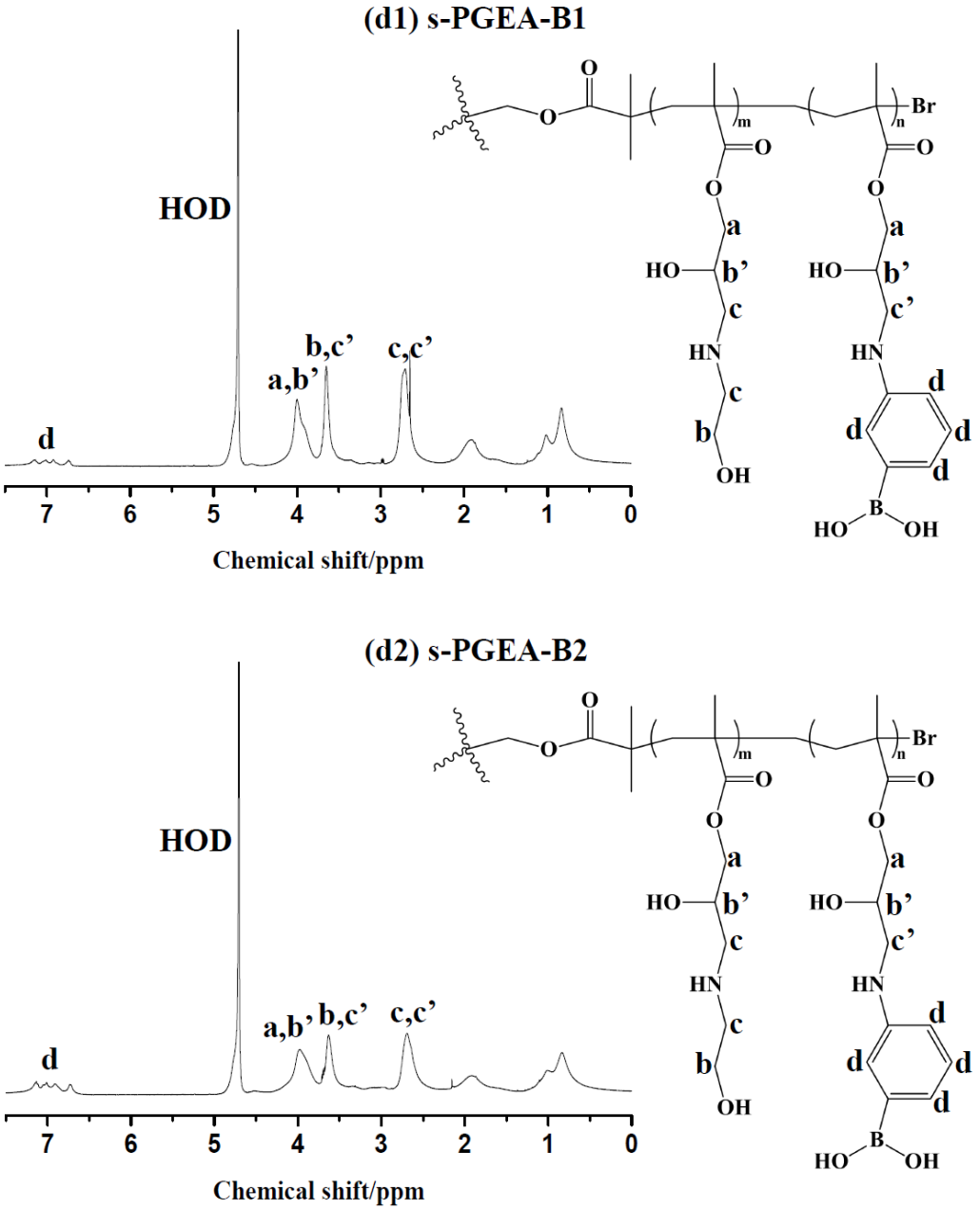


Fig. S1 400 MHz ^{1}H NMR spectra of (a) PER-Br in $CDCl_3$, (b) s-PGMA in $CDCl_3$, (c) s-PGEA in D_2O, and (d1,d2) s-PGEA-B in D_2O.

The chemical structures of representative polymers prepared in this work were characterized by ^{1}H NMR, and the spectrum were shown in Fig. S1. For the initiator PER-Br (Fig. S1(a)), the peaks at 4.23 and 1.91 ppm were attributed to methylene protons adjacent to the oxygen moieties of the ester linkages (a, -C-$\underline{CH_2}$-O-C=O) and

methyl protons (b, -$\underline{CH_3}$), respectively. The area ratio of peak a and b was about 1:3, which suggested that each initiator PER-Br molecule possessed four terminal four bromoisobutyryl groups. The NMR spectra of s-PGMA synthesized via ATRP of monomer GMA was shown in Fig. S1(b). The peaks located at 4.32 and 3.79 ppm were associated with the methylene protons adjacent to the oxygen moieties of the ester linkages (a, O=C-O-$\underline{CH_2}$-CH). The signal δ = 3.26 and 2.86 ppm belonged to the methylidyne protons (b, CH_2–$\underline{CH}$(O)–CH_2), and the peak at 2.65 ppm was related to the methylene protons (c, CH_2–CH(O)–$\underline{CH_2}$) of the epoxy ring. As expected, the area ratio of peak a, b and c was about 2:1:2, indicating that the epoxy rings were not damaged during the ATRP process. s-PGEAs were prepared through the ring-opening reaction of EA on the basis of s-PGMA. As shown in Fig. S1(c), the signal at the scope of 3.81-4.35 ppm (a, O=C-O-$\underline{CH_2}$-CH) was mainly (two-thirds of the peak area) attributed to the methylene adjacent to the ester linkages. While, the residual partial scope (one-thirds of the peak area) was assigned to the methylidyne (b', $\underline{CH}$–OH). Besides, the characterized chemical shift at 3.71 ppm belonged to the methylene protons adjacent to the hydroxyl groups (b, $\underline{CH_2}$–OH). The signal δ = 2.76 ppm belonged to the methylene protons adjacent to the secondary amine groups. The area ratio of peak a, b and c was about 3:2:4. This result indicated that s-PGEAs were prepared successfully. For s-PGEA-B1 (Fig. S1(d1)), the spectra was similar to that of s-PGEA, and included a extra typical signal at the range of 6.63 to 7.27 ppm, which was attributed to the protons of benzene ring (d, -NH-$\underline{C_6H_4}$-) of phenylboronic acid. In addition, the signal of the methylene protons adjacent to the amine groups of APBA residues was averagely distributed to the peaks at the 3.71 and 2.76 ppm, respectively. The area ratio of peak a and b', b and c', c and c', and d was about 3.75:2.25:4.25:1, demonstrating that the percentage of APBA residues to monomer units of s-PGEA-B was about 20%. The NMR spectra of s-PGEA-B2 (Fig. S1(d2)) was almost the same as that of s-PGEA-B1, except that the area ratio of a and b', b and c', c and c', and d was about 2.25:1.25:2.25:1, which revealed that the percentage of APBA to the opened epoxy groups was about 30%.