Supplementary information

1, Characterization of PAMAM G1 and G2

(1) The IR and ^{1}H NMR data of PAMAM G 0.5-G 2.0

G(-0.5): IR(KBr): 2965, 2829, 1737, 1436, 1200, 1040cm^{-1}.

^{1}H NMR(CDCl$_3$): δ_{ppm}=2.57(m,8H,4CH$_2$C**H**$_2$CO), 2.63(m,4H,2C**H**$_2$N), 2.9(m, 8H, 4C**H**$_2$ CH$_2$ CO), 3.8 (s,12H, 4C**H**$_3$).

G0: IR(KBr): 3279, 3046, 2932, 2882, 1649, 1553, 1462, 1356, 1115, 1028cm^{-1}.

^{1}H NMR(D$_2$O): δ_{ppm}=2.37 (m,8H,4CH$_2$C**H**$_2$CO), 2.5-2.7(m,12H,2C**H**$_2$N+4C**H**$_2$CH$_2$CO), 3.19(m, 8H, 4CH$_2$C**H**$_2$NH$_2$), 3.55(m, 8H, 4C**H**$_2$CH$_2$NH$_2$).

G0.5: IR(KBr): 3312, 2953, 2828, 1736, 1651, 1539, 1437, 1200, 1045 cm^{-1}.

^{1}H NMR(CDCl$_3$): δ_{ppm}=2.45(m,24H,12CH$_2$C**H**$_2$CO), 2.5-2.7(m,28H,2C**H**$_2$N+12C**H**$_2$CH$_2$CO), 2.8-2.9 (m, 8H, 4CH$_2$C**H**$_2$N), 3.3-3.4(m,8H, 4C**H**$_2$CH$_2$N), 3.7(s,24H, 8C**H**$_3$).

G1.0 IR(KBr): 3290, 3065, 2941, 2831, 1650, 1550, 1450, 1360, 1126, 1036 cm^{-1}.

^{1}H NMR (D$_2$O): δ_{ppm} =2.51 (t, 24H,12CH$_2$C**H**$_2$CO), 2.73 (t, 28H, 2C**H**$_2$N+12C**H**$_2$CH$_2$CO), 2.80-2.90(t,24H,4CH$_2$C**H**$_2$N+8CH$_2$C**H**$_2$NH$_2$),3.30-3.40(t, 24H, 4C**H**$_2$CH$_2$N+ 8C**H**$_2$CH$_2$NH$_2$).

G1.5: IR(KBr): 3306, 2953, 2830, 1736, 1651, 1541, 1436, 1200, 1045 cm^{-1}.

^{1}H NMR(CDCl$_3$): δ_{ppm}=2.3(m,56H,28CH$_2$C**H**$_2$CO), 2.4-2.6(m,60H,2C**H**$_2$N+28C**H**$_2$CH$_2$CO), 2.7(m,24H, 12CH$_2$C**H**$_2$N), 3.2-3.3(m,24H, 12C**H**$_2$CH$_2$N), 3.6(s,48H, 16C**H**$_3$).

G2.0 IR(KBr): 3290, 3065, 2941, 2831, 1650, 1550, 1450, 1360, 1128, 1033 cm^{-1}.

^{1}H NMR(D$_2$O): δ_{ppm}=2.55 (m,56H,28CH$_2$C**H**$_2$CO), 2.75 (m,60H,2C**H**$_2$N+28C**H**$_2$CH$_2$CO), 2.86-2.98 (m,56H,16CH$_2$C**H**$_2$NH$_2$+12CH$_2$C**H**$_2$N), 3.43(m,56H,16C**H**$_2$CH$_2$NH$_2$+12C**H**$_2$ CH$_2$N).

(2) MALDI-TOF mass spectra of PAMAM G1 and G2

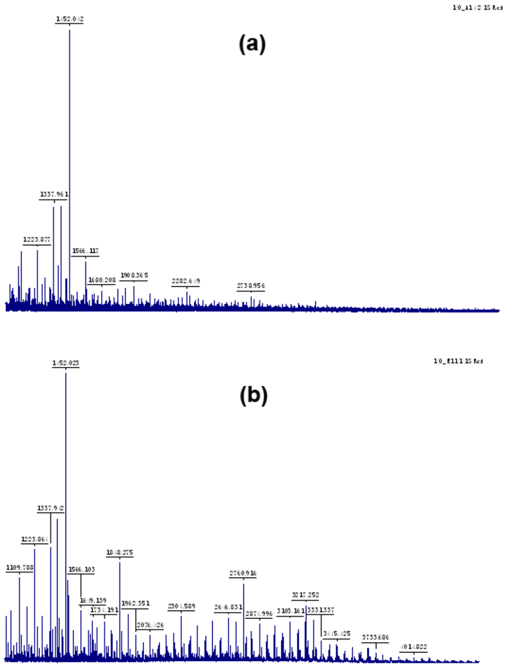

Figure S1 MALDI-TOF mass spectra of PAMAM G1 **(a)** and PAMAM G2 **(b).**

The molecular weight of PAMAM G1 and G2 measured by MALDI-TOF mass spectrum was 1452 or 3274 Da, respectively.

(3) DSC analysis of PAMAM G2 and G1

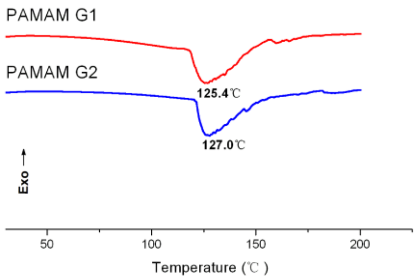

Figure S2 The DSC thermograms of PAMAM G2 and G1.

The endothermic peaks at 125.4 ℃ and 127.0 ℃ of PAMAM G2 or PAMAM G1 were seen, which were attributed to the isotropic liquid transition of the PAMAM G2 (or G1).

(4) Potentiometric titration of PAMAM G1 and G2

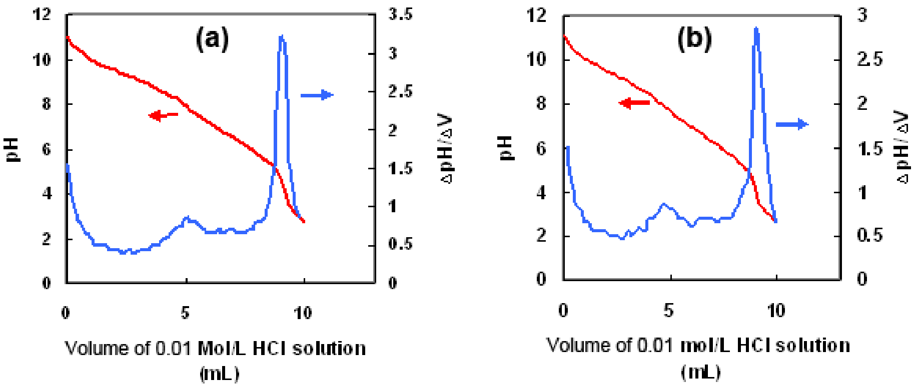

Figure S3 Curve of potentiometric titration of PAMAM G1 **(a)** and PAMAM G2 **(b)**.

The number of the primary amino groups of PAMAM G1 and G2 was 7.9 or 16.3, respectively. (The theoretical value of the primary amino groups of PAMAM G1 and G2 is 8.0 or 16.0, respectively.).

2, Characterization of EA-G2, EA-G1 and relative polymers

(1) IR analysis

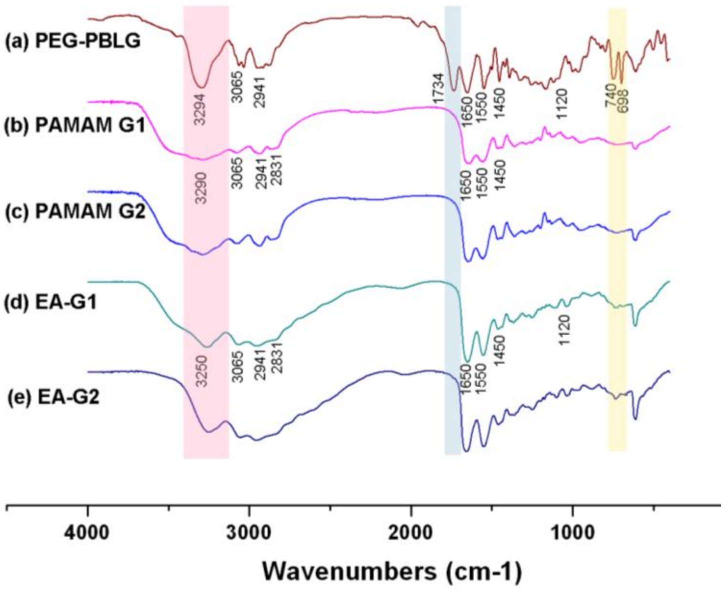

Figure S4 FT-IR spectra of PEG-PBLG **(a)**; PAMAM G1**(b)**; PAMAM G2**(c)**; EA-G1**(d)**; EA-G2**(e)**.

(2) ^{1}H-NMR analysis

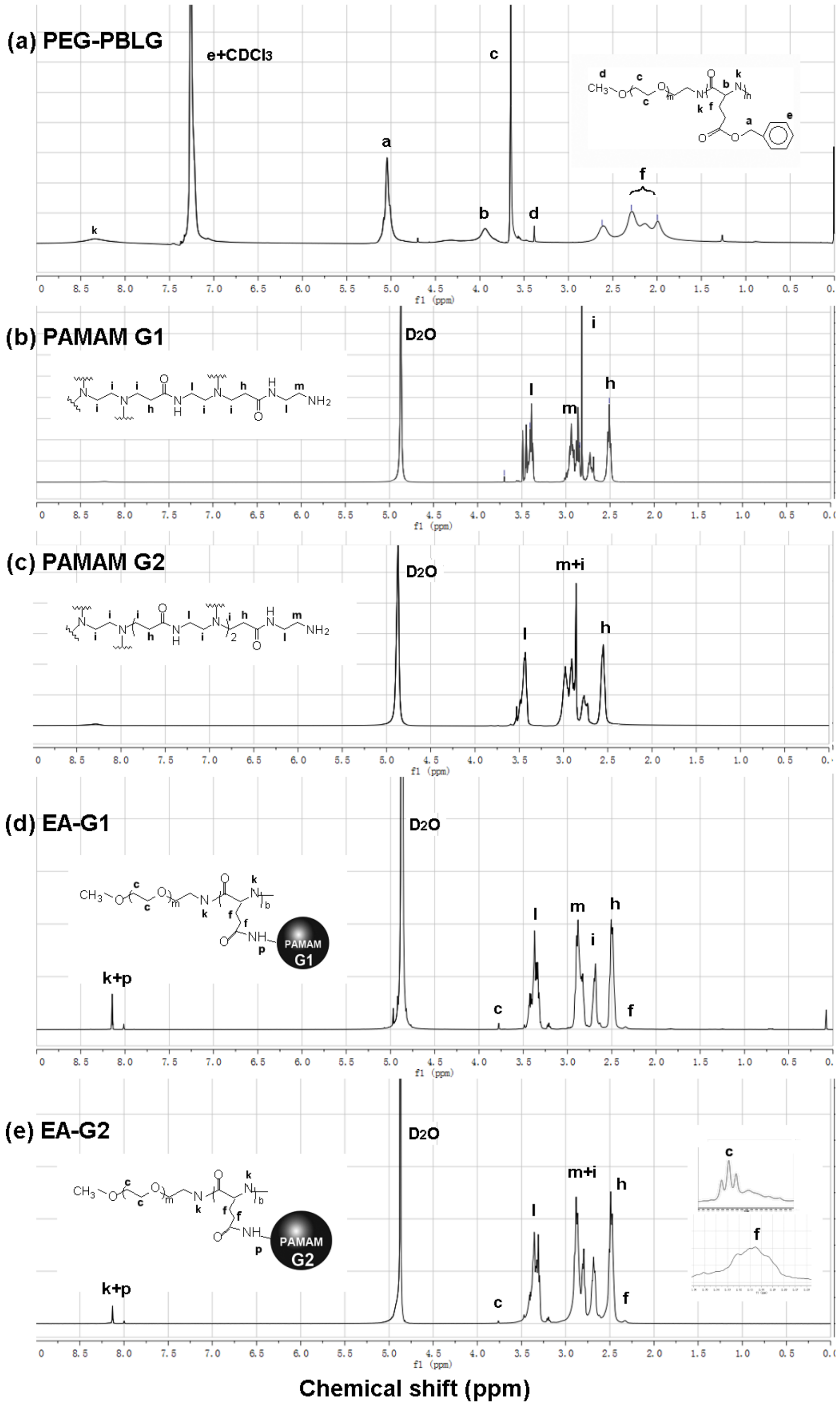

Figure S5 ^{1}H-NMR spectra of PEG-PBLG **(a)**; PAMAM G1**(b)**; PAMAM G2**(c)**; EA-G1**(d)**; EA-G2**(e)**.

(3) ^{1}H-NMR spectrum of re-synthesized EA-G2

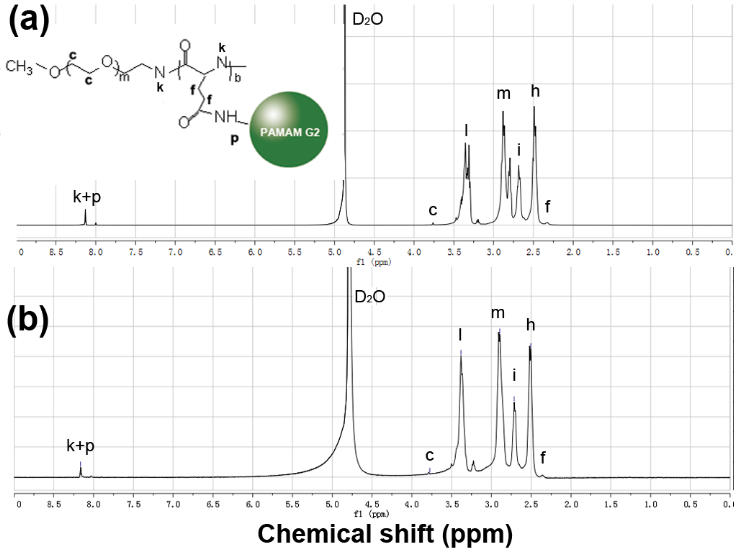

Figure S6 ^{1}H-NMR spectra of different EA-G2: synthesized in 03-2011 and dialyzed with dialysis tube (MWCO 3,500) for 48h **(a)**; synthesized in 07-2013 and dialyzed with dialysis tube (MWCO 14,000) for 72h **(b)**

The ^{1}H NMR of new EA-G2 (Fig.S6b) is quite similar to the of old EA-G2 (Fig.S6a). In Fig,S6b the **c** peak at 3.78 ppm is still very weak, but the **l**, **m**, **i** and **h** peaks at 3.38, 2.89, 2.72 and 2.52 ppm are still relatively strong suggesting PEG blocks occupy a very small proportion in both new EA-G2 or old EA-G2. Although the pores sizes of dialysis tube were increased and dialysis time was prolonged, but the situation of very small content of PEG blocks in EA-G2 did not changed.

(4) GPC analysis

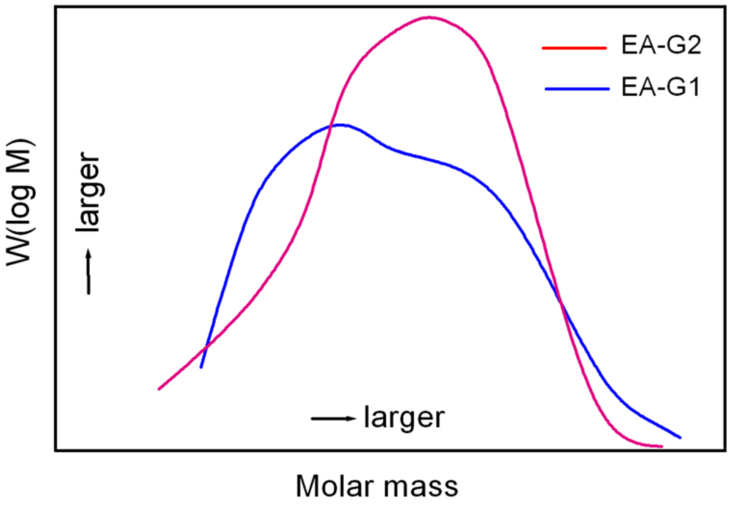

Figure S7 GPC of EA-G2 and EA-G1 copolymers

The GPC was measured on a chromatograph (Agilent 1100HPLC, USA), linear polyethylene glycol was used as standard polymer. As shown in Fig. S7 the molecular weight distribution of EA-G2 (or EA-G1) exihibited unimodal curve, and any other peak was not found, which proved the EA-G2 (or EA-G1) was a copolymer and not a mixture. The average molecular weight of EA-G2 was larger than that of EA-G1. Unfortunately, the molecular weight measured by GPC method was much smaller than that obtained from ^{1}H NMR method, because EA-G2 (or EA-G1) contained a great number of PAMAM G2 (or G1) with the highly-branched dendrimer structure and very small molecular volume.