Electronic Supplementary Material (ESI) for RSC Advances.

Supplementary information

Versatile Surface Charge-Mediated Anti-Fouling UF/MF Membrane Comprising Charged Hyperbranched Polyglycerols (HPGs) and PVDF Membranes

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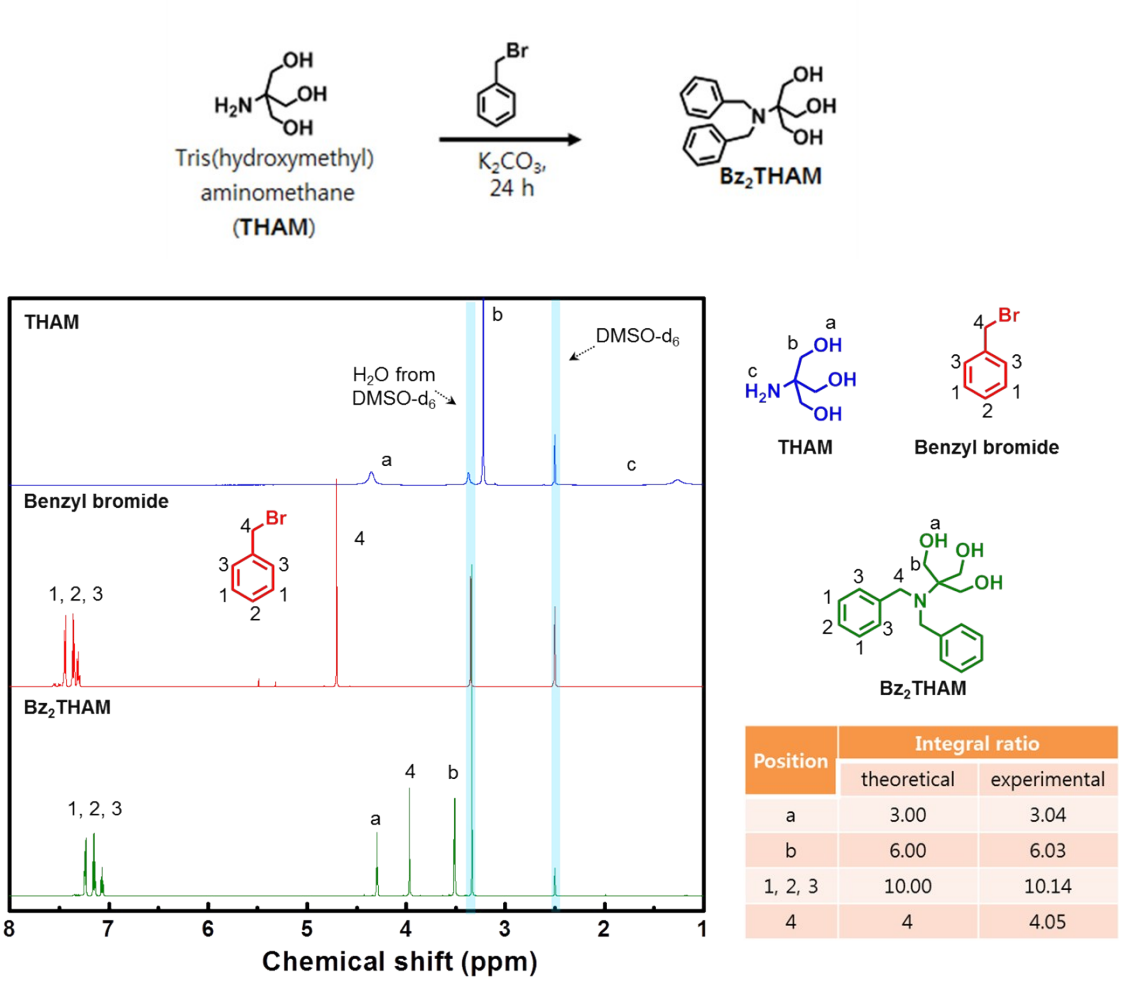
Synthesis of N,N-dibenzyl tris(hydroxymethyl) aminomethane (Bz2THAM)

Tris(hydroxymethyl) aminomethane (THAM) was reacted with benzyl bromide to synthesize the benzyl protected three armed initiator i.e., Bz_2THAM, which protected the amino functional group during anionic polymerization. The Bz2THAM was synthesized following description. The benzyl bromide (34 g, 0.2 mol) and the THAM (11 g, 0.09 mol) were dissolved into 150 mL of DMF solvent. After dissolution of the reagents, K_2CO_3 (27.6 g, 0.1 mol) was added to the above solution. The mixture was refluxed at 105 °C for 3 hours. The residual precipitates were filtered out and DMF solvent was then removed by evaporation. The residual product was dissolved into $CHCl_3$ and the solution was rinsed with saturated $NaHCO_3$ aqueous solution to eliminate residual salts. After obtain of $CHCl_3$ layer, the solvent was removed by evaporation. Next, the crude product was refined by recrystallization from ethyl acetate. The final product was dried under vacuum for overnight.



Position	Integral ratio	
	theoretical	experimental
a	3.00	3.04
b	6.00	6.03
1, 2, 3	10.00	10.14
4	4	4.05

Fig. S1. (top) Synthesis scheme and (bottom) ^{1}H NMR spectra of *N,N*-dibenzyl tris(hydroxymethyl) aminomethane (Bz_2THAM)

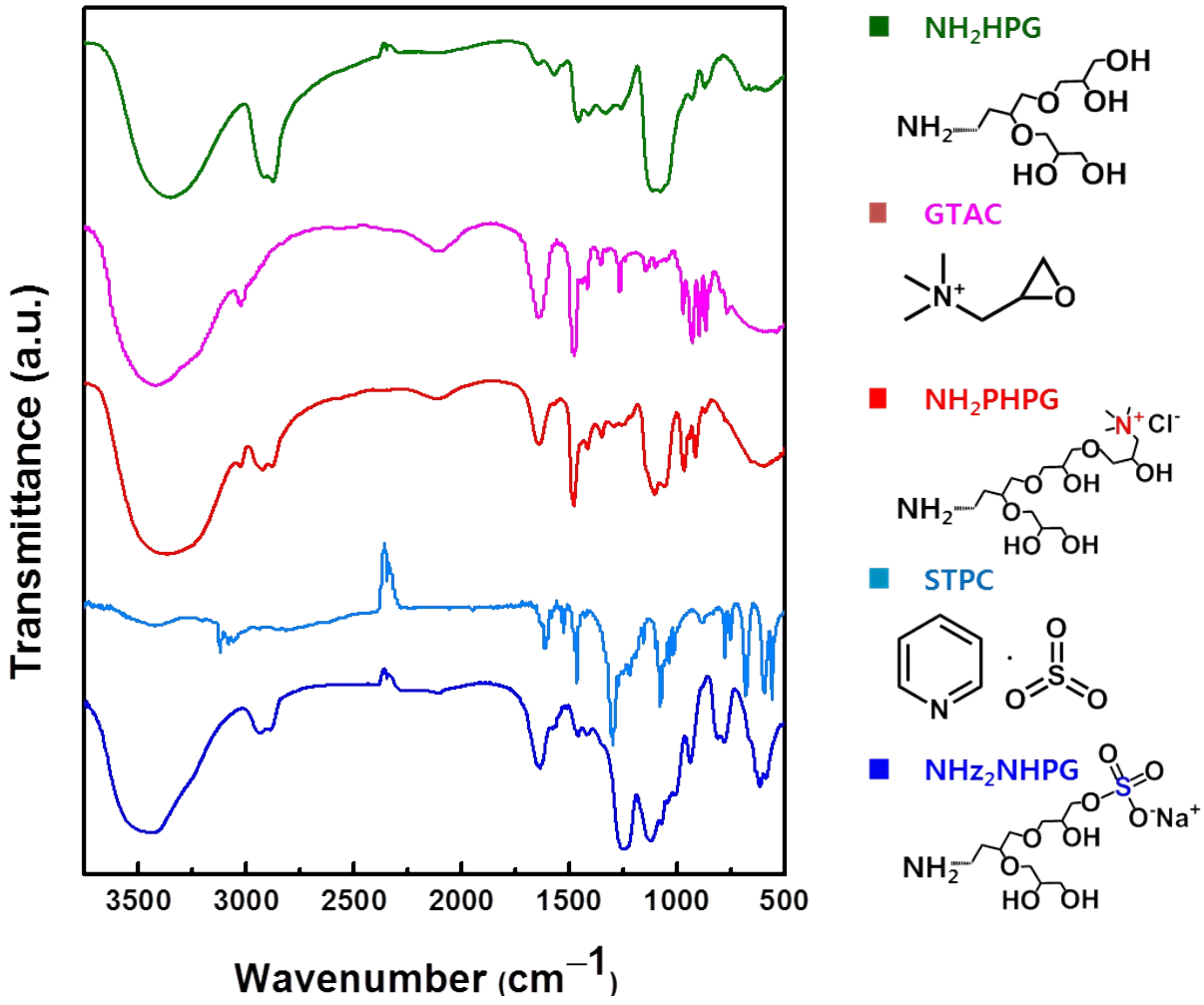
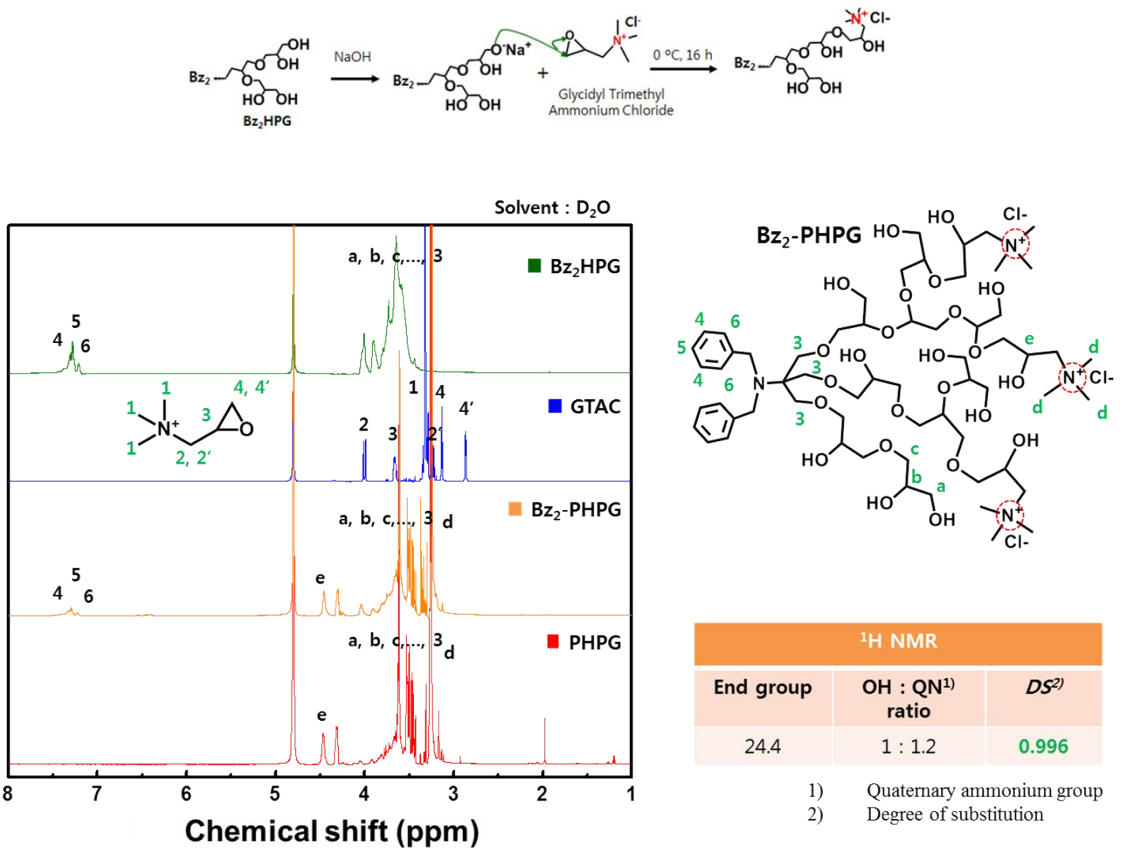


Fig. S2. FT-IR spectra of amino functionalized hyperbranched polyglycerol (NH_2-HPG), glycidyl trimethyl ammonium chloride (GTAC), positively charged modified hyperbranched polyglycerol (PHPG), Sulfur trioxide pyridine complex (STPC) and negatively charged modified hyperbranched polyglycerol (NHPG).



^{1}H NMR		
End group	OH : QN[1] ratio	*DS*[2]
24.4	1 : 1.2	0.996

1) Quaternary ammonium group
2) Degree of substitution

Fig. S3. (top) modification scheme for positively charged hyperbranched polyglycerol (PHPG) and (bottom) ^{1}H NMR spectra of benzyl protected HPG (Bz_2HPG), GTAC, Benzyl protected PHPG and debenzylated PHPG

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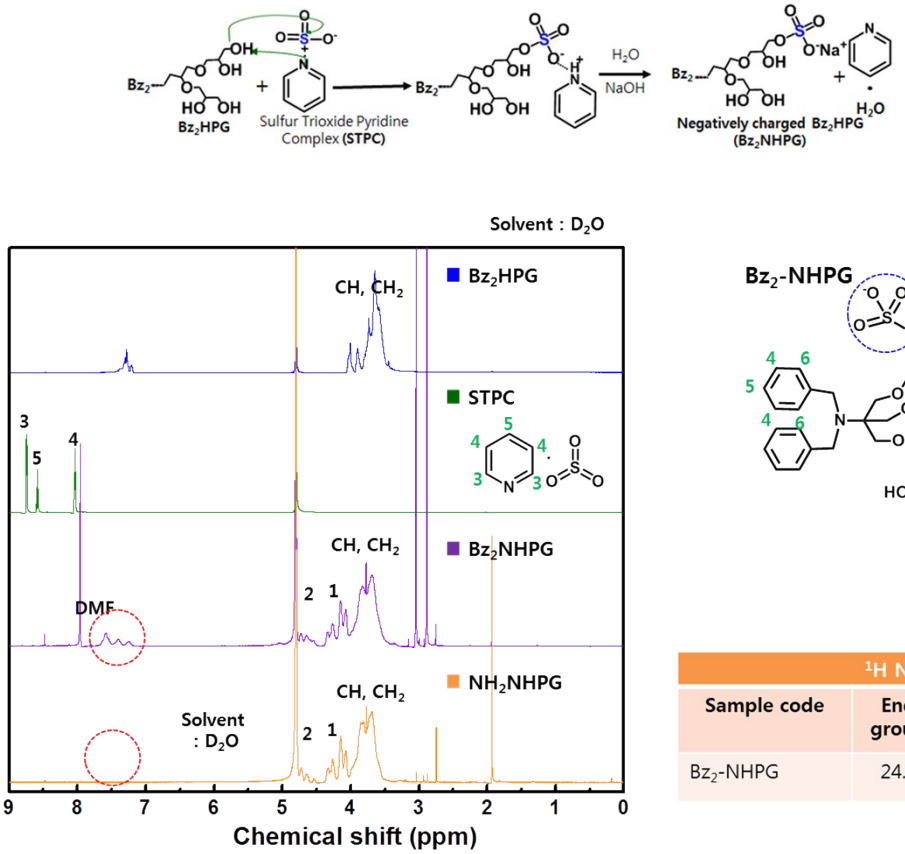

^{1}H NMR			
Sample code	End group	OH : ST ratio	*DS*
Bz_2-NHPG	24.4	1 : 1.01	0.67

Fig. S4. (top) modification scheme for negatively charged hyperbranched polyglycerol (NHPG) and (bottom) ^{1}H NMR spectra of benzyl protected HPG (Bz_2HPG), STPC, Benzyl protected NHPG and debenzylated NHPG.

Table S1. Atomic concentration of neat-PVDF, PVDF-HPG, PVDF-PHPG and PVDF-NHPG membranes detected by XPS analysis

Sample / Element	neat-PVDF	PVDF-HPG	PVDF-PHPG	PVDF-NHPG
C	48.73	52.55	54.42	55.21
N	NA	3.26	3.56	3.74
O	1.74	16.13	14.96	13.98
F	49.53	28.06	27.06	26.83
S	NA	NA	NA	0.24

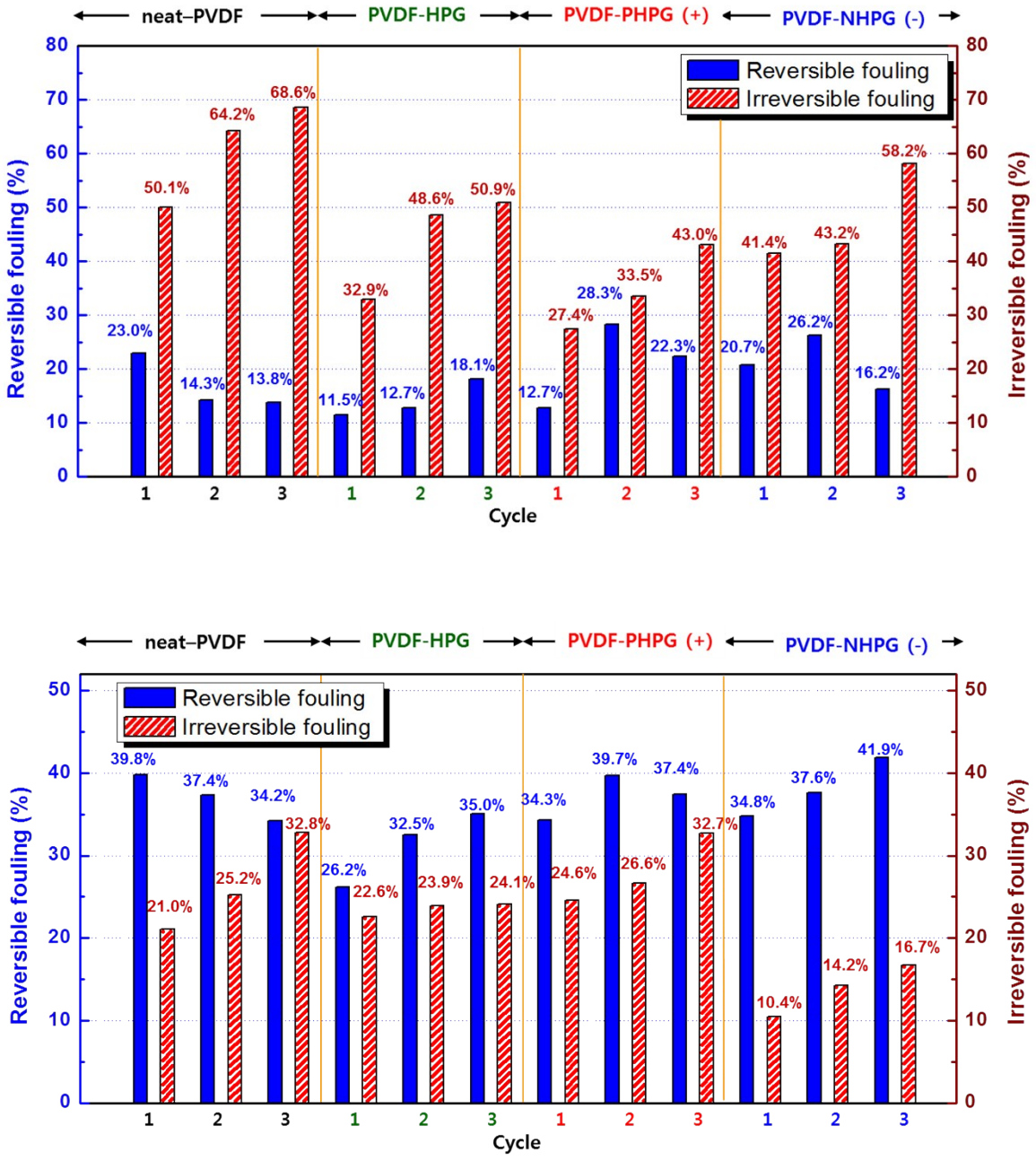

Fig. S5. Calculated reversible and irreversible fouling percentages of the neat-PVDF, PVDF-HPG, PVDF-PHPG and PVDF-NHPG for (top) 500 ppm lysozyme (LYZ) and 500 ppm bovine serum albumin (BSA) filtration tests.

Table S2. Summary of fouling recovery rate (FRR) for surface modified anti-fouling membranes in the literatures

Membrane material	Surface modification method	foulants	FRR (%)	ref
PVDF	Grafting charged hyperbranched polyglycerols	BSA LYZ	89.6 (BSA, PVDF-NHPG) 72.6 (LYZ, PVDF-PHPG)	This study
PVDF	Blending zwitterion	BSA	61.2 – 81.2	1
PP	Grafting zwitterion	BSA, LYZ	91.2 (BSA) 90.2 (LYZ)	2
PAN	Grafting zwitterion	BSA	85	3
PVDF	Grafting zwitterion	BSA	73-85.1	4
PAN	Grafting short-chain amino acid	BSA	68.6 (Gly) 77.2 (Ser) 96.9 (Lys)	5
PVDF	Blending poly(*N, N*-dimethyl acrylamide)	BSA, LYZ	82 – 95 (BSA) 82 – 95 (LYZ)	6
PES	Blending Pluronic F127®	BSA LYZ	91.6 – 94.0 (BSA) 88.0 – 91.7 (LYZ)	7
Poly(ether imide)	Grafting poly(ethylene glycol)	BSA	70.3 – 85.6	8
PES	Blending carbon nanotube	BSA	59.5 – 79.4	9
PSf	Coating organic/inorganic star-shape polymer	BSA	94 (30 min filtration) 86 (180 min filtration)	10
PVDF	Blending hyperbranched polymer functionalized multi-walled carbon nanotube	BSA	85.3 – 95.7	11

Abbreviations: PVDF: Poly(vinylidene fluoride), PP: Poly(propylene), PAN: Poly(acrylonitrile), PES: Poly(ether sulfone), PSf: Polysulfone

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