

Supporting Information

Construction of Hierarchical Fouling Resistance Surfaces onto Poly(vinylidene fluoride) Membranes for Combating Membrane Biofouling

Xue Li^a, Xuefeng Hu^b and Tao Cai^{a,*}

^aKey Laboratory of Biomedical Polymers of Ministry of Education, College of Chemistry and Molecular Science, Wuhan University, Wuhan, Hubei 430072, P. R. China

^bNational Engineering Research Center for Biomaterials, Sichuan University, Chengdu, Sichuan 610065, P. R. China

*Corresponding author.

Email address: chemcaitao@whu.edu.cn

Experiment Section

Materials

Sodium methoxide (NaOCH_3 , 95%), glycidol (96%) and 1,4-dioxane (99.8%) were obtained from Sigma-Aldrich Chem. Co. and used as received, unless otherwise stated. Glycidol and 1,4-dioxane were freshly distilled prior to use. *N,N*-dibenzyl tris(hydroxymethyl) aminomethane (B_2THAM) was prepared according to the methods reported in the literature.^{1,2}

Synthesis of the Amino-Terminated Hyperbranched Polyglycerol (HPG-NH_2)

Amino-terminated hyperbranched polyglycerol (HPG-NH_2) was synthesized in 1,4-dioxane from anionic ring-opening multibranching polymerization of glycidol, using *N,N*-dibenzyl tris(hydroxymethyl) aminomethane (B_2THAM) as the initiator and NaOCH_3 as the catalyst, followed by deprotection of benzyl groups in the $\text{HPG-B}_2\text{THAM}$ using palladium hydroxide on charcoal as the catalyst (Scheme S1). Briefly, B_2THAM (2.53 g, 8.39 mmol), NaOCH_3 (135.9 mg, 2.52 mmol) and anhydrous methanol (10 mL) were introduced into a 100 mL double-necked round bottom flask. The solution was stirred at room temperature for 2 h and evacuated at 80 °C for 6 h to remove methanol. Then 20 mL of anhydrous 1,4-dioxane was transferred into the round bottom flask. The mixture was purged with argon for 20 min to remove the dissolved oxygen. The reaction flask was sealed under an argon atmosphere, and the reaction was allowed to proceed at 100 °C with stirring. Glycidol (10 mL, 151 mmol) in 1,4-dioxane (20 mL) was purged with argon for 30 min. It was added slowly with a syringe to the reaction mixture over a period of approximately 12 h. After complete addition of the solution, the reaction mixture was allowed to stir for an additional 6 h. At the end of the reaction, the reaction flask was quenched in cold water and diluted with methanol, followed by pouring into

500 mL of diethyl ether. The adduct was purified twice by re-dissolving in methanol and re-precipitating in diethyl ether. The HPG-B₂THAM polymer was dried under vacuum at 80 °C to give a viscous liquid (yield ~84%). $[M]_0/[I]_0 = 18:1$; $M_{n,NMR} = 1380$ g/mol. ¹H NMR (DMSO-*d*₆, δ , ppm, TMS): 7.05-7.30 (10H, aromatic ring), 4.35-4.85 (H $\times(m+3)$, -OH), 3.9-4.0 (4H, PhCH₂N-), 3.25-3.85 (H $\times(5m+6)$, -OCH-, -OCH₂-), where the number *m* denotes the degree of polymerization of glycidol monomers in HPG-B₂THAM homopolymers.

In a typical reaction, HPG-B₂THAM (1.0 g) was dissolved in 30 mL of methanol. Palladium hydroxide on activated charcoal (200 mg) was added into the solution. The mixture was flushed with hydrogen and stirred at room temperature for 48 h. After that, the reaction mixture was filtered, followed by precipitating into 200 mL of diethyl ether. The crude product was redissolved in 30 mL of ethanol. The re-dissolution and precipitation process was repeated twice. Finally, the HPG-NH₂ polymer was obtained after drying under reduced pressure at room temperature for 24 h (yield ~95%). $M_{n,NMR} = 1200$ g/mol. ¹H NMR (DMSO-*d*₆, δ , ppm, TMS): 4.35-4.85 (H $\times(m+5)$, -OH, -NH₂), 3.25-3.85 (H $\times(5m+6)$, -OCH-, -OCH₂-), where the number *m* denotes the degree of polymerization of glycidol monomers in HPG-NH₂ homopolymers.

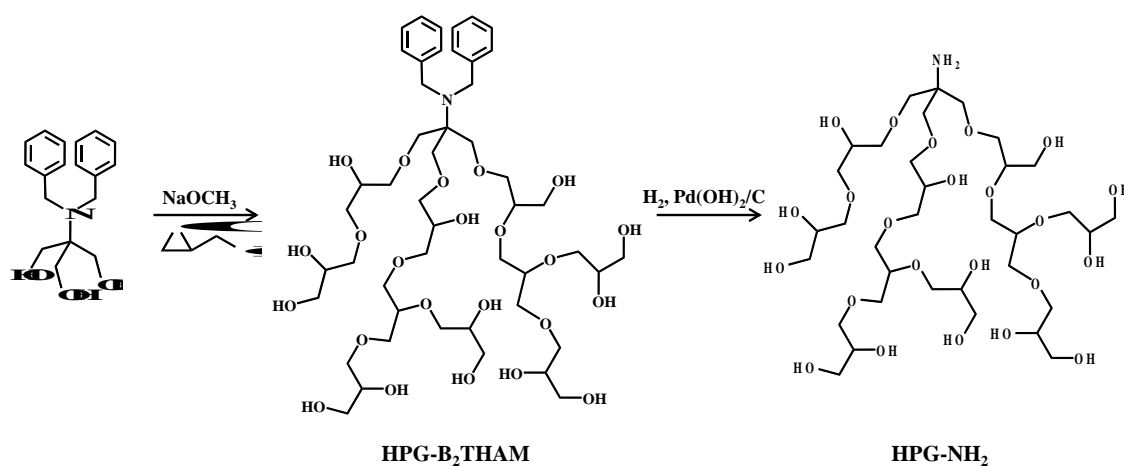
Determination of Peroxides Content in Ozone-Pretreated PVDF³

About 200 mg ozone-pretreated PVDF was dissolved into 20 mL of NMP containing 12 mg of 2,2-diphenyl-1-picrylhydrazyl (DPPH). The solution was degassed with purified argon for 30 min. The reaction mixture was then placed in a thermostated oil bath at 110 °C for 10 min. After that, the reaction mixture was quenched in an icy water bath,

followed by precipitated in excessive isopropanol. After 30 min, the solution was filtered and the residual DPPH concentration was determined by colorimetry at 520 nm. The number of moles of peroxides per gram of the ozone-pretreated PVDF can be calculated from the following equation.

$$T = [(C_0 - C) \times 180] / (2000 \times 394.33 \times m)$$

where C_0 and C are the initial and final DPPH concentration in g/L, respectively, and m is the weight of PVDF in grams.



Scheme S1. Synthesis of amino-terminated hyperbranched polyglycerol (HPG-NH₂).

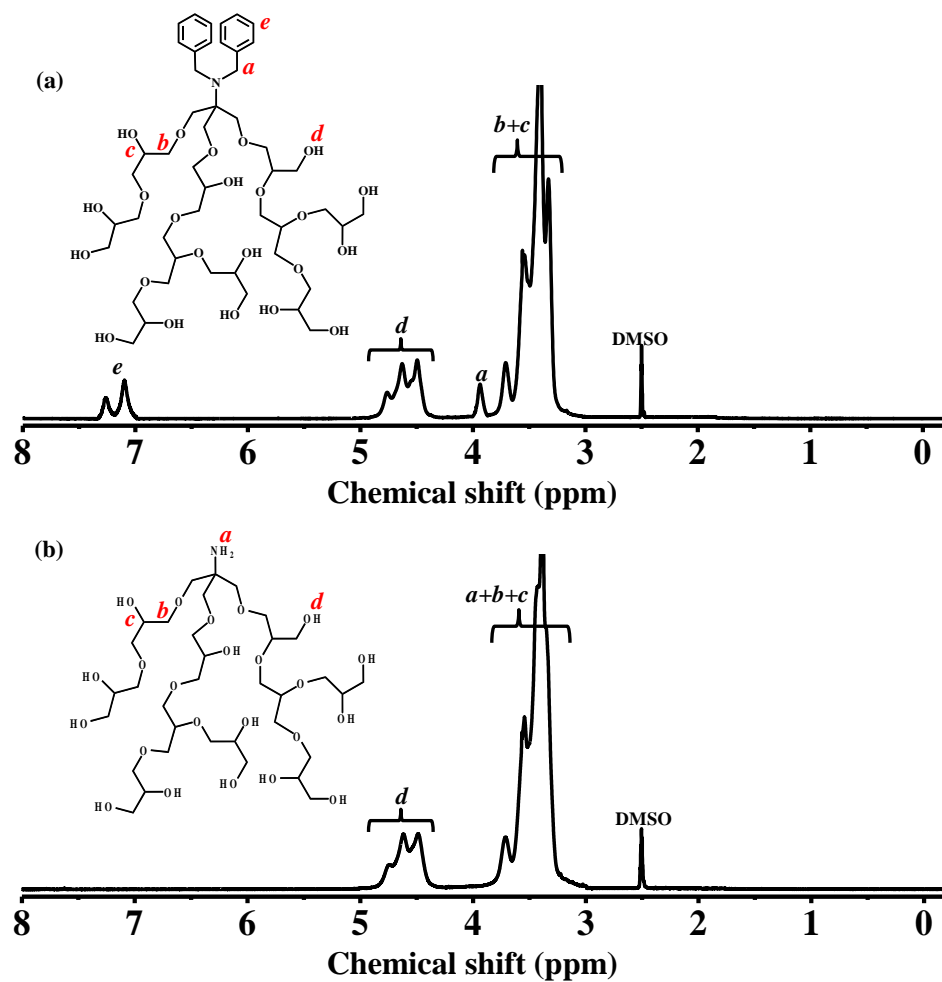


Figure S1. ^1H NMR spectra of the (a) HPG-B₂THAM and (b) HPG-NH₂ homopolymers in $\text{DMSO}-d_6$.

References

- (1) Nuhn, L.; Schull, C.; Frey, H.; Zentel, R. Combining Ring-Opening Multibranching and RAFT Polymerization: Multifunctional Linear-Hyperbranched Block Copolymers via Hyperbranched Macro-Chain-Transfer Agents. *Macromolecules* **2013**, *46*, 2892-2904.
- (2) Schull, C.; Nuhn, L.; Mangold, C.; Christ, E.; Zentel, R.; Frey, H. Linear-Hyperbranched Graft-Copolymers via Grafting-to Strategy Based on Hyperbranched Dendron Analogues and Reactive Ester Polymers. *Macromolecules* **2012**, *45*, 5901-5910.
- (3) Liu, Y.; Lee, J. Y.; Kang, E. T.; Wang, P.; Tan, K. L. Synthesis, Characterization and Electrochemical Transport Properties of the Poly(ethylene glycol)-Grafted Poly(vinylidene fluoride) nanoporous membranes. *React. Funct. Polym.* **2001**, *47*, 201-213.