Supporting Information

Stretchable Self-Healing Polymeric Networks with Recyclability and Dual Responsiveness

Xingyi Dai[†], Yuzhang Du[†], Yansong Wang,[,‡] Yuncong Liu[†], Nianxi Xu[‡], Yifan Li[‖], Dongzhi Shan[‡], Ben Bin Xu[‖] and Jie Kong[*,†]*

[†]MOE Key Laboratory of Materials Physics and Chemistry in Extraordinary Conditions, Shaanxi Key Laboratory of Macromolecular Science and Technology, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an, 710072, China

[‡]Key Laboratory of Optical System Advance Manufacturing Technology, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, 130033, China

[‖]Mechanical and Construction Engineering, Faculty of Engineering and Environment, Northumbria University, Newcastle upon Tyne, NE1 8ST, UK

*Corresponding Author, E-mail: kongjie@nwpu.edu.cn (J.K.), wangyansong99@163.com (Y.W.)

Synthesis of 1, 1, 1-tris[(4-tolylsulfonyl)methyl]ethane

The trimethylolethane (2.45g, 20 mmol) and triethylamine (12.6 mL, 90 mmol) were mixed in dichloromethane (100 mL). The solution was cooled to 0 °C in ice-water bath before p-toluenesulfochloride (13.34g, 70 mmol) was slowly added to the above mixture. The flask was then removed from the ice-water bath and the reaction was allowed to proceed at room temperature. After the reaction, the mixture was washed with 200 mL 1 M HCl solution (twice, 100 mL each), 200 mL water (twice, 100 mL each) and dried over anhydrous $MgSO_4$. After concentrated by rotary evaporation, the crude product was purified by crystallization from THF/ethanol/isopropanol (10/15/25 v/v) to obtain a white crystalline solid (9.8 g, yield: 84.1%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, 6H, ArH), 7.38 (d, 6H, ArH), 3.79 (s, 6H, -CH_2-), 2.49 (s, 9H, -CH_3), 0.92 (s, 3H, -CH_3).

Synthesis of 1, 1, 1-tris[(4-formylphenoxy)methyl]ethane

The 1, 1, 1-tris[(4-tolylsulfonyl)methyl]ethane (5.83g, 10 mmol), 4-hydroxybenzaldehyde (4.98g, 40 mmol) and potassium carbonate (5.58 g, 40 mmol) were mix together in 30 mL anhydrous DMF under nitrogen atmosphere. The reaction mixture was heated at 150 °C under reflux overnight. Then the mixture was extracted into 100 mL dichloromethane and washed with 200 mL water (twice, 100 mL each), 100 mL saturated brine and dried over anhydrous $MgSO_4$. The solvent was evaporated and the crude product was purified by silica gel column chromatography using dichloromethane as eluent to afford a white solid (3.2 g, yield: 74.1%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s 3H, -CHO), 7.87 (d, 6H, ArH), 7.05 (d, 6H, ArH), 4.22 (s, 6H, -CH_2-), 1.41 (s, 3H, -CH_3).

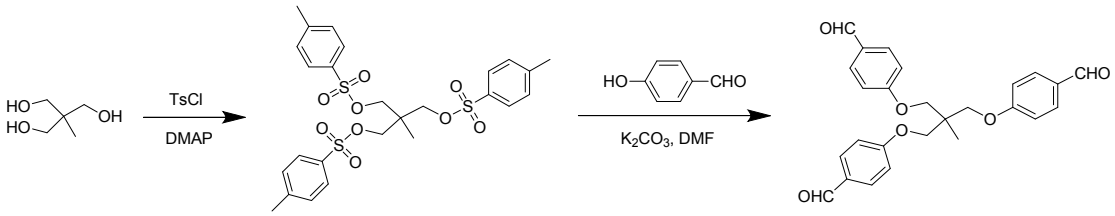

Figure S1 Synthesis of 1, 1, 1-tris[(4-formylphenoxy)methyl]ethane.

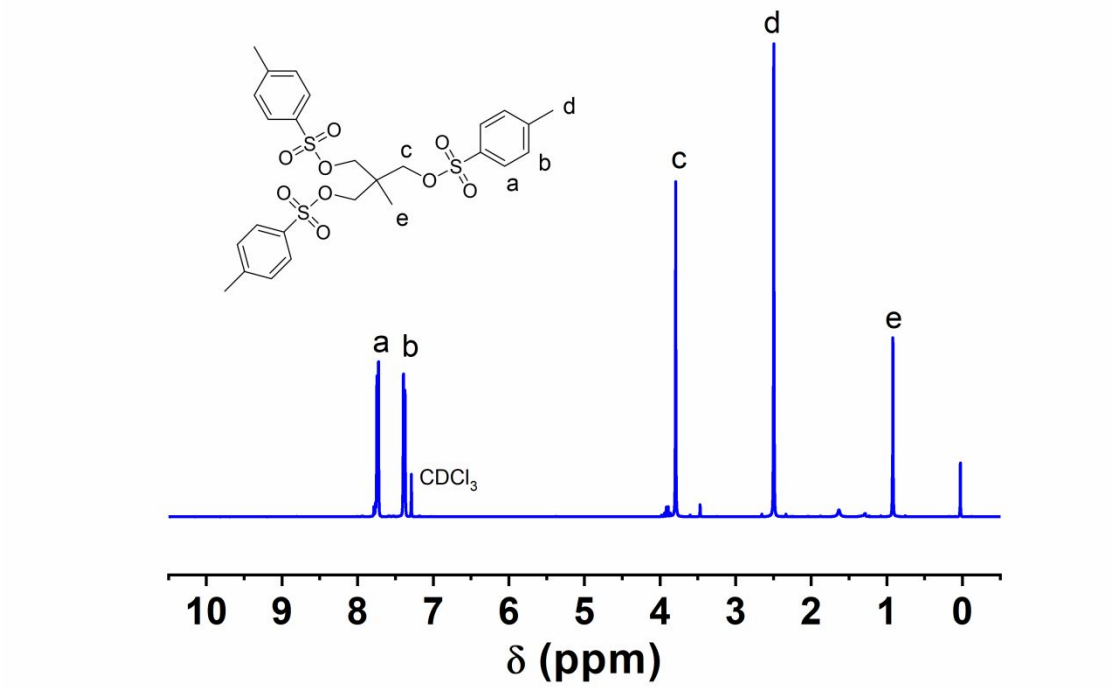

Figure S2 ^{1}H NMR spectra of tris[(4-tolylsulfonyl)methyl]ethane in $CDCl_3$.

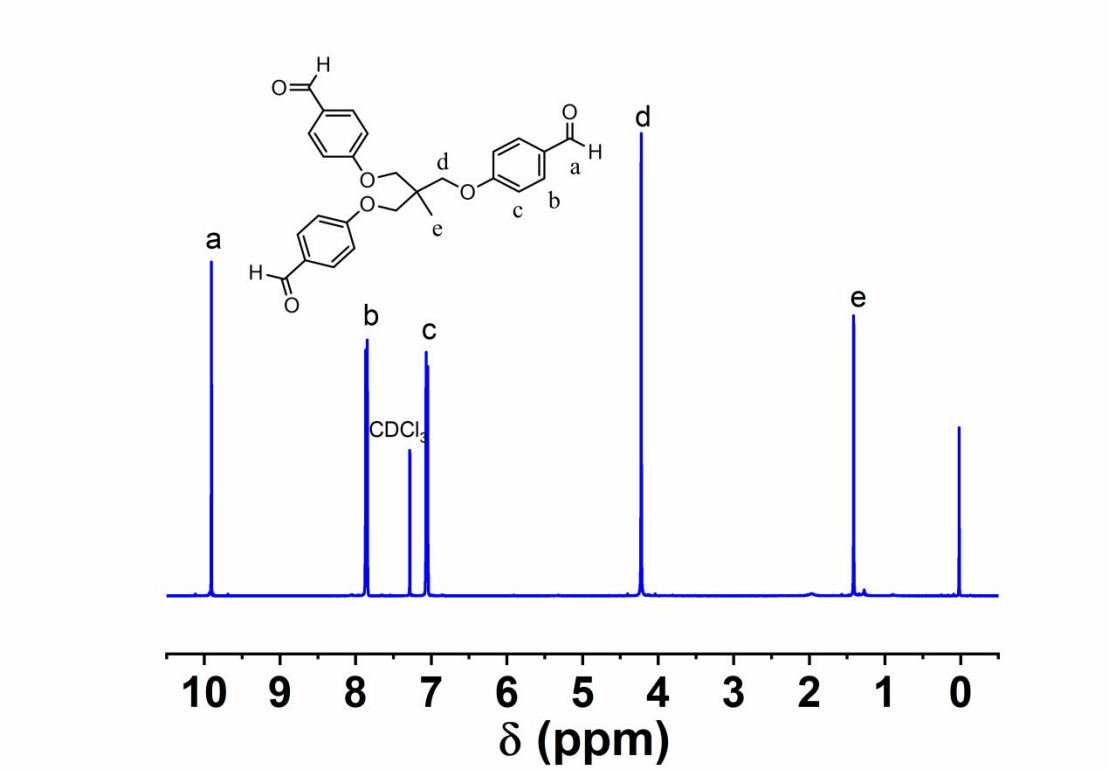

Figure S3 ^{1}H NMR spectra of 1, 1, 1-tris[(4-formylphenoxy)methyl]ethane in $CDCl_3$.

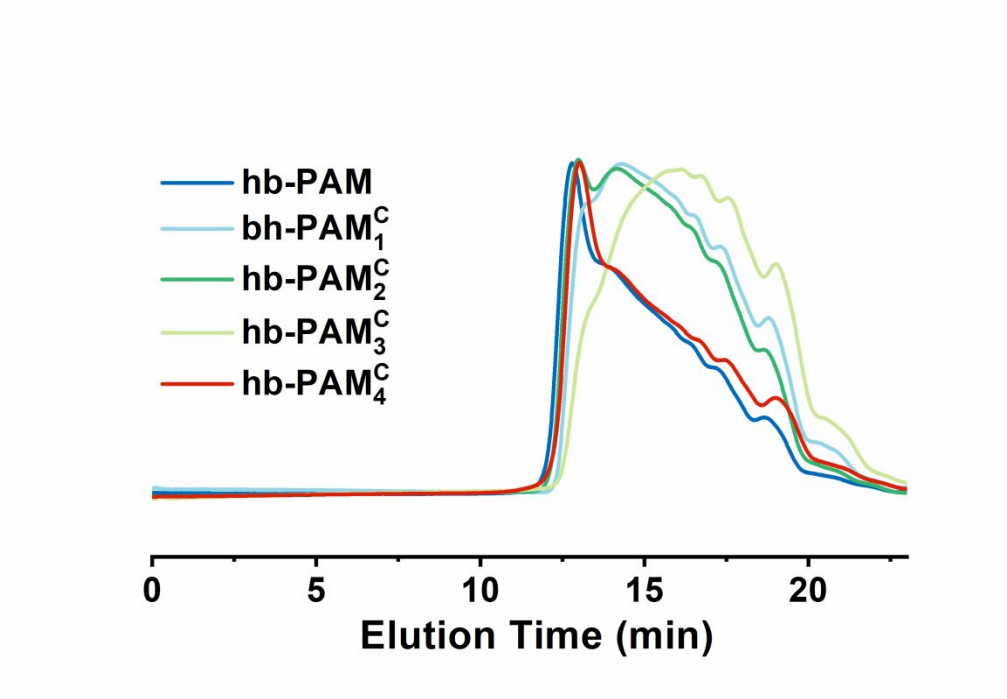

Figure S4 SEC traces of hyperbranched polyazomethines.