Supporting information

High strength biocompatible PEG single-network hydrogels

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Synthesis of tetrakis (2-propynyloxymethyl) methane (TPOM)

Tetrakis (2-propynyloxymethyl) methane (TPOM) was synthesized according to the reported method.[1] Briefly, KOH (15g, 268 mmol) was added into 30 ml of anhydrous DMF containing 14.7 mmol pentaerythritol. The solution was kept under magnetic stirring at room temperature for 90 min. Propargyl bromide (20g, 0.17mmol) was slowly added into the above solution over a 20 min-period. The reaction mixture was then heated at 40°C overnight. After being cooled, the mixture was quenched with water and extracted with 50 ml of ethyl ether thrice. The organic layers were combined, washed with water and brine in order, and dried over Na_2SO_4. After the removal of ethyl ether by rotary evaporation, the residue was further purified by passing a silica gel column using a mixed solution of ethyl acetate/hexane (v/v = 2:10) as an eluent. About 2.98 g of product was obtained (yield: 79%).

Synthesis of *α*, *ω*-diepoxy PEG_n (DEP_n)

DEP_{45} was prepared according to the method reported.[2] Briefly, PEG_{45} (M_n = 2000, 10 g) filtered through a neutral alumina column to remove excess NaH and byproducts. The filtered solution was concentrated by rotary evaporation. The concentrate was precipitated into cold diethyl ether. The precipitate was filtered, washed with diethyl ether thrice, and dried under reduced pressure. The obtained polymers were stored at 4 °C (yield: 96%). DEP_{22} was used in a similar manner to that of DEP_{45}. was first dissolved in dry THF (50 ml). The solution was then dropwise added into the slurry of NaH (0.45 g) in dry THF (100 ml) in a 250 mL three-necked round-bottom flask under nitrogen atmosphere. The reaction mixture was stirred at room temperature for 12 h. Epichlorohydrin (4 ml) was added into the reaction mixture and the solution was stirred for another 24 h. After that, the solution was filtered through a neutral alumina column to remove excess NaH and byproducts. The filtered solution was concentrated by rotary evaporation. The concentrate was precipitated into cold diethyl ether. The precipitate was filtered, washed with diethyl ether thrice, and dried under reduced pressure. The obtained polymers were stored at 4 °C (yield: 96%). DEP_{22} was used in a similar manner to that of DEP_{45}.

Synthesis of *α*, *ω*-diazido PEG_n ($PEG_n(N_3)_2$)

α, *ω*-diazido PEG_n ($PEG_n(N_3)_2$) was prepared from *α*, *ω*-diepoxy PEG_n (DEP_n) according to the method reported previously.[2] DEP_{45} (M_n = 2000, 5 g), sodium azide (1.4 g) and ammonium chloride (0.3 g) were added into 40 mL of DMF/water mixture (v/v = 1:3) in a 100 mL round-bottom flask. The mixture was stirred at 50 °C for 72 h. After the reaction, the solution was extracted using dichloromethane, and the organic phase was allowed to pass through a neutral alumina column to remove the unreacted NaN_3 and NaCl as a byproduct. After the removal of most of the solvent by rotary evaporation, the residue was precipitated in excess cold diethyl ether. The desired polymer was collected by filtration and dried under reduced pressure overnight (yield: 90 %). $PEG_{11}(N_3)_2$ and $PEG_{22}(N_3)_2$ were synthesized in a similar manner to that of $PEG_{45}(N_3)_2$.

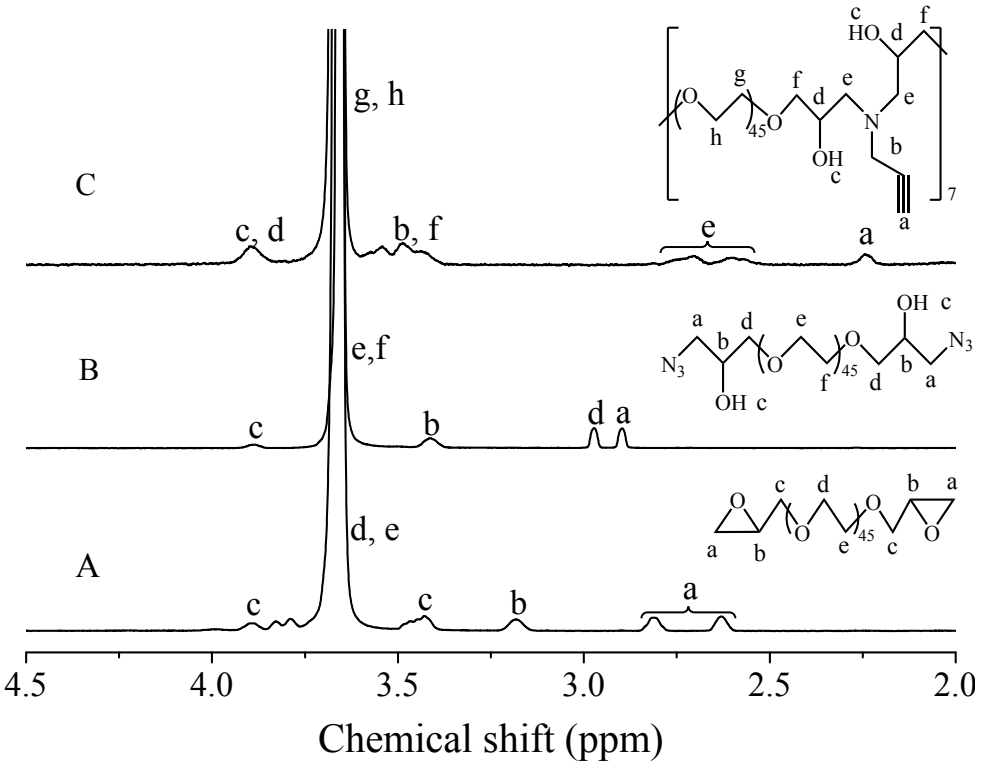

Figure S1. ^{1}H NMR spectra of (A) DEP_{45}, (B) $PEG_{45}(N_3)_2$ and (C) $(PEG_{45}(C{\equiv}CH))_7$ in $CDCl_3$-*d*.

References

1. L. Q. Xu, F. Yao, G. D. Fu and E. T. Kang, *Biomacromolecules*, 2010, **11**, 1810-1817.
2. G. D. Fu, H. Jiang, F. Yao, L. Q. Xu, J. Ling and E. T. Kang, *Macromol. Rapid Commun.*, 2012, **33**, 1523-1527.