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Supporting information for

Dopamine-assisted fixation of drug-loaded polymer multilayers to the osteoarticular implants for tuberculosis therapy

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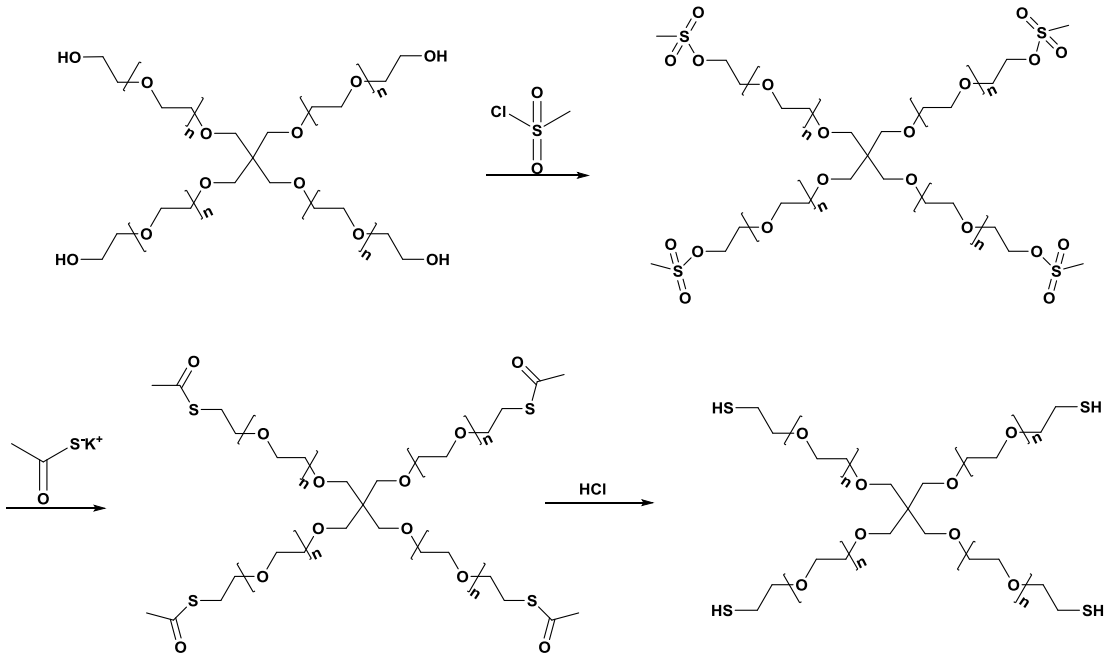
Materials and Methods

Synthesis of 4-armed PEG-SH



The three-step approach to 4-armed PEG-SH was modified based on our previous work.[1] First, 4-armed PEG-OH (10 g, 1 mmol) and triethylamine (1.38 mL, 10 mmol) were dissolved in anhydrous DCM (100 mL).The mixture was cooled down to 0 ℃ for 30 min, and then methanesulfonyl chloride (0.78 mL, 10 mmol) was added. After stirring for 8 h at room temperature, the mixture was quenched by $NaHCO_3$ saturated solution (80 mL). The organic phase was further washed with DI water (3×100 mL) and dried over $MgSO_4$. After evaporation, the 4-armed PEG-SO_3CH_3 (8.9 g, 85%) was dried in vacuum. ^{1}H NMR in $CDCl_3$: δ = 3.07 (s, –SO_3CH_3), 3.40 (s, –$C(CH_2)_4O$-), 3.46–3.75 (m, PEG main-chain protons), 4.36–4.38 ppm (t, –CH_2SO_3-).

Second, 4-armed PEG-SO_3CH_3 (8.9 g, 0.85 mmol) and potassium thioacetate (1.20 g, 8.5 mmol) were dissolved in anhydrous THF (150 mL). The mixture was stirred under a nitrogen atmosphere at 60 ℃. After stirring for 5 h, the reaction was quenched by DI water and extracted with chloroform. The chloroform layer was collected, dried over $MgSO_4$ and evaporated. The 4-armed PEG-$SCOCH_3$ (7.3 g, 83%) was obtained by precipitation three times from ice-cold diethyl ether and dried in vacuum. ^{1}H NMR in $CDCl_3$: δ = 2.34 (s, –$SCOCH_3$), 3.08–3.11 (t, –CH_2SCO–), 3.42 (s, –$C(CH_2)_4O$-), 3.46–3.83 ppm (m, PEG main-chain protons).

Third, 4-armed PEG-$SCOCH_3$ (7.3 g, 0.70 mmol) was dissolved in 100 mL of methanol. Concentrated hydrochloric acid (20 mL) was added to the solution. The mixture was refluxed at 80 ℃ for 72 h under a nitrogen atmosphere. Then the reaction was quenched by DI water and extracted with chloroform. The chloroform layer was collected, dried over $MgSO_4$ and evaporated. The 4-armed PEG-SH (6.3 g, 90%) was obtained by precipitation three times from ice-cold diethyl ether and dried in vacuum. ^{1}H NMR in $CDCl_3$: δ = 1.55–1.59 (m, –OCH_2CH_2SH), 2.64–2.69 (q, –CH_2SH), 3.42 (s, –$C(CH_2)_4O$-), 3.46–3.83 ppm (m, PEG main-chain protons). The spectra of each product are provided in supplementary information.

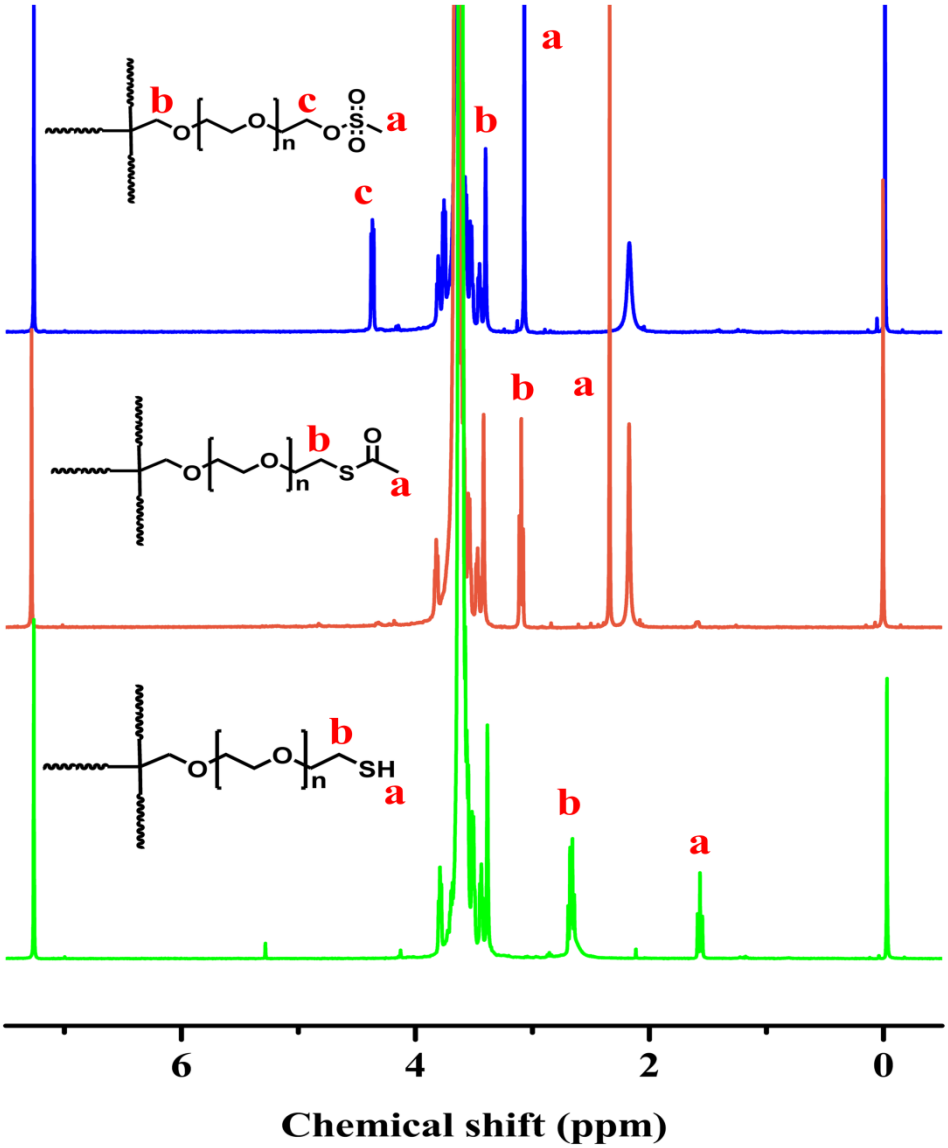


Figure S1. ^{1}H NMR spectra of (A) 4-armed PEG-SO_3CH_3, (B) 4-armed PEG-$SCOCH_3$ and (C) 4-armed PEG-SH.

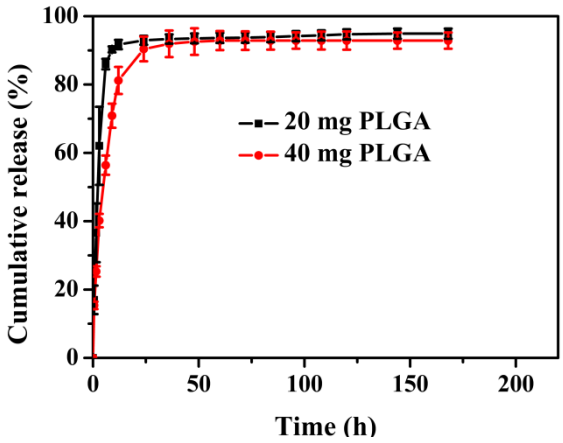


Figure S2. Effects of the thickness of the PLGA membranes on the release of INH directly entrapped in the PEG hydrogel films on Ti rods.

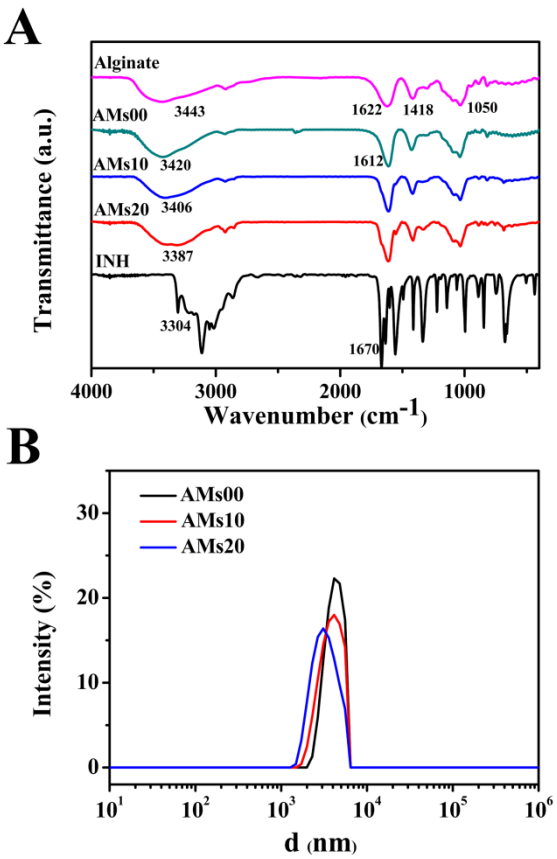


Figure S3. (A) FT-IR spectra of alginate, INH and alginate microparticles (AMs) with different INH contents. (B) Size distribution of blank and INH-loaded AMs.

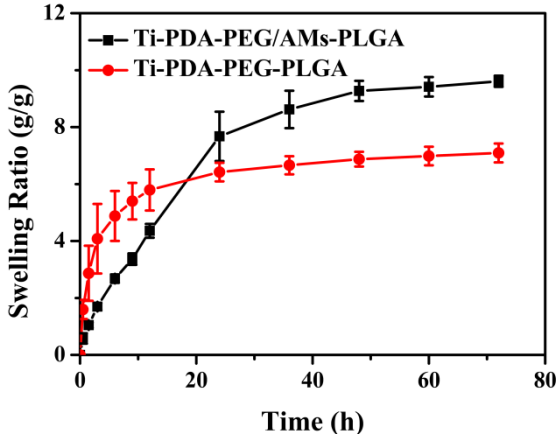


Figure S4. Swelling behaviors of the pure PEG gel film and PEG/AMs gel film on Ti substrates.

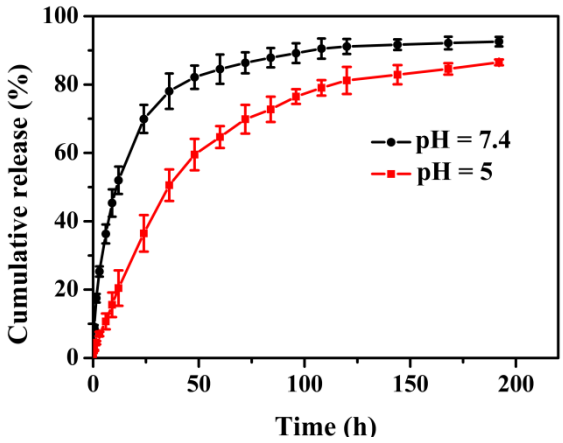


Figure S5. Effects of pH values on INH release from Ti rods.

Reference

1 X. Wang, D. Li, F. Yang, H. Shen, Z. Li and D. Wu, *Polym. Chem.*, 2013, **4**, 4596.