

Supporting Information

Sulfoxidation inside Hypercrosslinked Microporous Network Nanotubes Catalyst

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Experimental Section

Materials.

All reagents were used as received without any further purification unless stated otherwise. Glycidyl methacrylate (GM, Acros 97%) was distilled before use. Styrene (Sinopharm Chemical Reagent Co. Ltd 99%) was purified by passing over basic alumina. Dichloromethane (DCM) and N,N-dimethylformamide (DMF) were distilled from calcium hydride. 2,2-Azobisisobutyronitrile (AIBN) and D,L-lactide were purified by recrystallization from methanol and ethyl acetate, respectively. Trifluoromethanesulfonic acid was obtained from Energy Chemical Corporation. Sodium tungstate dihydrate was obtained from Aladdin Industrial Corporation. Tert-butyl (2-acrylamidoethyl)carbamate (BAEAM)¹, S-1-Dodecyl-S'-(α,α' -dimethyl- α' -acetic acid)trithiocarbonate (TC)², 2-cyanoprop-2-yl-4-cyanodithiobenzoate (CPD)³ were synthesized according to literature procedures.

Measurements.

All ¹H NMR spectra were recorded on a Bruker AVANCEIII™ 500 spectrometer (500 MHz) by using CDCl₃ or DMSO-d₆ as a solvent. GPC data were obtained from Waters GPC system equipped with a Waters 2414 refractive index (RI) detector, a 1515 isocratic HPLC pump, and two Waters HPLC columns. DMF (HPLC grade) with 0.1 M LiBr was used as the solvent for polymers and eluent for GPC with a flow rate of 1 ml/min at 65 °C. TEM images were obtained using a JEM-2100F TEM instrument. Samples were prepared by dip-coating a 400 mesh carbon-coated copper grid from the dilute sample solution allowing the solvent to evaporate. GC analyzed were recorded on an GC 7900 Series System with a Hewlett-Packard 5973 Mass Selective Detector (70 eV) using a HP-5MS fused silica capillary column and N₂ as a carrier gas (1 mL/min). The split ratio was 1:50. The injector temperature was 280 °C and detector was 280 °C. The column temperature was kept at 60 °C for 3 min, increased to 280 °C at a rate of 25 °C/min, and then held at 280 °C for 5 min. The W content in the material was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) method (IRIS INTREPID XPS, Thermo Electron, USA). Elemental analyses were conducted by using an elementalVario EL III and the sample was dried in vacuum at ambient temperature.

Synthesis

1. Synthesis of PGM backbone

GM (2 ml), CPD (18 mg), AIBN (2.4 mg) and benzene (2 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 15 h. The mixture was diluted with DCM, precipitated into methanol 3 times and dried under vacuum at room temperature for 24 h. Yield = 1.6 g (76%). GPC (PS standards): $M_n = 56,000$ g/mol, $M_w/M_n = 1.09$. ¹H NMR: n (GM) = 200.

2. Hydrolysis of PGM

PGM (1.0 g), THF (20 ml) and acetic acid (40 ml) were mixed in a 250 ml round-bottom flask. The reaction mixture was stirred and placed in an oil bath at 60 °C, followed by the slow addition of 61.5 ml water over the course of 2 h. After stirring for 24 h at 60 °C, the solvent was removed on a rotary evaporator. The isolated polymer was precipitated from MeOH into diethyl ether 3 times and dried under vacuum at 25 °C for 24 h. Yield = 0.93 g (82%). ¹H NMR: Conversion = 95%+.

3. Synthesis of Poly(GM-g-LA)

Hydrolyzed PGM (500 mg) was dissolved in 50 ml dry DMF in a 250 ml round bottom flask. D,L-lactide (11.7g) was added into the mixture and DBU (0.35ml) was followed. The reaction was continued for 1.5 h at room temperature and the reaction was quenched by 2.44 g benzoic acid. The resulting polymer was precipitated from THF into methanol:water = 1:1(V/V) 3 times and dried at 25 °C under vacuum for 24 h. Yield = 9.3 g (75%). GPC (PS standards): $M_n = 150,000$ g/mol, $M_w/M_n = 1.10$. ¹H NMR: $n(\text{PLA}) = 24$.

4. Synthesis of Poly(GM-g-LA-g-BAEAM)

Hydroxide end groups of the PLA polymer were then modified to install TC as described in the literature⁴. The RAFT modified polymer (240 mg) was mixed with BAEAM (1.2 g), AIBN (1.8 mg) and 1,4-dioxane (7.2 ml) in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The reaction was conducted at 60 °C for 12 h and stopped by opening the flask to air. The resulting reaction mixture was then precipitated into ethyl ether and precipitated from DCM into ethyl ether two more times. The yellow solid was dried under vacuum at 25 °C for 24 h. Yield = 800 mg (46.7%). GPC (PS standards): $M_n = 397,000$ g/mol, $M_w/M_n = 1.17$, ¹H NMR: $n(\text{BAEAM}) = 8$.

5. Synthesis of Poly(GM-g-LA-g-BAEAM-g-St)

Poly(GM-g-LA-g-BAEAM) (480 mg), Styrene (St) (5.9 g), AIBN (0.9 mg) and 1,4-dioxane (12 ml) were mixed in a reaction vessel and degassed by 3 freeze-pump-thaw cycles. The polymerization was conducted at 60 °C for 4 h. The resulting mixture was precipitated from DCM into MeOH 3 times and dried under vacuum at room temperature for 24 h. Yield = 540 mg (1.1%). ¹H NMR: $n(\text{St}) = 180$.

7. Hyper Crosslinking of Poly(GM-g-LA-g-BAEAM-g-St)

P(GM-g-LA-g-BAEAM-g-St) (400 mg, $n(\text{St}) = 2.3$ mmol), dimethoxymethane (350 mg, 4.6 mmol), anhydrous FeCl₃ (750 mg, 4.6 mmol) and dry dichloroethane (70 ml) were mixed in a reaction vessel at room temperature. The mixture was degassed by N₂ for 10 min. Then the mixture was heated to 80 °C for 24 h. The product was washed by MeOH 3 times and dried under vacuum

at room temperature for 24 h. Yield = 460 mg

8. Synthesis of amine supported microporous network nanotubes (Amine- MNNs)

The crosslinked precursor (200 mg), 50% NaOH aqueous 0.2 ml and 15 ml MeOH were mixed in a reaction vessel. The mixture was heated to 50 °C for 12 h. The impurities were separated by centrifugation and washed by MeOH 2 more times. The product was dried under vacuum at room temperature for 24 h. Yield = 220 mg.

9. Synthesis of ammonium triflate microporous network nanotube (AT-MNNs)

The Amine-MNNs (100 mg), trifluoromethanesulfonic acid (18 mg, 0.12 mmol) and dry dichloromethane 5 ml were mixed in a 50 ml flask. The mixture was stirred at room temperature for 24 h. The impurities were separated by centrifugation and washed by MeOH 2 more times. The product was dried under vacuum at room temperature for 24 h. Yield = 80 mg.

10. Synthesis of tungstate anions on microporous network nanotubes (TMNNs)

The tungstate anions on microporous network nanotubes were prepared through a simple ion exchange technique. In a 50 ml flask were mixed with 80 mg AT-MNNs, sodium tungstate dihydrate (60 mg, 0.18 mmol) and deionized water 5 ml. The mixture was stirred at room temperature for 24 h. The resulting ion-exchanged solid was obtained by centrifugation and washed by deionized water 3 times, ethanol 3 times. The material was then dried at room temperature under vacuum for 24 h. Yield = 60 mg.

11. General procedure for the selective oxidation.

To a solution of 0.1 mmol sulfide and 0.1 mmol H₂O₂ in 0.5 ml MeOH was added 4.5 mg of TMNNs (1 mol %), and the above solution was stirred at 30 °C for 1 h. The catalyst was separated by centrifugation, and washed by MeOH 2 more times. Then the combined solution was dried under vacuum. The obtained product was analyzed by ¹H NMR and GC.

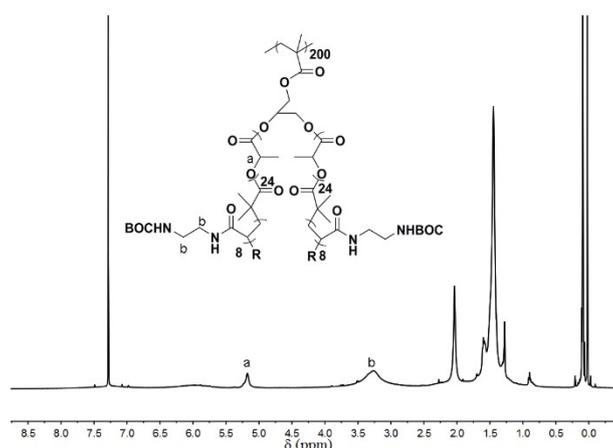


Figure 1. ¹H NMR of Poly(GM-g-LA-g-BAEAM) in CDCl₃

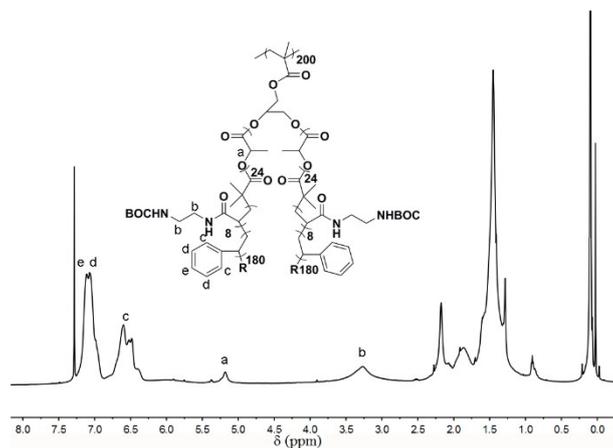


Figure 2. ^1H NMR of Poly(GM-g-LA-g-BAEAM-g-St) in CDCl_3

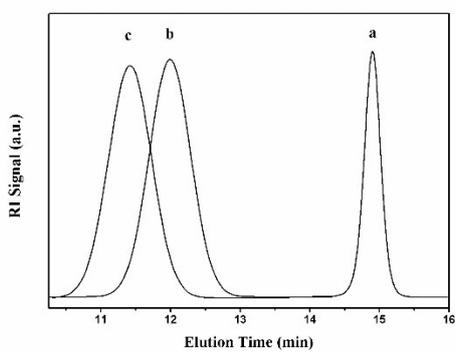


Figure 3. SEC traces of (a) PGM, (b) Poly(GM-g-LA), (c) Poly(GM-g-LA-g-BAEAM)

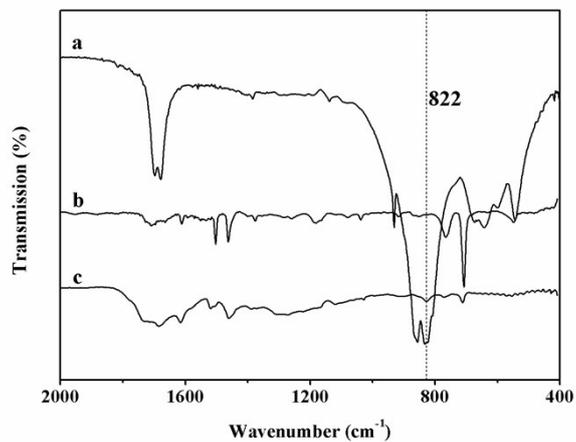


Figure 4. FTIR of (a) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, (b) AT-MNNs, (c) TMNNs

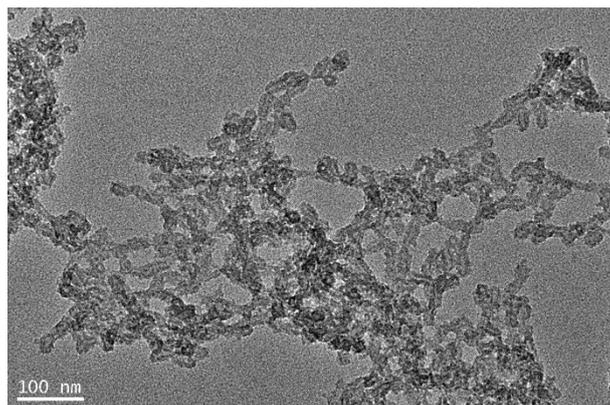


Figure 5. TEM image of TMNNs after recycled 8 times

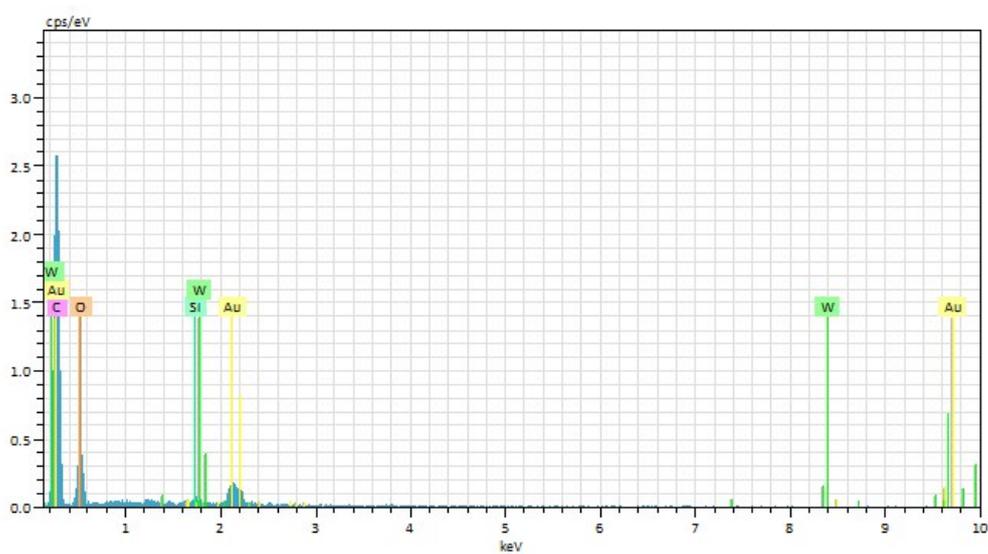


Figure 5. EDX analysis of TMNNs

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