Electronic Supplementary Information

A novel biodegradable hyperbranched polyester prepared from cellulose and tyrosine via the synthesis route of glycopeptides

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The ESI contains: Experimental section; supplementary solid-state ^{13}C-NMR, FT-IR spectra and GPC curve.

Experimental section

Materials

Cotton fibers were purchased from XinYi Surgical Dressing Products Factory, China. Cellulase (≥99%) was obtained from Shanghai Bo'ao Biotechnology Limited Company, China. Tyrosine (AR) was purchased from Tokyo Chemical Industry Limited Company, Japan. Other chemicals were used as received without further purification.

Synthesis of acetylated cellulose bromide (ACBr)

Cellulose was crushed with a laboratory-scale miller to reduce its molecular weight using physical methods, and was then degraded for 60 hours with 0.50 mg·mL^{-1} cellulase at pH=4.6 in the acetic acid-sodium acetate buffer solution after ultrasonic treatment for 30 minutes, yielding oligomeric cellulose with more functional groups. The resulting oligomeric cellulose was activated by immersion into 14% sodium hydroxide solution for 24 hours, then washed, and dried for the future use. The oligomeric cellulose (Oligo-Cell) was immersed into acetic acid solution to be activated for a second time while maintaining temperature at about 4 ºC in an ice bath. Excessive acetic anhydride was added into the mixture with pyridine as catalyst, allowing acetylation reaction to proceed for 6 hours. Afterwards, dilute acetic acid was added to hydrolyze the remaining acetic anhydride and the resulting acetylated cellulose was then thoroughly washed and filtrated. The obtained acetylated cellulose (Ace-Cell) was dissolved in 30% hydrogen bromide-acetic acid solution for 6 hours. The product was extracted with petroleum ether, and the obtained organic layer was successively washed with ice water and saturated sodium bicarbonate solution, and then dried with anhydrous sodium sulfate. The bromide-substituted cellulose derivative was finally obtained by vacuum distillation of organic phase. **FT-IR (cm^{-1}):**1750 (-CO-); 1375 (-CH_3, -CH_2); 1072 (C-O-C); 601 (-Br). **^{13}C NMR ($CDCl_3$, δ ppm)**:175.4 (-O-C_7O-); 103.0 (O-C_1-Br); 75.0 (C_4-O); 63.8(C_2-O, C_3-O, C_5-O); 29.2(C_6-O); 10.87(C_8-O).

Synthesis of CHBm

1mmol Tyrosine and silver carbonate were dissolved in dichloromethane and then stirred for 30 minutes. Equivalent molar amounts (1 mmol) of ACBr and dicyclohexyl carbodiimide (DCC) were added to the above mixture, and the reaction was maintained at ambient temperature for 12 hours in darkness. The reaction mixture was filtrated and the obtained filtrate was distilled under vacuum at 40 ºC. The resulting residues were dissolved in 200 mL chloroform, mixed with 300 mL of 10% ammonia solution to remove silver carbonate, and washed with distilled water for several times (100 ml each time). After being dried with calcium chloride, the chloroform phase was condensed into the dryness and then recrystallized with ethanol. The obtained cellulose-based glycopeptide-like derivative (CGPD) was added to the fresh 1.0 mol·L^{-1} sodium methoxide, and the mixture was stirred for 4 hours at ambient temperature. Afterwards, pH value of the solution was carefully adjusted to 7.0 with 10% acetic acid solution. After evaporation, the solid CHBP's monomer (CHBm) was finally obtained. **FT-IR (cm^{-1}):**3649 (-OH); 1750 (C=O); 1600~1450(C=C of benzene ring). **^{13}C NMR ($CDCl_3$, δ ppm)**:175.2 (O-C_{10}O); 158.7 (C_{15}-O); 123.1 (C_{14}); 104.8 (C_{13}); 103.3 (C_{12}); 75.1 (C_1-O); 67.8(C_4-O); 49.9 (C_2-O, C_3-O, C_5-O); 38.7 (C_6-O, C_9-N); 65.5 (C_{11}).

Synthesis of CHBP

5.0 g CHBM was dissolved in 200 mL toluene. After stirring for 30 minutes, 1 g *p*-toluenesulfonic acid (*p*-TSA) and 0.1g DCC were added into the above mixture. While the mixture was refluxed in the oil bath, 2 droplets of glycerol were added as the central core to adjust molecular weight of CHBP. The solvent was exchanged with ethanol and the reaction was allowed to proceed for another 8 hours. The solid product after the distillation, i.e. the first generation CHBP ('*CHBP-1*'), was obtained. It needs to be noted that pH value of reaction system during the polycondensation has to be carefully controlled. High pH value would led to rapid solidification of the monomer, whereas low pH one would lower the reaction rate. The process was repeated using the '*CHBP-1'* as the starting material to yield the second generation CHBP ('*CHBP-2')*. In the similar manner, the third and fourth generations of CHBPs designated as "*CHBP-3*" and "*CHBP-4*", were also synthesized, respectively. **FT-IR (cm^{-1}):** 3650 (-OH); 2950 (-CH_3, -CH_2-); 1750 (C=O); 1600~1450(C=C of benzene ring); 1200-1090 (C-O-C). **^{13}C NMR ($CDCl_3$, δ ppm)**: 182.7 (O-C_{10}O); 164.8 (C_{15}-O); 120.8(C_{14}); 116.5 (C_{13}); 113.8 (C_{12}); 91.03(O-C_1-O); 74.7(C_4-O); 49.8(C_2-O, C_3-O, C_5-O); 38.7(C_6-O); 33.0(C_9-N); 24.8 (C_{11}).

Characterization

IR spectra of samples were recorded on the Fourier transform infrared spectrometer (FT-IR Prestige-21, Shimadzu Corporation, Japan) in the wavenumber range of 500-4000 cm^{-1}. A small amount of samples were grinded with dried KBr powder and then compressed into disks for the FT-IR test. ^{13}C NMR spectra of samples were recorded on Bruker DRX 400 MHz solids CP/MAS NMR spectrometer (ADVANCE NMR, Bruker Corporation, Swiss). Molecular weight and its polydispersity index (PDI) were determined with GPC (Waters 2695, USA). Measurements were performed at 35 ºC in tetrahydrofuran (THF) as mobile phase with a nominal flow rate of 1.0

$mL \cdot min^{-1}$. A certain amounts of samples were dissolved in THF, filtered through a 0.45 μm filter, and injected into the column (200 μL). The standard curve was made with standard sample of linear polystyrene.

Thermal stability of samples were measured using a STA 409 PC instrument (Netzsch, Germany) under nitrogen atmosphere at a heating rates of 20 ºC·min^{-1}. About 9.20-10.40 mg sample was heated from room temperature to 600 ºC at a nitrogen flow rate of 25 $mL \cdot min^{-1}$

Biodegradation test was performed using incubation medium as the only carbon source and its composition of the medium included sample fine powder (0.15%), $MgSO_4 \cdot 7H_2O$ (0.05%), NH_4Cl (0.1%), $CaCl_2 \cdot 2H_2O$ (0.0005%), KH_2PO_4 (0.554%), and $Na_2HPO_4 \cdot 12H_2O$ (1.194%). NaOH solution with the concentration of 0.01 $mol \cdot L^{-1}$was used to adjust pH value of culture medium to 6.8-7.0. Under the sterile condition, the strain materials were prepared as the solution containing 4.6×10^6 single *aspergillus niger* per milliliter. After a certain amount of sample powder was evenly spreading on the incubation media, the asepsis gun was used to inoculate strain in the middle of the incubation media. The treated incubation media was cultivated at 28°C in the oven. The growing status of fungus in the samples was observed under different periods.

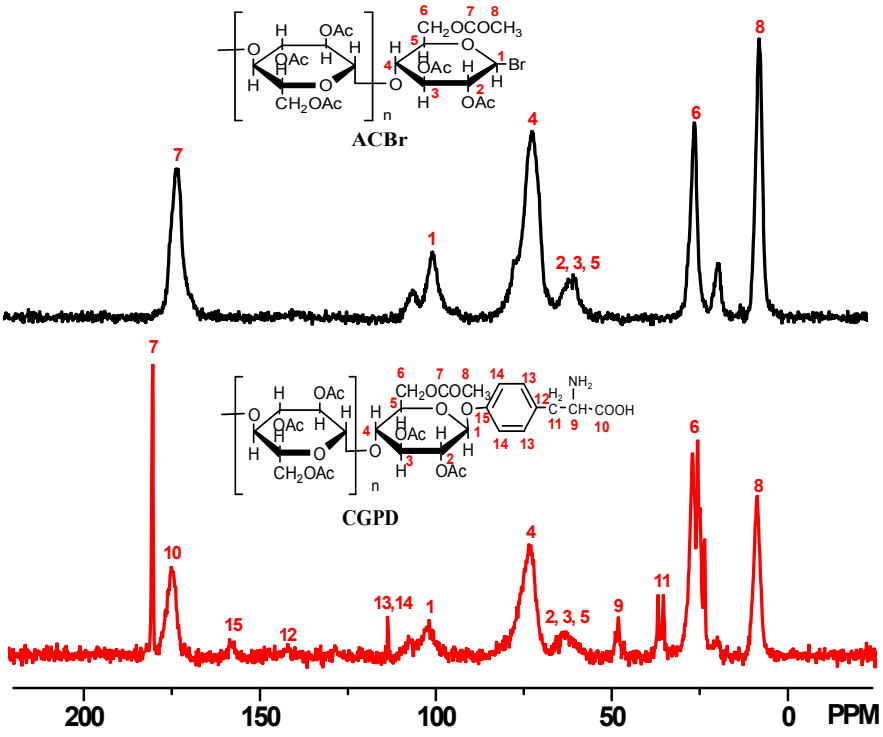

Figure S1. CP/MAS ^{13}C-NMR spectra of ACBr and CGPD.

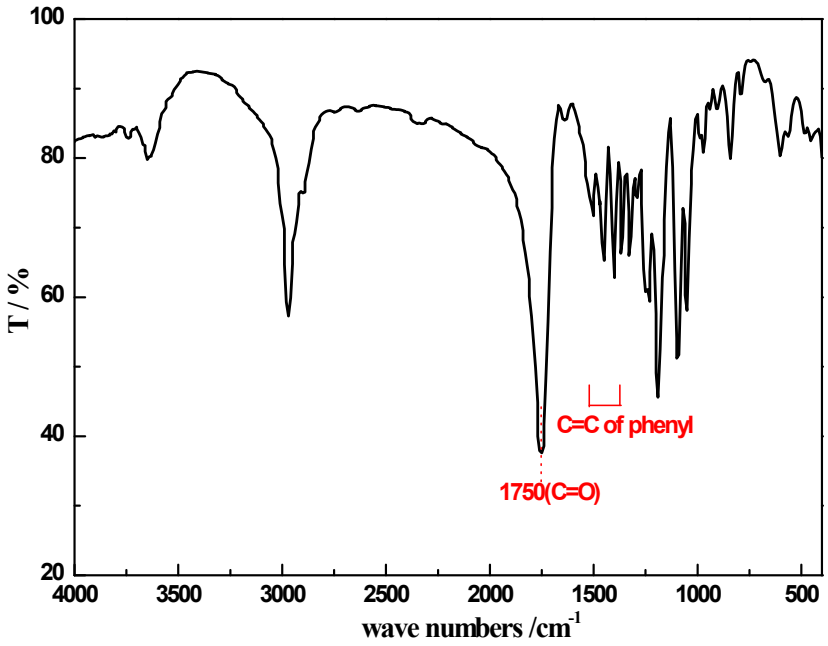

Figure S2. FT-IR spectrum of CHBP-3.

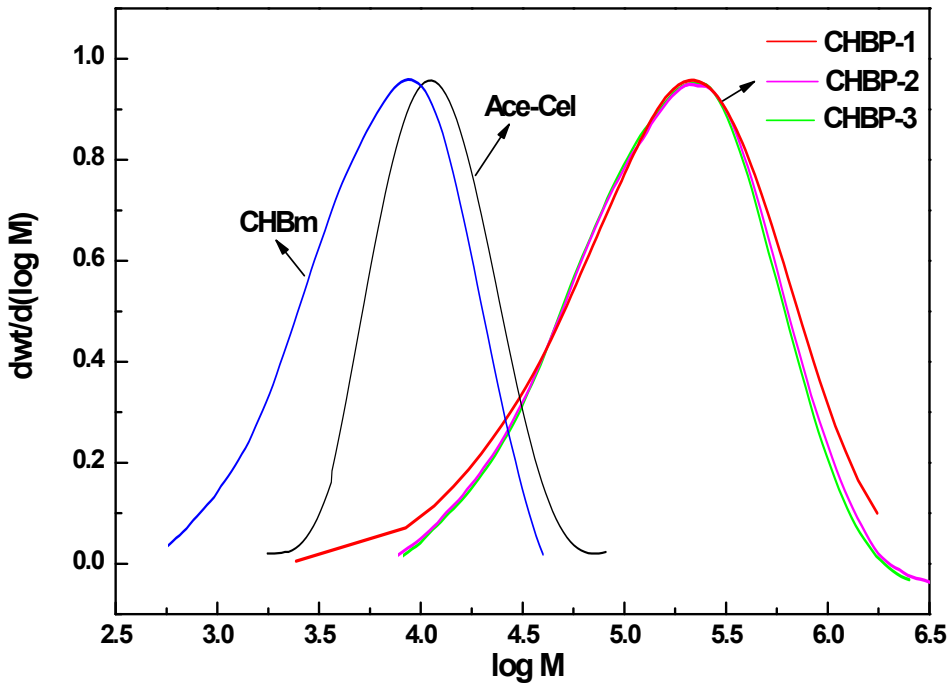

Figure S3. The molecular weight distribution curves of samples.