A facile route to fabricate biodegradable hydrogel for controlled pesticide release

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Materials and Methods

1. Chemicals and materials

Aminoacetaldehyde dimethyl acetal (Aladdin, 98%), methacryloyl chloride (Aladdin, purum), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, Aladdin, 98%), tert-butyl methyl ether (Aladdin, 99.9%), 2,2-azobisisobutryic acid dimethyl ester (AIBMe, Aladdin, 98.5%), acrylic acid (AA, Aladdin, 99%), thioglycolic acid (TGA, Aladdin, 98%), N'-ethyl-N-(3-dimethylaminopropyl)-carbodiimide (EDC, Aladdin, 98.5%), adipic acid dihydrazyde (ADH, Aladdin, 98%) were used as received. Oligo(ethylene glycol) methyl ether methacrylate with an average number-average molecular weight of 475 g/mol ($OEGMA_{475}$, Sigma Aldrich, 95%) was purified by passing it over a column of basic aluminum oxide. Dioxane was purchased from Tianjin Chemical Reagent Co., China. Avermectin (96.3%) was supplied by Hebei Veyong Animal Pharmaceutical, China. Tris (hydroxymethyl) aminomethane (TRIS) and hydrochloric acid were purchased from Beijing Chemical Reagents Company, China. Petroleum ether, sodium chloride, and sodium hydroxide were analytical chemicals purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd, China. Deionized water was prepared with an ion-exchange system.

2. Synthesis of free and Av hydrogel

First, hydrazide-functionalized precursors (POH), the N-(2,2-dimethoxyethyl) methacrylamide (DMEMAm) monomer, and aldehyde-functionalized POEGMA precursors (POA) were prepared following a published procedure.[18] Second, free hydrogel (HG) and Av loaded hydrogel (Av-PG) were synthesized, respectively. Briefly, Av (0.2 g) was added in a beaker with deionized water (20 mL) to disperse Av. Then 0.37 g POH and POA were added in two round-bottom flask dissolved in 5 mL of Av solution, respectively. Subsequently, the solution was stirred for at room temperature for 0.5 h. Av loaded POH and POA precursor (POH-Av, POA-Av) was prepared under continuous agitation. Both precursors (POH-Av, POA-Av) were added into the round bottom flask at the same time with magnetic stirring for 20 min. The Av-HGs were obtained and placed in the previous rubber molds incubated at room temperature for at least 12 hours to ensure complete gelation prior to testing. Then Av-HGs were washed thrice successively with ethanol to remove the unloaded avermectin. The free HG was prepared as the same with Av-HG.

3. Controlled release of avermectin

Samples that contain the same amount of Av gel (97.4% w/w) were suspended with 100 mL of an

ethanol/water mixture in 150 mL conical flask, respectively, which was used as the release medium to dissolve Av, and then were placed in a constant shaking incubator at a stirring speed of 100 rpm. The cumulative release rate of Av from the hydrogel was calculated by measuring the concentration of Av dissolved in the mixture solution at different times to evaluate the sustained release from Av gel. To measure the concentration, 2.0 mL of mixture was collected at different intervals from the suspension in the constant shaking incubator. 2.0 mL supernatant obtained by centrifugation (10000 rpm) was monitored by UV-vis absorption spectroscopy analysis and 2.0 mL of mixture was added to the constant shaking incubator.

4. ^{1}H-NMR and GPC curves of samples

The NMR spectra were recorded and shown in Fig. S1 and Fig. S2, which are in accordance with previous report. DMSO and chloroform were used as the solvent for ^{1}H-NMR. ^{1}H-NMR (DMSO, 600 MHz): δ = 1.75 (s, 3H, -CH_3), δ = 2.92-3.23 (m, 8H, O-CH_3 and -N(H)-CH_2), δ = 4.33 (t, 1H, -CH), δ = 5.24 (s, 1H, =CH_2) , δ = 5.57 (s, 1H, =CH_2), δ = 7.89 (s, 1H, -NH).

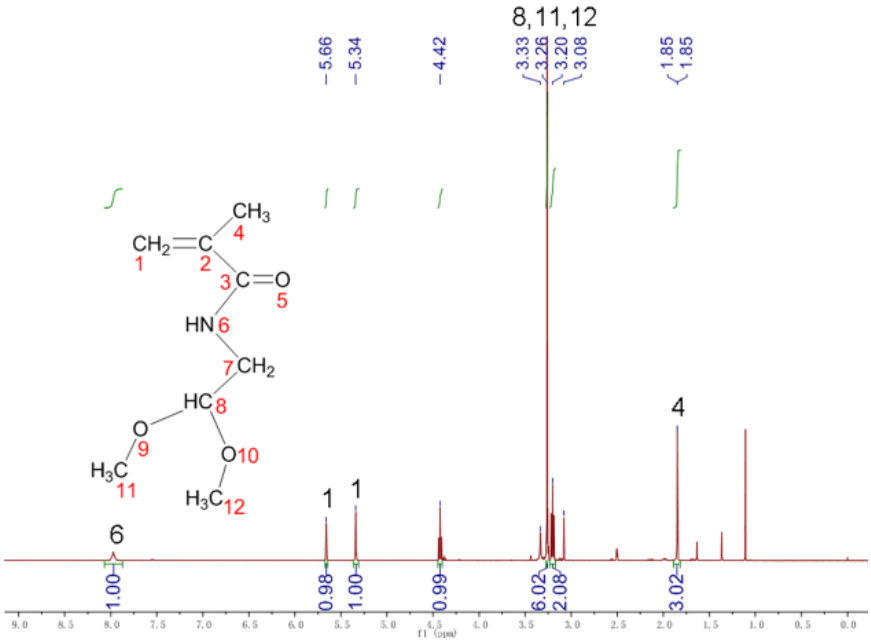

Fig. S1 ^{1}H-NMR spectrum of N-(2,2-dimethoxyethyl)methacrylamide (DMEMAm) monomer.

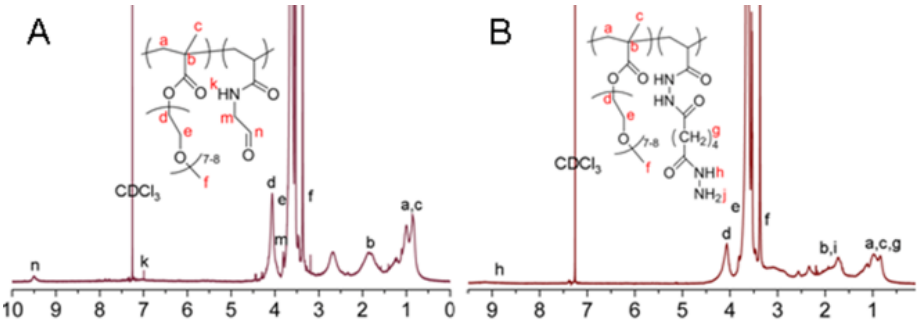

Fig. S2 ^{1}H-NMR spectra of precursors: (A) aldehyde-functionalized precursors; (B) hydrazide-functionalized precursors.

The results of the synthesized samples were further verified, as confirmed by the GPC (Fig. S3),

including Mn and PDI of both precursors. Determined using aqueous GPC with a mobile phase consisting of 0.3 M sodium nitrate and 0.05 M phosphate buffer at pH=7.2.

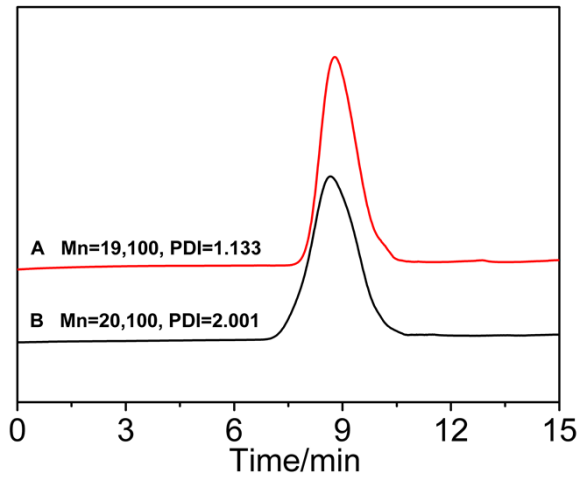

Fig. S3 GPC curves of samples: (A) aldehyde-functionalized precursors; (B) hydrazide-functionalized precursors.

5. The effects of pH on the samples

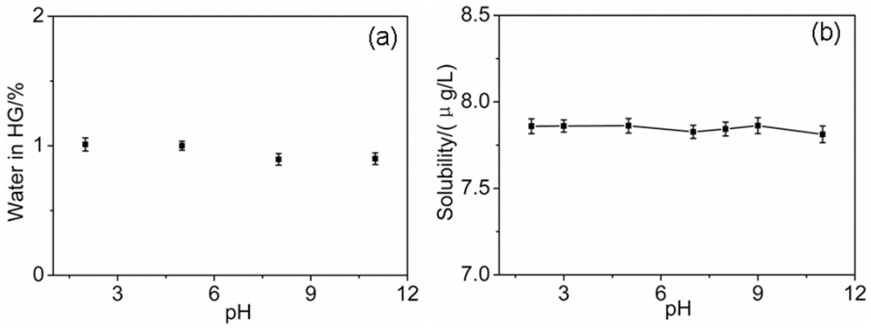

Fig. S4 (a) the effects of pH on the swelling ratio of HG; (b) the effects of pH on the solubility of avermectin in water.

Reference

18 N. M. Smeets, E. Bakaic, M. Patenaude, T. Hoare, *Chem. Commun.*, 2014, **50**, 3306-3309.