

Electronic Supporting Information

A Smart Bottom-up Strategy for Fabrication of Complex Hydrogel Constructs with 3D Controllable Geometric Shapes through Dynamic Interfacial Adhesion

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1. Materials

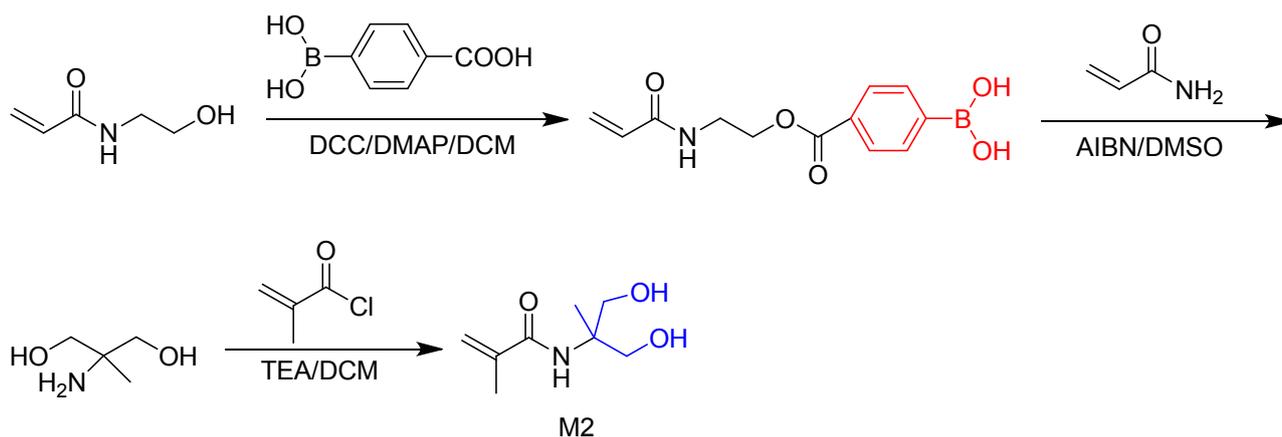
4-Carboxybenzeneboronic acid was purchased from Aladdin Co., Ltd (Shanghai, China). N-(2-Hydroxy-ethyl) acrylamide and methacryloyl chloride (both stabilised with 4-methoxyphenol) were obtained from TCL (Shanghai, China). 2-Amino-2-methyl-1, 3-propanediol (AMPO), 4-(dimethylamino)pyridine (DMAP) and N, N'-dicyclohexyl carbodiimide (DCC) were purchased from Adamas Reagent Co., Ltd (Shanghai, China). N, N'-methylenebis(acrylamide) (BIS) was obtained from Sigma-Aldrich (Shanghai, China). 2, 2'-Azobisisobutyronitrile (AIBN) (Sigma, 98%) was recrystallised from ethanol. Acetonitrile was distilled over P₂O₅ after refluxing until becoming colourless. Triethylamine (Et₃N) was distilled over calcium hydride after refluxing for 12 h. The water used in this study was distilled and further purified using a filtration system. All other reagents were commercial chemicals and they were used without further purification unless otherwise noted.

2. Characterisations

¹H and ¹³C NMR spectra were recorded on a 300 MHz Bruker Avance-300 NMR spectrometer. A Bruker AvanceII-600 spectrometer was used to collect solid ¹¹B NMR data using BF₃·OEt₂ as an external standard (0 ppm). Chemical shifts were reported in parts per million (ppm) with reference to the residual protons of the deuterated solvents. Stress-strain measurements for the assembled gel samples were analysed by a commercial test machine (Electronic Testing Machine, RGM-6005, China). Movies and pictures were obtained by a digital camera.

3. Synthesis of monomers

M1 and M2 was prepared according to a published method.



Scheme S1 Synthesis of monomers M1 and M2

3.1 Synthesis of 4-((2-acrylamidoethoxy)carbonyl)phenylboronic acid (M1)

N, N'-dicyclohexyl carbodiimide (DCC) (6.98 g, 33.5 mmol) in CH_2Cl_2 (50 mL) were added dropwise to a suspension of 4-carboxyphenylboronic acid (5.01 g, 30.2 mmol), N-(2-hydroxyethyl)acrylamide (4.18 g 36.3 mmol) and 4-(dimethylamino)pyridine (DMAP) (379 mg, 3.07 mmol) in CH_2Cl_2 (100 mL) over 3 h. After 24 h, the reaction solution was filtered and purified via flash chromatography (gradient 30:1 DCM:MeOH). A white solid was obtained (2.38 g; yield: 31.9 %). ^1H NMR (300 MHz, D_2O) δ 7.90 (d, $J = 8.1$ Hz, 2H), 7.82 (d, $J = 8.2$ Hz, 2H), 6.18 (dd, $J = 17.0, 9.6$ Hz, 1H), 6.08 (t, $J = 8.5$ Hz, 1H), 5.62 (dd, $J = 9.7, 2.2$ Hz, 1H), 4.28 (t, $J = 5.1$ Hz, 2H), 3.51 (t, $J = 5.0$ Hz, 2H). ^{13}C NMR (75 MHz, DMSO-d_6) δ 165.90, 164.94, 134.17, 133.55, 131.57, 130.84, 128.33, 125.41, 63.49, 37.77.

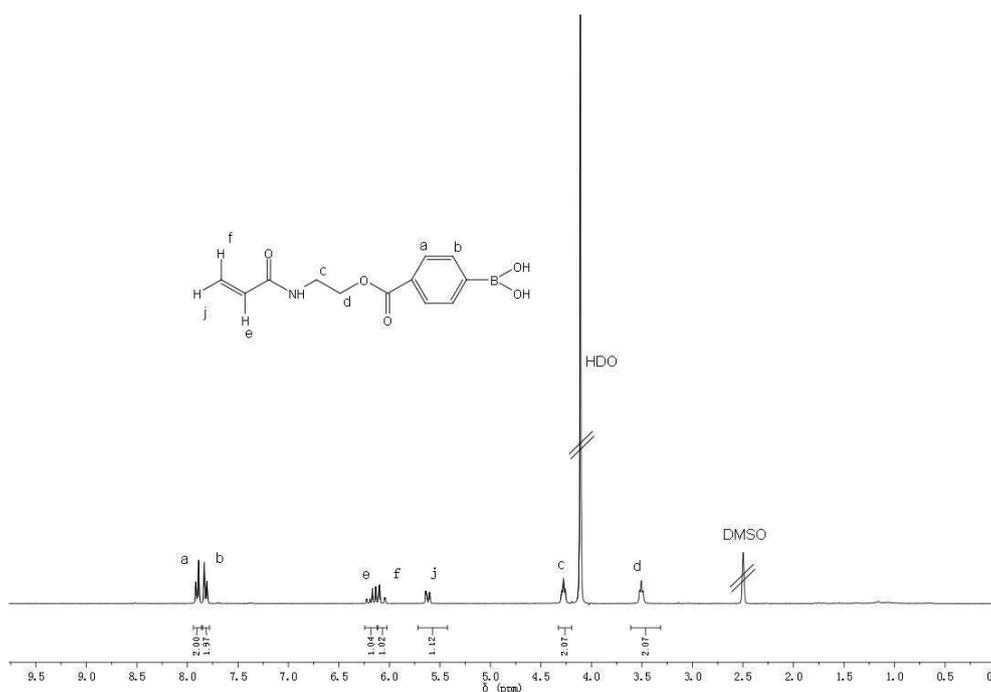


Fig.S1 ^1H NMR of M1

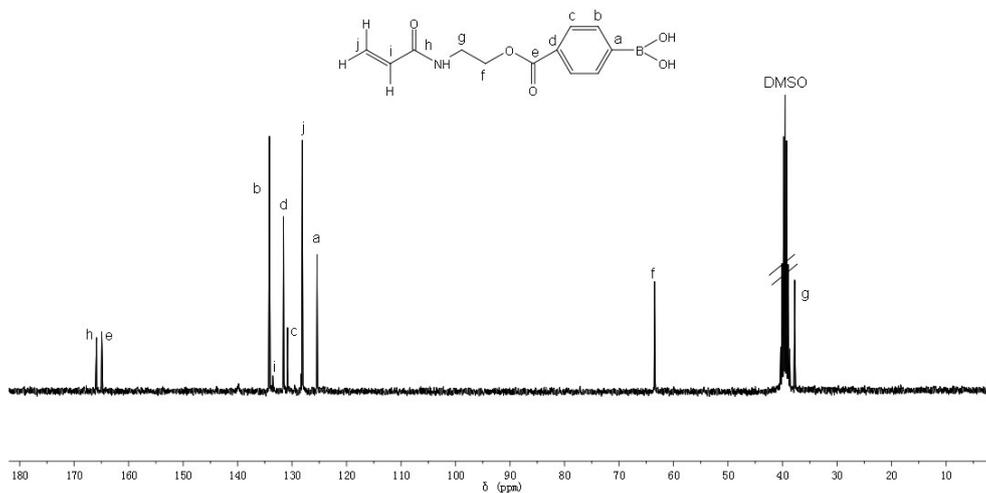


Fig.S2 ^{13}C NMR of M1

3.2 2-Acryloylamino-2-methyl-propan-1, 3-diol (M2)

Methacryloyl chloride (2.4 ml, 20 mmol) was added in drops into a cold suspension of AMPO (2.10 g, 20 mmol) and triethylamine (8.4 mL, 60 mmol) in acetonitrile (200 mL) under nitrogen atmosphere. The reaction was allowed to proceed under stirring at 0 °C for 6 h. Subsequently, the suspension was heated to 60 °C and filtered while hot to remove the insoluble hydrochloride salt. The filtrate was concentrated to 20 mL, followed by being stored at room temperature (RT). Finally, the white crystal was formed and isolated by filtration (2.70 g; yield: 77.9%). ^1H NMR (300 MHz, DMSO- d_6) δ 6.82 (s, 1H), 5.58 (s, 1H), 5.30 (s, 1H), 4.81 (t, J = 5.9 Hz, 2H), 3.53 (dd, J = 10.8, 5.8 Hz, 2H), 3.43 (dd, J = 10.8, 6.0 Hz, 2H), 1.83 (s, 3H), 1.18 (s, 3H). ^{13}C NMR (75 MHz, DMSO- d_6) δ 168.02, 140.73, 118.81, 63.74, 58.34, 18.71, 18.32.

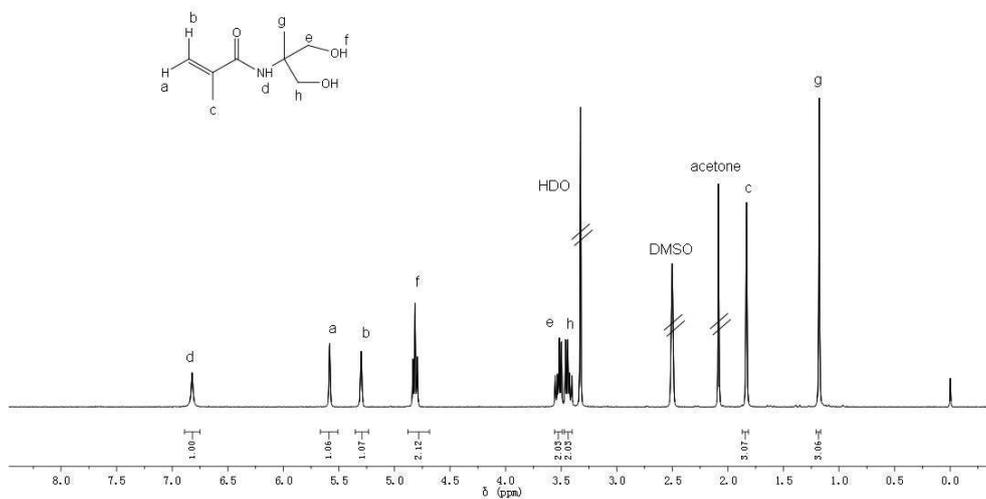


Fig.S3 ¹H NMR of M2

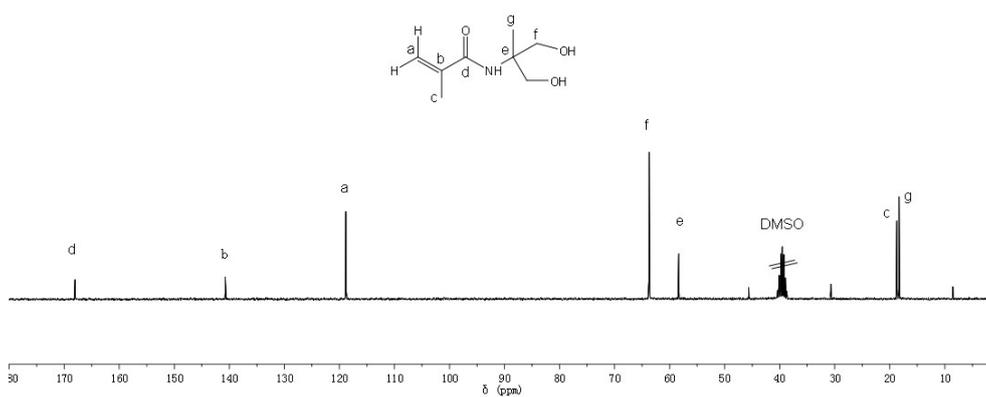


Fig.S4 ¹³C NMR of M2

4. Preparation of the PBA- gel

The PBA-gel were also prepared by radical polymerisation. Predetermined amounts of AAm, BIS and M1 were dissolved in DMSO (3 ml). The solution was purged with nitrogen for 15 min to remove oxygen, and then AIBN was added. The reaction mixture was transferred to a

tetrafluoroethylene mould, and the mould was sealed immediately. Gelation was carried out in an oven at 70 °C for 24 h. The mould was then removed from the oven, and the bulk gel obtained from the mould was purified by washing with a large amount of DMSO to remove unreacted monomers and initiators. This was followed by soaking in water for hours, then repeatedly washing with water. Subsequently, the gels were cut into different shapes with a knife.

5. Preparation of the NIPAM-diol-gel

The NIPAM-diol-gel was also prepared by radical polymerisation. Predetermined amounts of NIPAM, BIS and M2 were dissolved in DMSO (3 ml). The solution was purged with nitrogen for 15 min to remove oxygen, and then AIBN was added. The reaction mixture was transferred to a tetrafluoroethylene mould, and the mould was sealed immediately. Gelation was carried out in an oven at 70 °C for 24 h. The mould was then removed from the oven, and the bulk gel obtained from the mould was purified by washing with a large amount of DMSO to remove unreacted monomers and initiators. This was followed by soaking in water for hours, then repeatedly washing with water. Subsequently, the gels were cut into different shapes with a knife.

6. References

- 1 Y. Lin, J. W. Gao, H. W. Liu and Y. S. Li, *Macromolecules*, 2009, 42, 3237-3246.
- 2 D. Roy, B. S. Sumerlin, *ACS Macro Letters*, 2012, 1, 529-532.