

Supporting Information

Effect of molecular weight and polymer composition on galloI-functionalized underwater adhesive

Jinhong Yu^a, Bohan Cheng^a and Hirotaka Ejima^{*a}

^aDepartment of Materials Engineering, School of Engineering, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku 113-8656, Japan.

*E-mail address: ejima@material.t.u-tokyo.ac.jp

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Materials

Methyl gallate, *N,N*-diisopropylethylamine (DIEA), chloromethyl methyl ether (MOMCl), and methyltriphenylphosphonium bromide were purchased from Tokyo Chemical Industry and were used as received. Lithium aluminium hydride (LiAlH₄), anhydrous tetrahydrofuran (THF), anhydrous dichloromethane (DCM), potassium *tert*-butoxide (*t*-BuOK), 2,2'-azobis(2-methylpropionitrile) (AIBN), and styrene (St) were purchased from Wako Pure Chemical Industry. Activated manganese dioxide was purchased from Sigma Aldrich and used as received.

Experimental Methods

1. Synthetic route for gallol-functionalized polymers

1.1 Synthesis of methyl 3,4,5-tris(methoxymethoxy)benzoate (MTMB)

Under nitrogen atmosphere at 0 °C, 25.2 g (126 mmol) of methyl gallate, 62.4 g (756 mmol) of chloromethyl methyl ether and 50 mL of THF was first added to a flask. After stirring for 5 min, *N,N*-diisopropylethylamine (DIEA) (65.5 g, 504 mmol) in 50 mL THF solution was added dropwise. The mixture was then stirred at 45 °C for 24 h and then concentrated under vacuum. The resulting reaction mass was extracted twice with 50 mL of diethyl ether and washed with brine, dried over MgSO₄, filtered, and evaporated to yield a colourless oil. The crude product was then directly moved to the next step without further purification.

1.2 Synthesis of 3,4,5-tris(methoxymethoxy)benzyl alcohol (TMBA)

At 0 °C, the crude product obtained from step 1.1 was added dropwise to a suspension of LiAlH₄ (7.74 g, 200 mmol) in 150 mL anhydrous THF. After reacting 24 h at room temperature, the reaction was quenched with 8 mL water, 8 mL 15% NaOH, and 24 mL water. Then, 36 g of MgSO₄ was added to the mixture, and the mixture was stirred for 30 min. The reaction mass was filtered, washed with THF, and evaporated to yield white crystals (97 mmol, 71% in two steps). ¹H NMR (400 MHz, CDCl₃): (δ, ppm) 6.85 (s, 2H), 5.21 (s, 4H), 5.11 (s, 2H), 4.60 (s, 2H), 3.61 (s, 3H), 3.49 (s, 6H).

1.3 Synthesis of 3,4,5-tris(methoxymethoxy)benzaldehyde (TMMB)

To a solution of the TMBA 2.88 g (10.0 mmol) in DCM (150 mL) was added activated MnO₂ 6.09 g (70.0 mmol). The reaction mixture was stirred overnight at room temperature. The solids were removed via filtration, and the filtrate was concentrated. The resulting material was purified by silica gel chromatography (hexane:ethyl acetate = 9:1) to obtain a white solid (2.53 g, 8.8 mmol). The yield was 88.5%. ¹H NMR (400 MHz, CDCl₃): (δ, ppm) 9.87 (s, H), 7.40 (s, 2H), 5.28 (s, 4H), 5.25 (s, 2H), 3.62 (s, 3H), 3.52 (s, 6H).

1.4 Synthesis of 1,2,3-tris(methoxymethoxy)-5-vinylbenzene (TMMS)

Under nitrogen atmosphere at 0 °C, 2.40 g *t*-BuOK (23.1 mmol) and 8.25 g methyltriphenylphosphonium bromide (23.1 mmol) were stirred in 100 mL THF for 30 min. Then, the reaction solution was brought to r.t., 4.05 g (14.2 mmol) of 3,4,5-tris(methoxymethoxy) benzaldehyde was added, and the mixture is stirred overnight

at 45 °C. Pure water (10 mL) was added, extracted with diethyl ether, dried over MgSO₄, concentrated, and purified by silica gel column chromatography (hexane:ethyl acetate = 9:1) to obtain a white solid (3.22 g, 11.3 mmol). The yield was 79.5%. ¹H NMR (400 MHz, DMSO-d₆, Figure S1): (δ, ppm) 6.89 (s, 2H), 6.60 (dd, 1H, *J* = 17.40 Hz, *J'* = 10.99 Hz), 5.71 (dd, 1H, *J* = 17.40 Hz, *J'* = 0.92 Hz), 5.21 (dd, 1H, *J* = 10.99 Hz, *J'* = 0.92 Hz), 5.20 (s, 4H), 5.04 (s, 2H), 3.50 (s, 3H), 3.40 (s, 6H).

1.5 Synthesis of poly(TMMS-co-styrene)

In a test tube, TMMS (0.28 g, 1 mmol), styrene (0.94 g, 9 mmol), and initiator 2,2'-azobis(2-methylpropionitrile) (AIBN) (2.5 mg, 0.0015 mmol) were dissolved in 2 mL anisole. Polymerization was conducted at 80 °C for 24 h under nitrogen atmosphere. The mixture was then precipitated in methanol. The resulting white solids were dried under vacuum to yield 0.63 g of polymer (51.6%). ¹H NMR (400 MHz, DMSO-d₆): (δ, ppm) 7.21–6.20 (5H, Ar-H), 6.20–5.75 (2H, Ar-H), 5.16–4.71 (6H, -CH₂-), 3.71–3.00 (9H, -CH₃), 2.40–0.80 (Polymer backbone).

1.6 Deprotection of poly(TMMS-co-styrene)

Under nitrogen atmosphere, the polymer obtained from step 1.5 was dissolved in 10 mL methanol and THF solution (1:1), followed by dropwise addition of 1 mL of 1 M HCl in diethyl ester. After stirring at room temperature for 24 h, the mixture was evaporated and dried under vacuum to yield a pink solid. The yields of deprotection were all above 80%. ¹H NMR (400 MHz, DMSO-d₆, Figure S2): (δ, ppm) 8.70–7.50 (OH), 7.50–6.00 (5H, Ar-H), 6.01–5.75 (2H, Ar-H), 2.50–0.80 (Polymer backbone).

2. Measurement of molecular weight

M_n and PDI were measured by gel permeation chromatography (GPC) (SHIMAZU Prominence-i GPC System) using THF as the eluent. The calibration curve was prepared using polystyrene as a standard.

3. Oxidation characterization by X-ray Photoelectron Spectroscopy

The elemental compositions of the surfaces were investigated by XPS (AXIS-His, Shimadzu/Kratos Co. Ltd., Kyoto, Japan) with a Mg Kα (12 kV) radiation source at the anode. The photoelectron take-off angle was fixed at 90°. All the spectra were referred to the C_{1s} peak at 284.5 eV of the binding energy.

Table S1. Composition , PDI, and M_n of the synthesized polymers used in this study.

Feed			Product			
TMMS (mol%)	Styrene (mol%)	TMMS: Styrene: Initiator	TMMS (mol%) ^a	Styrene (mol%) ^a	PDI ^b	M_n ($\times 10^4$) ^b
5	95	1: 19: 0.03	5	95	2.1	6.5
10	90	1: 9: 0.01	10	90	1.8	10.3
10	90	1: 9: 0.01	13	87	2.1	9.7
10	90	1: 9: 0.012	9	91	2.5	8.3
10	90	1: 9: 0.015	10	90	1.7	6.9
10	90	1: 9: 0.015	10	90	2.0	6.4
10	90	1: 9: 0.014	7	93	1.8	5.8
10	90	1: 9: 0.03	8	92	2.7	3.7
10	90	1: 9: 0.05	8	12	1.7	4.2
10	90	1: 9: 0.01	12	88	1.7	2.7
20	80	2: 8: 0.015	21	79	1.6	8.8
30	70	3: 7: 0.015	33	67	2.0	9.6
40	60	4: 6: 0.015	42	58	1.9	11.1

a: measured by ¹H NMR

b: measured by GPC

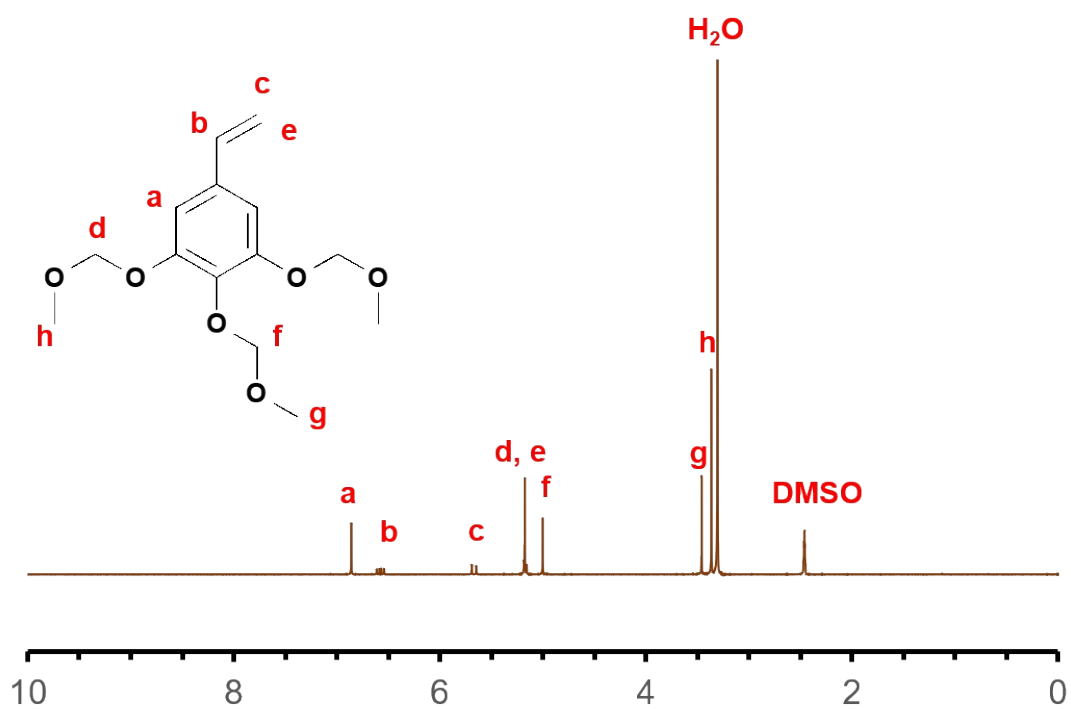


Figure S1. ¹H NMR spectrum of TMMS (400 MHz, DMSO-d₆).

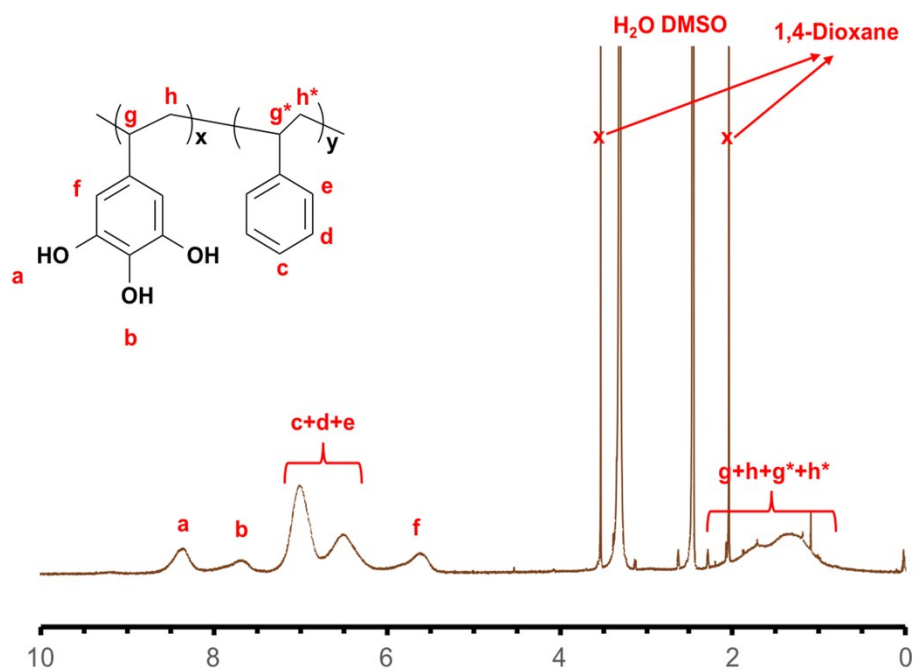


Figure S2. ¹H NMR spectrum of P(VGal-co-St) (400 MHz, DMSO-d₆)

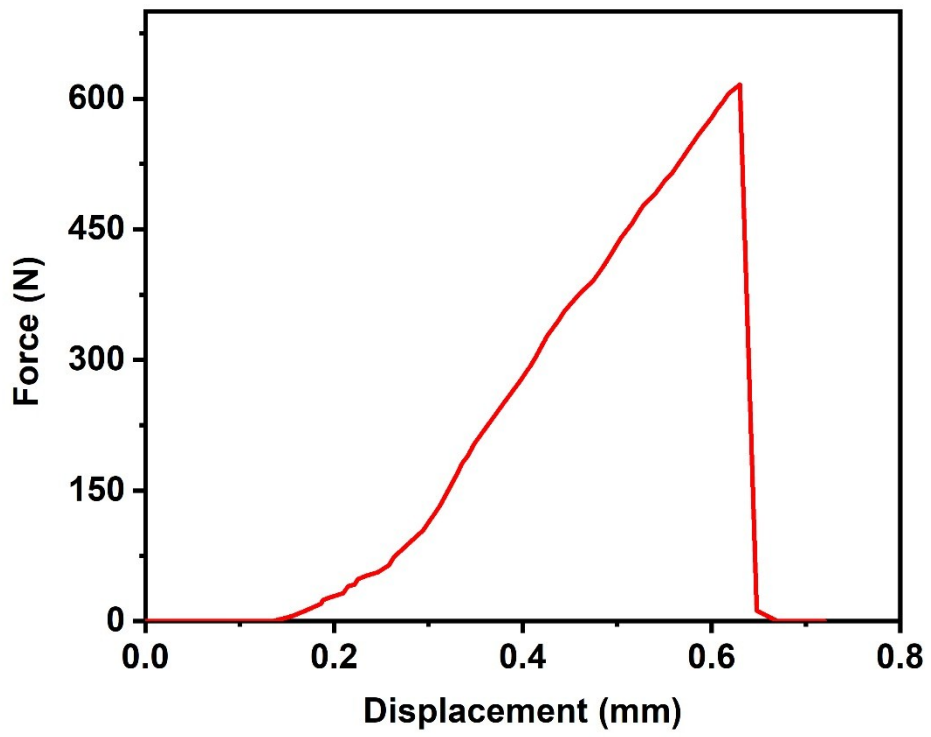


Figure S3. Typical force-displacement curve of the adhesion tests.

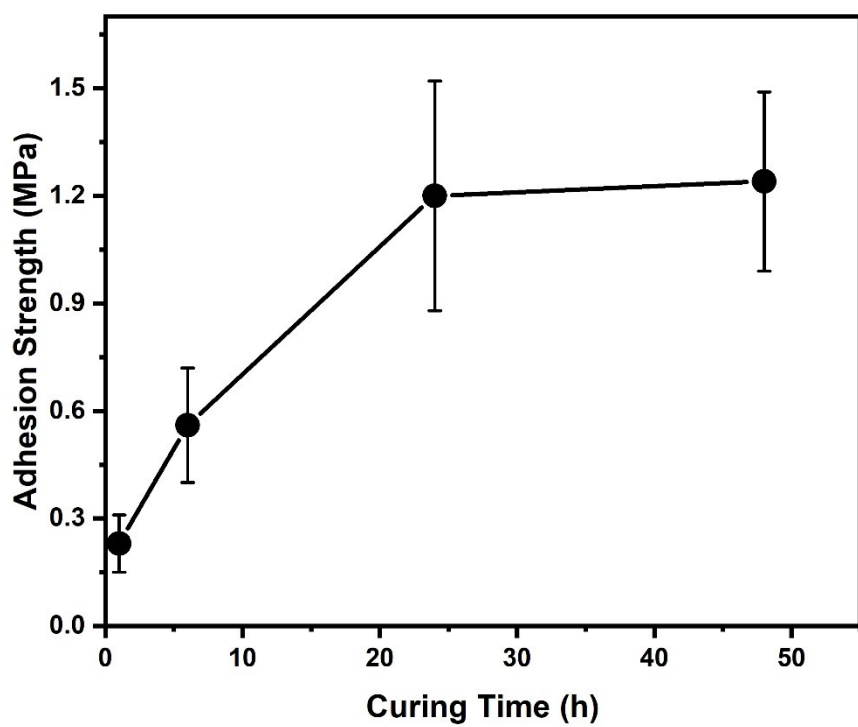


Figure S4. Adhesion strength against curing time of P(VGal-co-St) with low molecular weight ($M_n = 4.2 \times 10^4$)

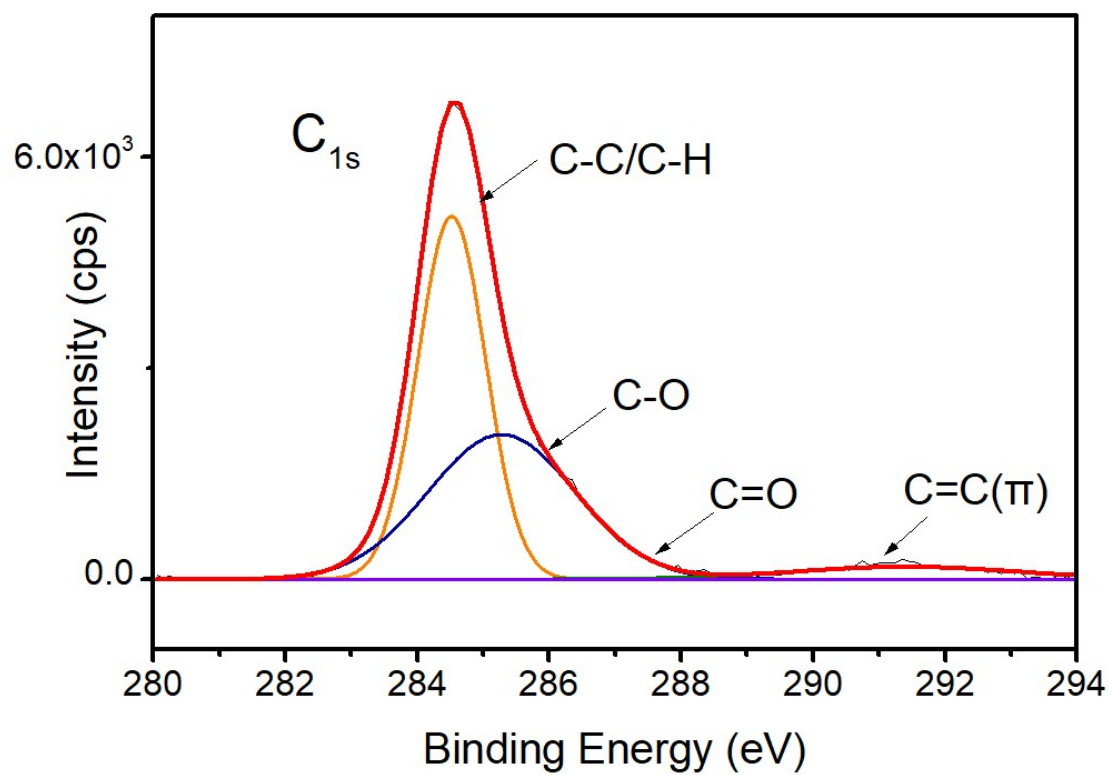


Figure S5. XPS spectrum of fresh P(VGal_{10%}-co-St_{90%}) on alumina substrate.