Electronic Supplementary Information

Modification of amine-cured epoxy resins by boronic acids based on their reactivity with intrinsic diethanolamine units

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Materials and instruments

All reagents and solvents used for this study were commercially available and used as supplied. ¹H nuclear magnetic resonance (NMR) spectra and diffusion-ordered spectroscopy (DOSY) spectra were recorded on a Bruker topspin AVANCE III HD500 spectrometer, using hexadeuterodimethyl sulfoxide (DMSO-*d*₆) or CDCl₃ as solvents. Unless otherwise mentioned, the spectra were taken at room temperature. In NMR spectra, the signals of residual undeuterated solvent were used as the internal standard. Differential scanning calorimetry (DSC) measurements were carried out on a SHIMADZU DSC-60A Plus with a heating rate of 10 °C/min. Fluorescence spectra were measured on a JASCO FP-6600 spectrofluorometer. Tensile tests were performed with an elongation rate of 100 mm/min at room temperature on a Shimadzu EZ-L instrument equipped with 50 N load cell. Gel permeation chromatography (GPC) was performed at 30 °C using a JASCO HSS-1500 system with a refractive index (RI) detector, using *N*,*N*-dimethylformamide (DMF) as eluent. The number average molecular weight (*M*_n) and polydispersity index (*M*_w/*M*_n) of the polymers were calculated on the basis of a polystyrene calibration.

Synthesis of DEAal: 3,3'-(octylazanediyl)bis(1-phenoxypropan-2-ol)

Glycidyl phenyl ether (2.23 g, 14.9 mmol) and *n*-octylamine (0.800 mL, 4.99 mmol) were mixed in a round-bottom flask and stirred at 80 °C for 20 h. The crude product was chromatographed on a silica gel using chloroform/methanol (v/v = 80/1) as the eluent. After drying under vacuum, 1.13 g of **DEAal** was obtained as viscous liquid (53% yield). ¹H NMR (500 MHz, DMSO-*d*₆) : δ /ppm 0.80–0.84 (m, 3H, CH₂C*H*₃), 1.14–1.22 (m, 10H, CH₂), 1.33–1.36 (m, 2H, NCH₂C*H*₂), 2.41–2.66 (m, 6H, NCH₂), 3.81–3.86 (m, 4H, OCH₂), 3.92–3.99 (m, 2H, CHOH), 4.81, 4.82, 4.84, 4.85 (dd, *J* = 3.90, 2H, OH), 6.84–6.92 (m, 6H, aromatic), 7.22–7.27 (m, 4H, aromatic); ¹³C NMR (125 MHz, DMSO-*d*₆): δ /ppm 14.42, 22.56, 27.28, 27.33, 27.35, 29.22, 29.44, 31.72, 55.92, 56.07, 58.31, 58.9, 67.72, 68.05, 70.76, 70.91, 114.7, 114.80, 120.79, 120.81, 129.85, 129.86, 159.17, 159.18; FT-IR (NaCl): v⁻/cm⁻¹ 3330, 2922, 1599, 1520, 1496, 1457, 1361, 1301, 1244, 1173, 1078, 1042, 805, 753, 690, 504, 457, 435, 423; MS (FAB⁺) *m/z* = 430.30 [**DEAal** + H]⁺.

Synthesis of DEAar: 3,3'-(p-tolylazanediyl)bis(1-phenoxypropan-2-ol)

p-Toluidine (0.353 g, 3.29 mmol) was dissolved in a round-bottom flask at 50 °C. Then, glycidyl phenyl ether (0.99 g, 6.58 mmol) was added into the flask. The mixture was stirred at 80 °C for 7.5 h. The crude product was chromatographed on a silica gel using hexane/ethyl acetate (v/v = 4/1) as the eluent. After drying under vacuum, 0.496 g of **DEAal** was obtained as white solid (37% yield). ¹H NMR (500 MHz, DMSO-*d*₆) : δ /ppm 2.15 (s, 3H, CH₃), 3.30–3.71 (m, 4H, NCH₂), 3.89–3.95 (m, 4H, OCH₂), 4.04–4.06 (m, 2H, CHOH), 5.16–5.34 (m, 2H, OH), 6.67, 6,68, 6,69, 6,70 (dd, *J* = 4.60, 2H, aromatic), 6.92–6.95 (m, 8H, aromatic), 7.27–7.31 (m, 4H, aromatic); ¹³C NMR (125 MHz, DMSO-*d*₆): δ /ppm 19.87, 39.02, 39.18, 39.61, 39.78, 39.85, 39.94, 40.02, 54.71, 55.29, 66.51, 66.57, 70.06, 70.11, 112.05, 112.10, 114.48, 114.52, 120.58, 123.79, 123.84, 129.51, 145.58, 145.76, 158.57; FT-IR (NaCl): v^{-} /cm⁻¹ 3330, 2922, 1599, 1520, 1496, 1457, 1361, 1301, 1244, 1173, 1078, 1042, 805, 753, 690, 504, 457, 435, 423; MS (FAB⁺) *m/z* = 430.20 [**DEAar** + H]⁺.

Synthesis of DOAB

Equimolar amount of **DEAal** and 4-methylphenyl boronic acid (**BA**) were dissolved in chloroform and mixed thoroughly in a glass vial. After drying the solvent in air, solid product was obtained. ¹H NMR spectra were recorded for each reaction to assess the generation of DOAB. All model reactions using reactants shown in **Scheme 1** and listed in **Table S1** were conducted in the same manner.

| Reactant name | | Reaction |
|---------------|-----------------------------|--------------------------------------------------|
| DEA | Boronic acid | |
| DEAal | 4-methylphenyl boronic acid | + |
| DEAar | 4-methylphenyl boronic acid | _ |
| DEAal | 2-anthracene boronic acid | + |
| DEAal | 9-anthracene boronic acid | _ |
| | | + : DOAB was formed. - : DOAB was NOT formed. |

Table S1 Reactants of model reactions

DOAB from **DEAal** + **BA**: ¹H NMR (500 MHz, DMSO-*d*₆) : δ/ppm 0.81–0.85 (m, 3H, CH₃), 0.98–1.22 (m, 10H, CH₂), 1.44–1.53 (m, 2H, CH₂), 2.21–2.30 (m, 3H, PhCH₃), 2.68–3.49 (m, 6H, NCH₂), 4.06–4.16 (m, 4H, OCH₂), 4.42–4.58 (m, 2H, CH₂C*H*O), 6.86–7.05 (m, 8H, aromatic), 7.30–7.34 (m, 4H, aromatic), 7.43–7.49 (m, 2H, aromatic); ¹³C NMR (125 MHz, DMSO-*d*₆): δ/ppm 14.38, 21.52, 22.48, 22.58, 24.49, 24.69, 26.84, 28.88, 29.05, 29.10, 29.24, 31.58, 31.74, 56.46, 58.31, 60.10, 60.78, 62.21, 69.98, 70.08, 70.66, 70.73, 71.45, 72.40, 114.74, 114.90, 114.98, 121.07, 127.90, 127.98, 129.83, 129.96, 133.83, 133.89, 136.09, 136.13, 159.08, 159.10; FT-IR (NaCl): v⁻/cm⁻¹ 3873, 3856, 3843, 3753, 3737, 3713, 3692, 3679, 3651, 3631, 3336, 3033, 2925, 2857, 1600, 1588, 1497, 1455, 1377, 1300, 1247, 1225, 1200, 1178, 1122, 1079, 1045, 879, 798, 753, 691, 666, 650, 514.

DOAB from **DEAal** + 2-anthracene boronic acid: ¹H NMR (500 MHz, DMSO-*d*₆) : δ /ppm 0.66–0.71 (m, 3H, CH₃), 0.96–1.11 (br, 10H, CH₂), 1.41–1.50 (br, 2H, CH₂), 2.81–3.54 (m, 6H, NCH₂), 4.14–4.24 (m, 4H, OCH₂), 4.56–4.67 (m, 2H, CH₂CHO), 6.96–7.08 (m, 6H, aromatic), 7.31–7.37 (m, 4H, aromatic), 7.43–7.47 (m, 2H, aromatic), 7.70–7.77 (m, 1H, aromatic), 7.88–7.92 (m, 1H, aromatic), 7.99–8.05 (m, 2H, aromatic), 8.23–8.25 (m, 1H, aromatic), 8.44–8.45 (br, 2H, aromatic); ¹³C NMR (125 MHz, DMSO-*d*₆): δ /ppm 14.38, 21.52, 22.48, 22.58, 24.49, 24.69, 26.84, 28.88, 29.05, 29.10, 29.24, 31.58, 31.74, 56.46, 58.31, 60.10, 60.78, 62.21, 69.98, 70.08, 70.66, 70.73, 71.45, 72.40, 114.74, 114.90, 114.98, 121.07, 127.90, 127.98, 129.83, 129.96, 133.83, 133.89, 136.09, 136.13, 159.08, 159.10; FT-IR (NaCl): ν^{-} /cm⁻¹ 2925, 1599, 1496, 1456, 1300, 1246, 1173, 1044, 878, 752, 690, 481, 473, 453, 437.

Determination of binding constant

The binding constant (K_a) for DEA and boronic acid was determined by using ¹H NMR spectrum based on the following equation:²

$$K_a = \frac{I_{DOAB}}{I_{DEA} \left(n_{BA} - \frac{I_{DOAB}}{I_{DEA} + I_{DOAB}} n_{DEA} \right)}$$

where I_{DOAB} is the integral value of protons in DOAB; I_{DEA} is the integral value of protons in DEA; n_{BA} is the initial molar concentration of the boronic acid; n_{DEA} is the initial molar concentration of the DEA.

Synthesis of linear epoxy polymer (EP)

Scheme S1. Synthesis of EP.¹



2,2-Bis(4-glycidyloxyphenyl)propane (DGEBA) (0.820 g, 2.42 mmol) and 1-propylamine (0.200 mL, 2.42 mmol) were dissolved in 0.900 mL of DMF in a glass vial. After being stirred at 100 °C for 3 h, the reaction mixture was precipitated into a mixture of acetone/hexane (v/v = 3/2). The obtained white solid was dried under vacuum to give **EP** (0.617 g, 64% yield). M_n = 33,800, M_w/M_n = 2.36. ¹H NMR (500 MHz, DMSO-*d*₆) : δ /ppm, 0.73–0.77 (m, 3H, CH₂CH₃), 1.35-1.39 (m, 2H, CH₂CH₃), 1.53 (br, 6H, CCH₃), 2.40–2.62 (m, 6H, NCH₂), 3.78–3.93 (m, 6H, OCH₂CHOH), 4.81–4.84 (m, 2H, OH), 6.74–6.78 (m, 4H, aromatic), 7.03–7.05 (m, 4H, aromatic); FT-IR (NaCl): v⁻/cm⁻¹ 3383, 2962, 1607, 1509, 1461, 1296, 1248, 1182, 1038, 827, 755, 663, 629, 593, 577, 560, 539.

Reaction of EP with boronic acid

EP (5.03 mg with approx. 12.6 μmol of DEA units) and **BA** (1.20 mg, 8.83 μmol) were dissolved in chloroform and mixed thoroughly in a glass vial. After drying the solvent in air, white solid was obtained. ¹H NMR spectrum and DOSY spectrum were recorded to assess the generation of the adduct (**EP-BA**). ¹H NMR (500 MHz, DMSO- d_6) : δ/ppm 0.62 (br, 3H, CH₃), 1.40–1.57 (br, 8H, CH₂CH₃, CCH₃), 2.11, 2.43, 2.59–2.67, 2.84, 3.42 (br, 6H, NCH₂), 3.79–4.08 (br, 4H, OCH₂), 4.41–4.51 (br, 2H, CH₂CHO), 6.87 (br, 4H, aromatic), 7.00 (br, 2H, aromatic), 7.10 (br, 4H, aromatic), 7.40–7.46 (m, 2H, aromatic); FT-IR (NaCl): v^{-} /cm⁻¹ 2967, 2872, 1607, 1581, 1509, 1455, 1384, 1362, 1296, 1249, 1182, 1042, 828, 799, 756, 665, 560.

Gelation of EP

DMF solutions of **EP** (0.278 g with approx. 0.696 mmol of DEA units in 0.80 mL of DMF) and 4,4'biphenyldiboronic acid (**diBA**) (72.4 mg 0.299 mmol in 0.70 mL of DMF) were prepared. Then, the **diBA** solution was added dropwise to the **EP** solution that was being mixed by using magnetic stirrer (Movie S1). Gelation was no more observed after ~62 % of the prepared **diBA** solution was dropped.

Synthesis of cross-linked epoxy resin (ER)

Scheme S2. Synthesis of ER.



DGEBA (0.800 g, 2.35 mmol) and poly(propylene glycol) bis(2-aminopropyl ether) (D2000, average $M_n \sim 2000$) (2.35 g, 1.18 mmol) were mixed thoroughly in a glass vial by using magnetic stirrer. After degassed under vacuum, the mixture was poured into a Teflon mold and heated at 120 °C for 4 h followed by 140 °C for 2 h. The cured sample was removed from the mold as a transparent elastomer, **ER**.

Modification of ER by fluorescent boronic acid

ER cut into squares by razor blade was immersed in 3 mL of tetrahydrofuran (THF) solution of an anthracene boronic acid (2-anthracene boronic acid or 9-anthracene boronic acid) $(5.0 \times 10^{-2} \text{ M})$ for 5 minutes. The sample was then washed with THF/methanol (v/v = 2/1) in a Soxhlet extractor and dried in the ambient condition. Fluorescence spectra of the treated sample were measured to evaluate the incorporation of boronic acid into **ER**.

Modification of ER by diboronic acid

ER cut into a dumbbell shape (ISO 37-4 specimen) was immersed in 30 mL of THF solution of 1,4phenylene diboronic acid (5.0×10^{-2} M) for 15 minutes. The sample (**ER-diBA**) was then washed with THF/methanol (v/v = 2/1) in a Soxhlet extractor and dried in the ambient condition. Completion of washing was confirmed by observing no exothermic peaks in its DSC profile. A reference sample treated with 4-methylphenyl boronic acid (**ER-BA**) was prepared in the same manner. Tensile stress tests were performed to evaluate the incorporation of boronic acid into **ER**.



Fig. S1 ¹H NMR spectrum of DEAal (DMSO-*d*₆, 500 MHz).



Fig. S2 13 C NMR spectrum of DEAal (DMSO- d_6 , 500 MHz).



Fig. S3 FAB mass spectrum of DEAal.



Fig. S4 ¹H NMR spectra of the mixture of equimolar **DEAal** and **BA** (black), **BA** (blue), and **DEAal** (red) (DMSO-*d*₆, 500 MHz).



Fig. S5 ¹³C NMR spectrum of the mixture of equimolar DEAal and BA (DMSO-*d*₆, 500 MHz).



Fig. S6 ¹H NMR spectrum of DEAar (DMSO-*d*₆, 500 MHz).



Fig. S7 ¹³C NMR spectrum of **DEAar** (DMSO-*d*₆, 500 MHz).



Fig. S8 FAB mass spectrum of DEAar.



Fig. S9 ¹H NMR spectra of the mixture of equimolar **DEAar** and **BA** (black), **BA** (blue), and **DEAar** (red) (DMSO-*d*₆, 500 MHz).



Fig. S10 ¹H NMR spectra of DOAB formed with equimolar **DEAal** and 2-anthracene boronic acid (black), 2-anthracene boronic acid (blue), and **DEAal** (red) (DMSO-*d*₆, 500 MHz).



Fig. S11 ¹³C NMR spectra of DOAB formed with equimolar **DEAal** and 2-anthracene boronic acid (DMSO-*d*₆, 125 MHz).



Fig. S12 ¹H NMR spectrum of the mixture of equimolar **DEAal** and 9-anthracene boronic acid (black), 9-anthraceneboronic acid (blue), and **DEAal** (red) (DMSO-*d*₆, 500 MHz).



Fig. S13 Fluorescence emission spectra of DEAal mixed with the equimolar amount of an anthracene boronic acid, an anthracene boronic acid, and DEAal in chloroform at room temperature. Sample concentration was 1.0×10^{-5} M for all measurements. $\lambda_{ex} = 365$ nm. (a) Spectra of samples using 2-anthracene boronic acid. λ_{em} shifted from 418 nm to 415 nm after addition of DEAal to 2-anthracene boronic acid. (b) Spectra of samples using 9-anthracene boronic acid. λ_{em} remained at 413 nm.



Fig. S14 ¹H NMR spectra of **DEAal-BA** with various **DEAal/BA** ratio shown on the right of spectra. Rectangles in gray represent **DEAal-BA** signals (DMSO-*d*₆, 500 MHz).



Fig. S15 Binding constant of DEAal-BA at 25-100 °C in DMSO-d₆.



Fig. S 16. FT-IR spectra of EP (black) and EP-BA (blue) (NaCl).



Fig. S17 Stacked DOSY spectra of EP (black) and EP-BA (blue) in DMSO-d₆.



Fig. S18 DSC profiles of EP (black) and EP-diBA (red).



Fig. S19 Photograph of ER.



Fig. S20 DSC profiles of ER (black), ER-BA (blue), ER-diBA (red).



Fig. S21. Solid-state fluorescence emission spectra of ER treated with an anthracene boronic acid, an anthracene boronic acid, and ER at room temperature. $\lambda_{ex} = 365$ nm. (a) Spectra of samples using 2-anthracene boronic acid. λ_{em} of treated ER was 415 nm. (b) Spectra of samples using 9-anthracene boronic acid.

| Sample name | Fracture stress ^a [MPa] | Strain ^a [%] | Young's modules [®] | [MPa] T_g^b [°C] | |
|-------------|------------------------------------|-------------------------|------------------------------|--------------------|--|
| ER | 0.94 | 72 | 1.4 | -44.5 | |
| ER-BA | 1.2 | 98 | 1.3 | -44.7 | |
| ER-diBA | 1.8 | 71 | 2.6 | -45.5 | |

Table S2 Mechanical and thermal characteristics of cross-linked epoxy polymers

^aAverage value of four measurements.

^bDetermined by DSC.

Reference

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