

## Supporting Information

### Readily Self-healing and Recyclable Silicone Elastomer via Boron–Nitrogen Noncovalent Crosslinking

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## Experimental

### Materials

Octamethylcyclotetrasiloxane (D<sub>4</sub>) and 3-aminopropylmethyldiethoxysilane were obtained as the commercial products and used directly. Dichloromethane, acetic acid, ethanol, N-butyl amine, trichloromethane, and methanol were obtained from Tianjin Fuyu Chemical Co., Ltd. 4-(methylol) benzyl alcohol ester and acryloyl chloride were supplied by Energy Chemical Technology Co., Ltd.

### Characterization and measurements

The proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectra were recorded on a Bruker AVANCE 400 spectrometer at 25 °C using CDCl<sub>3</sub> as the solvent and without tetramethylsilane as an interior label. The scanning electronmicroscopy (SEM) images were obtained using a Hitachi S-4800(7 kV). The samples were cut and coated with a thin layer of platinum before the investigation. X-ray photoelectron spectroscopy was performed by using a Thermo Fisher Scientific Escalab 250 spectrometer with a monochromated Al<sub>Kα</sub> X-ray source at a residual pressure of 10<sup>-7</sup>pa. Rheological measurements were performed by using a Haake Rheostress 6000 rheometer with a cone-plate system (L1) at 25.0 °C. The dynamic frequency sweep measurements were carried out in the linear viscoelastic region, which was determined from dynamic stress sweep measurements. The healing efficiency of the materials could be indicated as  $\eta, \eta = T_{\text{healed}}/T_{\text{initial}}$ , where  $T_{\text{healed}}$  and  $T_{\text{initial}}$  are the tensile strengths of the healed and initial samples, respectively.

### Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-boroxo) benzyl acrylate (TBBA)

4-(methylol) benzyl alcohol ester (2.88 g) and triethylamine (3.0 g) were dissolved in 25 mL trichloromethane. Then, acryloyl chloride (1.5 g) was added dropwise to the reaction mixture. The resulting mixture was sealed and stirred for 2 h in an ice bath. The solvent and the unreacted acryloyl chloride were removed under vacuum. Next, triethylamine salt was removed by column chromatography using ethyl acetate as an eluent. A yellow liquid (3.0 g) was obtained after vacuum drying (yield 85%). <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): 7.84 (d, 2H, -C<sub>2</sub>H<sub>2</sub>BOOC<sub>2</sub>H<sub>12</sub>), 7.40 (d, 2H, CH<sub>2</sub>=CHCOOCH<sub>2</sub>C<sub>2</sub>H<sub>2</sub>), 6.47 (dd, 2H, CH<sub>2</sub>=CHCOOCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>BOOC<sub>2</sub>H<sub>12</sub>), 5.87 (dd, 1H, CH<sub>2</sub>=CHCOOCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>BOOC<sub>2</sub>H<sub>12</sub>), 5.24 (s, 2H, -CH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>BOOC<sub>2</sub>H<sub>12</sub>), 1.36 (s, 12H, -C<sub>2</sub>H<sub>12</sub>).

### Synthesis of the polymer (PAPMS).

PAPMS was synthesized by ring opening polymerization. Typically, 100 g D<sub>4</sub> and 10 g 3-aminopropylmethyldiethoxysilane were added to a 250 mL three-neck flask equipped with a mechanical stirrer. 0.053 g (0.05 wt%) KOH, 1.88 g water, and 1.1 g (1.0 wt%) DMSO were added to the mixture. The mixture was refluxed and stirred for 4 h at 100 °C and ethanol and water were removed by

reduced pressure distillation. The resultant mixture was stirred slowly at 120 °C for 15 h, and cooled to room temperature. KOH was neutralized by acetic acid. The low-boiling components were removed by reduced pressure distillation at 180 °C, and a colorless viscous liquid was obtained. GPC data:  $M_n=39894$  g/mol,  $M_w=43752$  g/mol,  $M_z=48416$  g/mol, PDI=1.10.  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ): 2.67 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), 1.58–1.25 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), 0.60–0.46 (m, 2H,  $-\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), 0.25–0.10 (m, 73H,  $-\text{SiCH}_3$ ).

### **Preparation of elastomers**

PAPMS (3.92 g), TBBA (0.54 g), methanol (1 mL) and trichloromethane (9 mL) were added to a 100 mL flask with reflux condenser. Then, the mixture was stirred gently and refluxed at 65 °C for 6 h. Most of the solvent was removed by rotary evaporation, and the thick precursor was placed in a mold for the remaining solvent to volatilize slowly at room temperature. Transparent elastomer films with light yellow color were obtained with high yield (99%).