

Supporting Information for

A Stretchable and Rapidly Self-healable Polysiloxane Elastomer Based on Reversible Aluminum-amino Coordination

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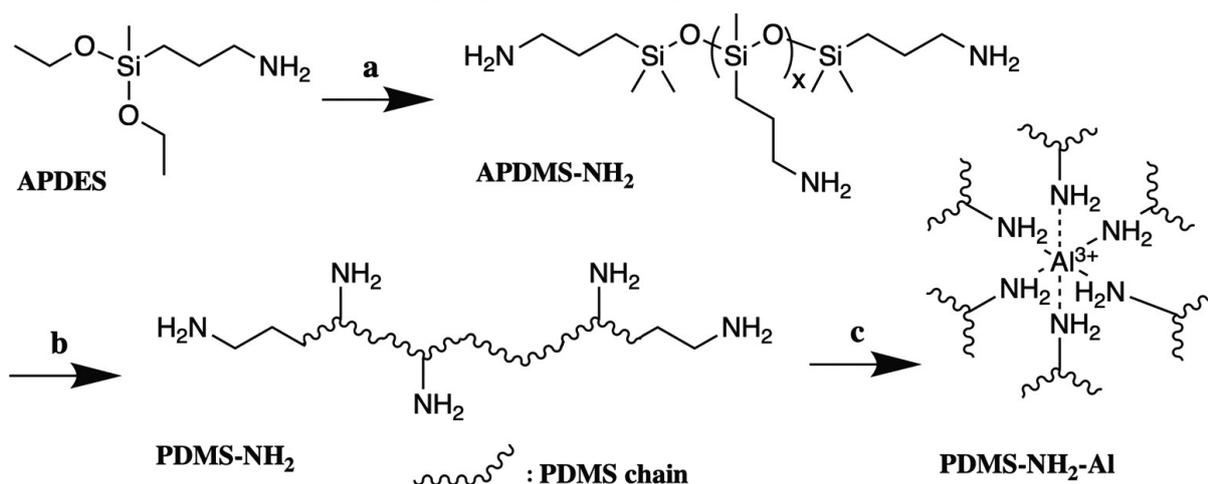
Experimental Details

Materials

Octamethylcyclotetrasiloxane (D4, 99%) was supplied by Dow Corning Silicones (USA). 3-Aminopropyldiethoxymethylsilane (APDES, 96%) was purchased from Qufu Chenguan Chemical Co. Ltd. (Shandong, China). 1, 3-bis(3-aminopropyl)-tetramethyldisiloxane (AMM, 97%) and tetramethylammonium hydroxide pentahydrate ($\text{Me}_4\text{NOH}\cdot 5\text{H}_2\text{O}$, 99%) were purchased from Macklin (Shanghai, China). Aluminum chloride hexahydrate ($\text{AlCl}_3\cdot 6\text{H}_2\text{O}$), dichloromethane (DCM), methanol (MeOH), and other solvents were supplied by Guangzhou Chemical Reagent Factory (Guangzhou, China). All of the chemicals were used as received without further purification.

Synthesis of amino-grafted polydimethylsiloxanes (PDMS-NH₂)

As is presented in **Scheme S1**, PDMS-NH₂ were synthesized *via* two steps of reactions. Firstly, APDES (95.67 g, 0.5 mol), H₂O (18.00 g, 1.0 mol), and AMM (2.13 g, 8.6 mmol) were added into a round-bottom flask equipped with a stirring system. The mixture was stirred for 4 h at room temperature. Volatile compounds were removed by rotary evaporation at 150 °C and 0.1 MPa to obtain the colorless and clear liquid product APDMS-NH₂. In the second step, D₄ (100 g, 0.34 mol), APDMS-NH₂ (18.50 g, 2.71 mmol), AMM (2.13 g, 8.6 mmol), $\text{Me}_4\text{NOH}\cdot 5\text{H}_2\text{O}$ (catalyst, 0.02 g) were added into a round-bottom flask equipped with a stirring system and a condenser under nitrogen atmosphere. The mixture was stirred for 10 h at 90 °C and then heated to 150 °C for 1.5 h to decompose the catalyst. Volatile compounds were removed by rotary evaporation at 150 °C and 0.1 MPa to obtain the colorless and clear liquid product PDMS-NH₂. Yields: 95%. FT-IR (KBr, cm⁻¹): 2963, 2904, 1580, 1414, 1260, 1089, 1024, 868, 800, 706. ¹H NMR (CDCl_3 , 600 MHz, ppm): 0 – 0.18 (*m*, Si-CH₃), 0.46 – 0.57 (*t*, Si-CH₂), 1.38 – 1.53 (*m*, -CH₂-CH₂NH₂), 2.63 – 2.68 (*m*, -CH₂-NH₂). GPC (see Characterization part): $M_n = 14.6$ kDa, $D = 1.86$, concentration of amino groups = 1.404 mmol·g⁻¹ (calculated from ¹H NMR).



Scheme S1. Synthesis route of PDMS-NH₂-Al. Conditions: a. AMM, H₂O, RT; b. D₄, AMM, $\text{Me}_4\text{NOH}\cdot 5\text{H}_2\text{O}$, 1. 70 °C 10min, 2. 90 °C 10h, 3. 150 °C 1.5 h; c. $\text{AlCl}_3\cdot 6\text{H}_2\text{O}$, dichloromethane/methanol (v/v, 1/1)

Preparation of Al³⁺-coordinated elastomers (PDMS-NH₂-Al)

As is presented in **Scheme S1**, The PDMS-NH₂ was dissolved in DCM/MeOH (1/1, v/v), and then $\text{AlCl}_3\cdot 6\text{H}_2\text{O}/\text{CH}_3\text{OH}$ solution was added dropwise under stirring. The same PDMS-NH₂ (M_n : 14.6 kDa, D : 1.86)

was used for the preparation of elastomers containing different amount of Al^{3+} . The mixture was stirred for 4 h at room temperature, and transferred into a petri dish to evaporate the solvents at 90 °C for 4 h. The resulting product was further dried in vacuum for 12 h and the transparent solids were collected, pressed into testing films for 2 h at room temperature.

Characterizations

Liquid ^1H NMR spectra was acquired at room temperature using Bruker Avance III-600 (600 MHz) spectrometer. Solid-state ^{27}Al and ^{13}C NMR spectra were acquired at 25 °C using Bruker Avance III-400. ^{27}Al chemical shifts was referenced to a 1.0 M aqueous solution of aluminium nitrate as an external standard ($\delta = 0$). ^{13}C chemical shifts were referenced to tetramethylsilane as external standard ($\delta = 0$). FTIR-ATR spectra were recorded using a Nicolet iS5 Fourier-transform infrared spectrometer (Thermo Scientific, USA) equipped with an iD5-ZnSe ATR accessory. The molecular weight of PDMS-NH₂ was measured on a gel permeation chromatography (GPC) system with a Waters 515 pump, Shodex F-804L column and Waters 2414 reflective index detector. Toluene was used as the eluent and narrow-dispersed polystyrene as the standards for calibration. The amino groups of PDMS-NH₂ were protected *via* reaction with *m*-toluene isocyanate to avoid the interaction with the column fillers. Differential scanning calorimetry (DSC) measurements were carried out with a DSC 200F3 apparatus (Netzsch, Germany). The specimens were first heated and held at 80 °C for 5 min and then cooled and held at -150 °C, after that were heated to 150 °C. The heating and cooling rate were 10 °C·min⁻¹. X-ray diffraction analysis was performed with an X' Pert-Pro X-ray diffractometer (PANalytical X' Pert Pro, The Netherlands) with filtered monochromatic Cu $K\alpha$ radiation in the 2θ range of 5° to 90°. The scanning electron microscopy (SEM) images were obtained on an LEO1530VP at 5 kV.

Small angle X-ray scattering (SAXS) measurement was performed using a SAXSess camera (Anton Paar, Austria). A PW 3830 X-ray generator with a long fine focus sealed glass X-ray tube (PANalytical) was operated at 40 kV and 50 mA. A focusing multilayer optics and a block collimator provide an intense monochromatic primary beam (Cu $K\alpha$, $\lambda = 0.1542$ nm). A semi-transparent beam stop enables measurement of attenuated primary beam at zero scattering vector. The film trip was fixed with a sample holder and placed in a TCS 120 temperature-controlled unit along the line shaped X-ray beam in the evacuated camera housing. The sample-to-detector distance was 261.2 mm and the temperature was kept at 26 °C. The 2D scattered intensity distribution recorded by an imaging-plate (IP) detector was read out by a Cyclone storage phosphor system (Perkin Elmer). The 2D data were integrated into the one-dimensional scattering function $I(q)$ as a function of the magnitude of the scattering vector q defined as: $q = 4\pi \sin \theta / \lambda$, where λ is the wavelength and 2θ is the scattering angle. The measurement was collected for 10 min.

Rheological measurements were performed with a MCR102 rheometer (Anton Paar, Austria). The 25 mm aluminum plates were used. The dynamic temperature (20-100 °C) sweep was performed at a strain amplitude of 0.1% and a frequency of 1 Hz. The dynamic frequency sweep (0.1 - 100 rad/s) was performed at a strain amplitude of 0.1% at 80 °C, 70 °C, 60 °C, 50 °C, 40 °C, 30 °C, and 20 °C.

Tensile experiments were performed on rectangular specimens (50 mm × 10 mm × 1 mm) using a KJ-2091 tensile testing machine (Kejian Instruments Co. Ltd, China) at a stretching rate of 100 mm·min⁻¹. For the cyclic tensile test, both loading and unloading were performed at a strain rate of 100 mm·min⁻¹ at 20 °C. Stress relaxation tests was measured at 25 °C and 50% relative humidity (RH) under a constant strain of 50% strain.

Healing efficiency was used to evaluate the self-healing property of different samples. The samples were cut from the middle, and then the cut surfaces were brought attached immediately. After that, samples were

horizontally set without applied stress for 30 min or 60 min at 20 °C or -20 °C before the tensile testing. The healing efficiency (*HE*) was calculated as follows:

$$HE = \frac{EB_{healed}}{EB_{virgin}} \times 100\%$$

where EB_{healed} and EB_{virgin} represent the elongation at break of healed samples and virgin samples.

Supplementary Figures

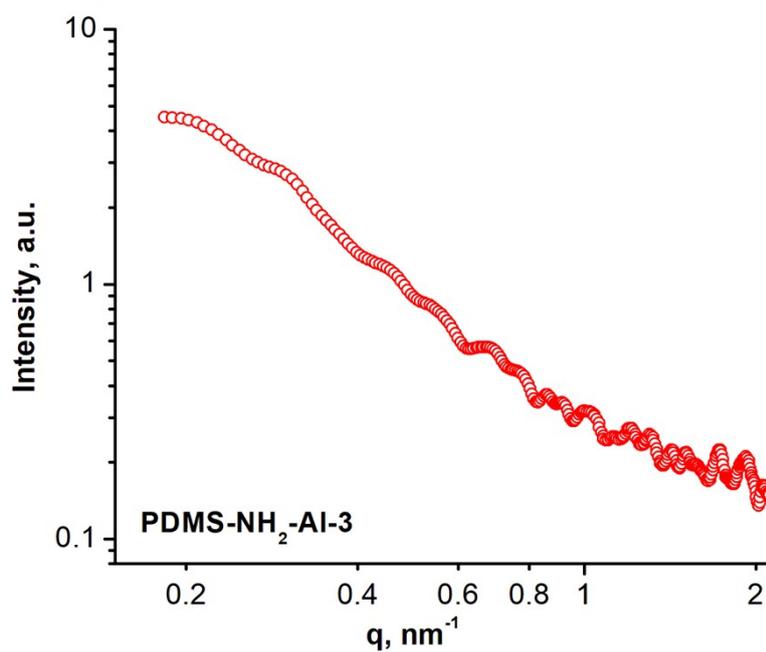


Figure S1. Small angle X-ray scattering profiles of PDMS-NH₂-Al-3.

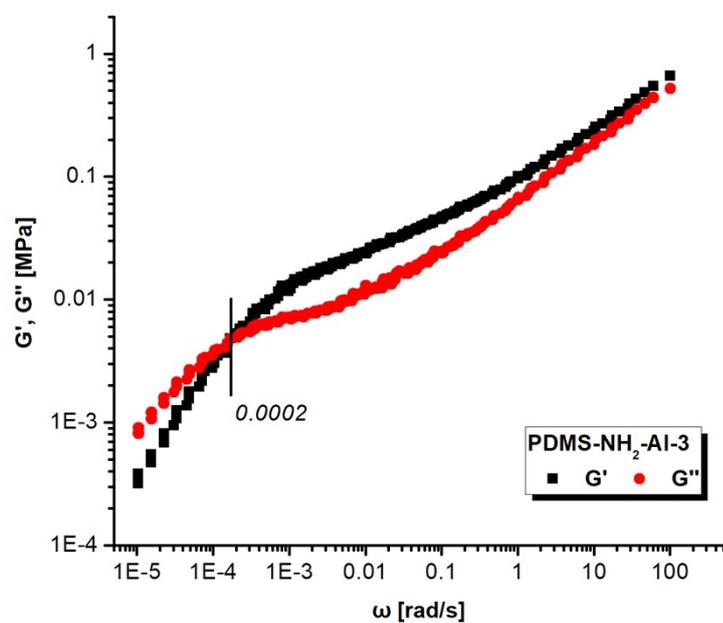


Figure S2. Master curve of frequency dependency of G' and G'' of PDMS-NH₂-Al-3 at a reference temperature of -20 °C.