CO_2 switchable adhesion of ionic polydimethylsiloxane elastomers

Yohei Miwa, [a,b,]* *Masatoshi Tsunoda,*[a] *Shoei Shimozaki,*[a] *Rina Sawada,*[a] *and Shoichi Kutsumizu,*[a]

[a]Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan.

[b]PRESTO, Japan Science and Technology Agency.

*Author to whom correspondence should be addressed.

E-mail: miwa.yohei.y6@f.gifu-u.ac.jp

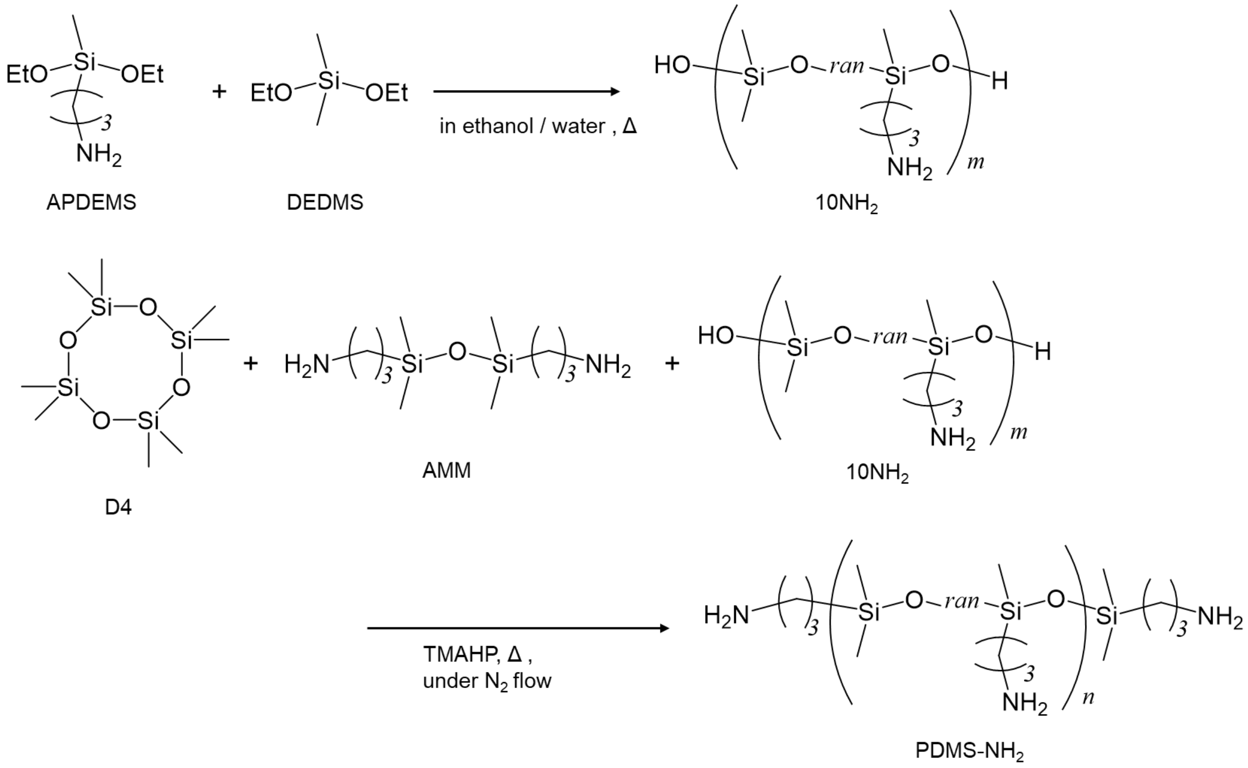
Table of Contents

1. Supplementary Methods

1.1 Sample Preparation.

Materials. Diethoxydimethylsilane (DEDMS, >98%), 3-aminopropyldiethoxymethylsilane (APDEMS, >97%), butyl isocyanate (> 98.0 %), and octamethylcyclotetrasiloxane (D4, >98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. 1,3-bis(3-aminopropyldiethoxymethylsilane (97%) was purchased from Shin-Etsu Chemical Co., Ltd. Molecular sieves (3A 1/16), succinic anhydride (SA, ≥98.0%), lithium hydroxide monohydrate (LiOH, ≥95%), sodium hydroxide (NaOH, 97%), cesium hydroxide monohydrate (CsOH, ≥95%), deuterated chloroform (CDCl3, 99.8%), and deuterated dimethyl sulfoxide (DMSO-d6, 99.8%) were purchased from Nacalai Tesque, Inc. Tetramethylammonium hydroxide pentahydrate (>99%), aluminum oxide, acetone (extra-pure (EP) regent grade), tetrahydrofuran (THF, EP), chloroform (EP), methanol (EP), and ethanol (EP) were purchased from Kanto Chemical Co., Inc.

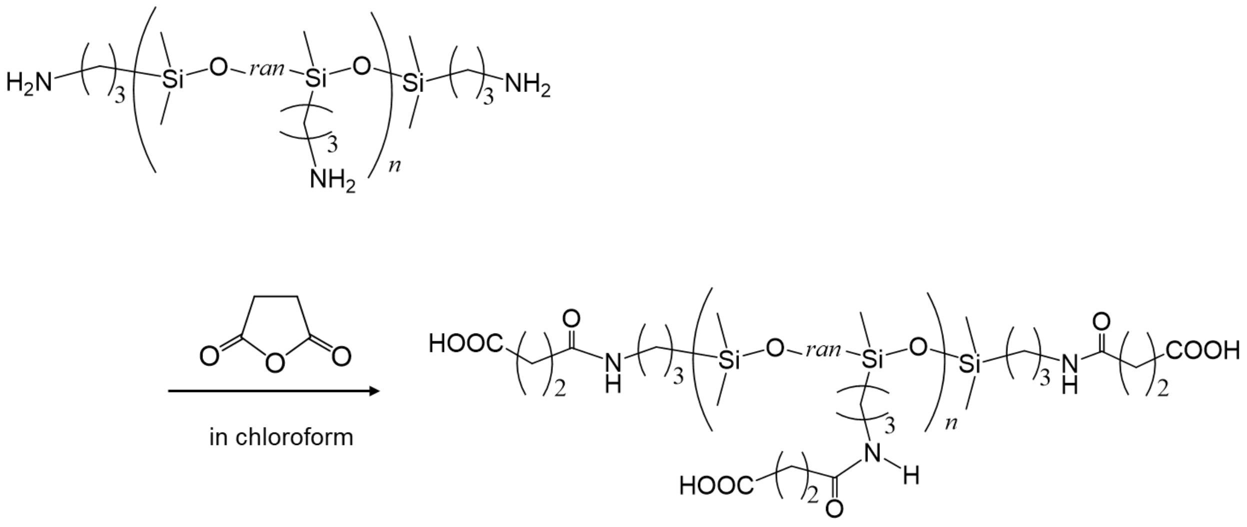
Preparation of PDMS-NH$_2$. DEDMS (416 g, 2.81 mol), APDEMS (59.7 g, 3.12×10^{-1} mol), water (561 g, 31.2 mol), and ethanol (800 g) were stirred at room temperature for 110 h. The reaction mixture was further stirred at 80 °C for 48 h to remove the solvents. And then, the reaction mixture was further heated at 85 °C and 140 ºC for 9 h and 14 h, respectively, in a vacuum. The resultant polymer is called $10NH_2$. A mixture of D4 (500mL, 1.62 mol), $10NH_2$ (189 g), and AMM (1.7 mL, 6.17×10^{-3} mol) was stirred under N_2 gas flow for 1 h in a 1000 mL three-necked flask. Then, TMAHP (1.09×10^{-1} g, 5.65×10^{-4} mol) was quickly added to the mixture. The mixture was heated and stirred at 100 ºC for 46 h under N_2 gas flow. During the reaction, the viscosity of the mixture increased. To terminate the reaction, the mixture was heated at 150 ºC and stirred for 2 h. After that, the reaction mixture was slowly cooled to room temperature. The resultant polymer, PDMS-NH_2, was transferred to a Teflon container and vacuum-dried at 110 ºC for 6 h. The amine concentration of PDMS-NH_2 was determined to be 3.2 mol% via neutralization titration with HCl and bromophenol blue as an indicator. ^{1}H-nuclear magnetic resonance (NMR) spectrum of PDMS-NH_2 is shown in Fig. S1a.



Scheme S1

Preparation of PDMS-COOH. 81.4 g of PDMS-NH_2 (81.4 g) and SA (10.6 g, 1.06 × 10^{-1} mol) were separately dissolved in 300 ml and 200 mL of dehydrated chloroform, respectively. The SA/chloroform solution was stirred at 50 °C until clear solution was obtained. These solutions were mixed and stirred overnight at room temperature. The precipitated SA was removed by filtration, and the solution was subjected to an evaporator to remove the solvent. Here, since some unreacted

SA precipitated as a powder, the polymer was dissolved in hexane containing small amount of chloroform and SA was removed by filtration. After that, the solvent was removed from the polymer using an evaporator. This procedure was repeated three times. Then, the polymer was further purified via precipitation from acetone solution to methanol. This precipitation was repeated twice. Finally, the precipitated polymer was carefully washed with methanol in a Teflon container. The polymer was dried at room temperature for 24 h, and further dried at 35 °C for 48 h in vacuum. The resultant polymer is named as PDMS-COOH. The concentration of carboxy group in PDMS-COOH was determined to be 3.5 mol% via the neutralization titration with NaOH/methanol solution and phenolphthalein. ^{1}H-NMR spectrum of PDMS-COOH is shown in Fig. S1b.



Scheme S2

Preparation of PDMS-*M*. Methanol solution of LiOH, NaOH, or CsOH was added dropwise to stirred THF solution of PDMS-COOH. The carboxy groups of PDMS-COOH were fully neutralized. The neutralized solution was gently poured into a Teflon petri dish, covered with aluminum foil with small holes. The solution was dried at 35 °C for 24 h in air to make a sheet. The sheet was further dried at 35 °C for more than 48 h in vacuum. The thickness of the sheet was ca. 0.5 mm. Fourier transform infrared (FT-IR) spectra of PDMS-*M* are shown in Fig. S2.

1-2. Measurements.

A Perkin Elmer Spectrum 400 (MIR/FIR) was used for FT-IR spectroscopy measurement. Measurements were performed on the transmittance mode with the optical resolution of 4.00 cm^{-1}.

NMR measurements were performed on a JEOL FT-NMR spectrometer α-400. PDMS-NH_2 was dissolved in CDCl3. For PDMS-COOH, a mixture of CDCl3 and DMSO-d6 at a volume ratio of 9:1 was used as a solvent.

Small-angle X-ray scattering (SAXS) measurements were carried out at the beamline BL-15A2 at the Photon Factory (PF) of the High Energy Accelerator Research Organization (KEK) in Tsukuba, Japan. The sample sheets were vacuum-dried for more than two nights and stored in an aluminum package with molecular sieves. Before the measurement, the package was opened, and the sample sheets were quickly set at the sample chamber at the beamline. Dry N_2 or CO_2 gas was flown into the sample chamber. The wavelength of X-ray was 1.2 Å. X-ray scattering from the specimen was recorded using PILATUS-2M detector. Silver behenate and stearic acid were used as standards.

Anton Paar MCR302 was used for rheology measurements. The measurement temperature was controlled using a Peltier temperature controller. Dry N_2 or CO_2 gas was flow into a Peltier hood to control the gaseous atmosphere during the measurements. A stainless-steel parallel plate with a diameter of 4 mm was used as a jig. Before measurement, a sample sheet was vacuum-dried at room temperature for more than 48 h. The measurements were performed at 25° C and a strain of 0.2 % with a frequency of 1 Hz. During the measurement, the inflow gas was switched in the order of $N_2 \rightarrow CO_2 \rightarrow N_2$.

The probe tack tests were conducted at 25°C under controlled gas atmosphere (N_2 or CO_2) using Anton Paar MCR302. A stainless-steel parallel plate with a diameter of 4 mm was used as a probe. The measurements were performed for a sample sheet attached on a copper plate. The sample sheet on a copper plate was vacuum-dried at room temperature for more than 48 h and fixed with screws to an iron cover placed on the Peltier plate at the MCR302. Furthermore, the sample sheet was covered with a Peltier hood and dried by flowing dry N_2 gas overnight. The probe approached at a speed of 10 $\mu m\ s^{-1}$ and contacted with a load of 0.5 N to the sample sheet for 30 s. And then, the probe was removed from the sample sheet with a speed of 10 μm s^{-1}. The measurements were repeated with an interval of 5 min. During the repeated measurements, the inflow gas was changed in the order of N_2 → CO_2 → N_2.

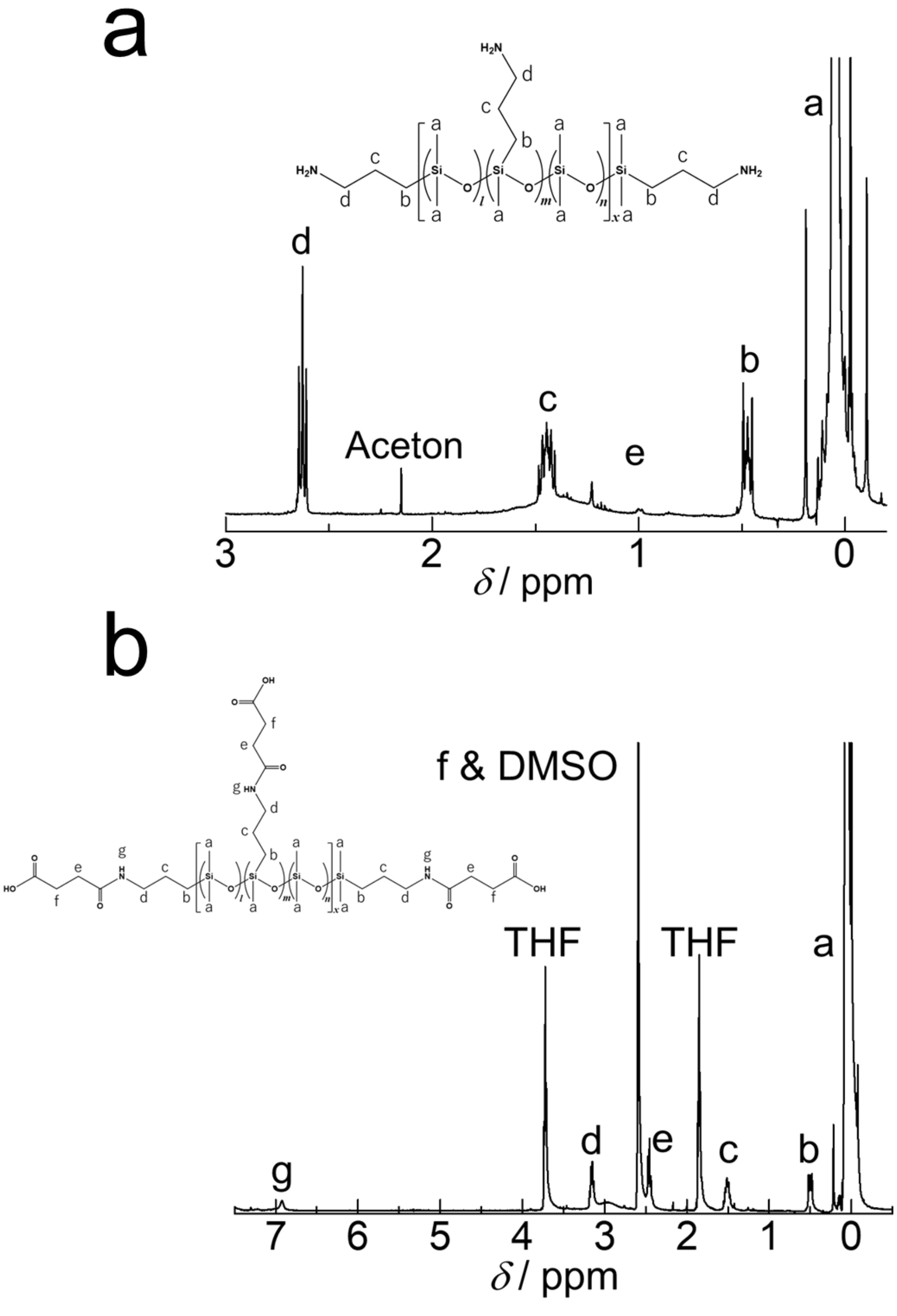


Fig. S1. ^{1}H-NMR spectra of (a) PDMS-NH_2 and (b) PDMS-COOH.

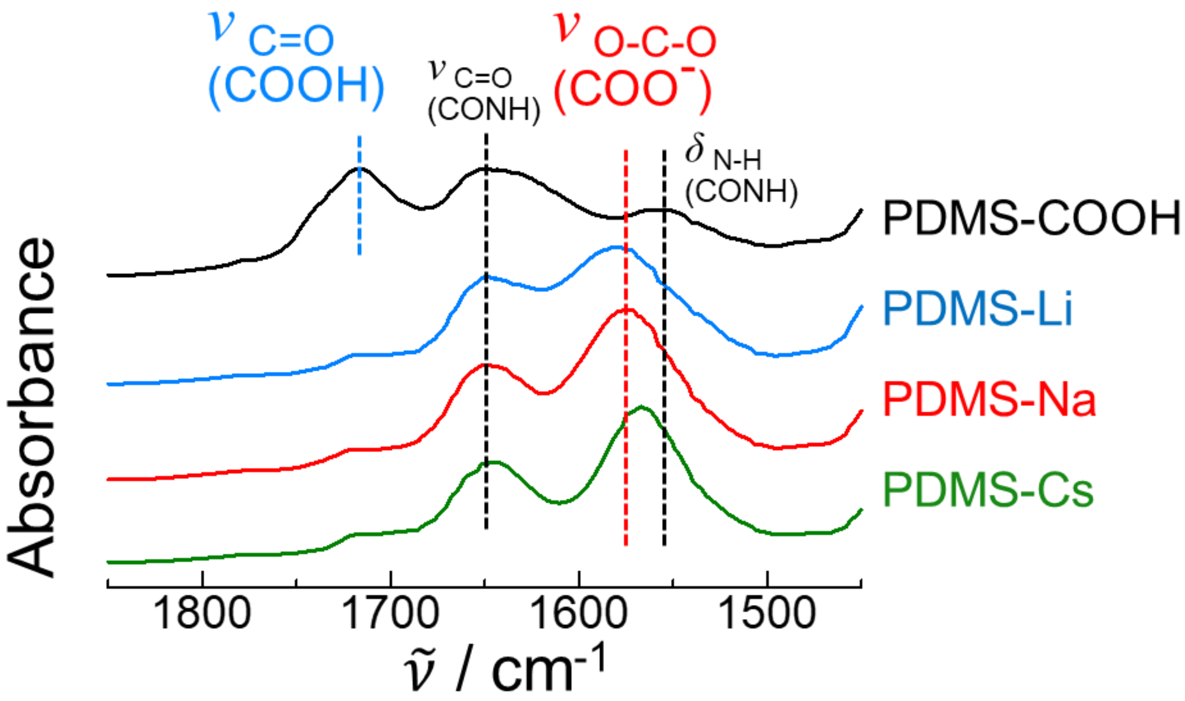


Fig. S2. FT–IR spectra of the indicated samples.

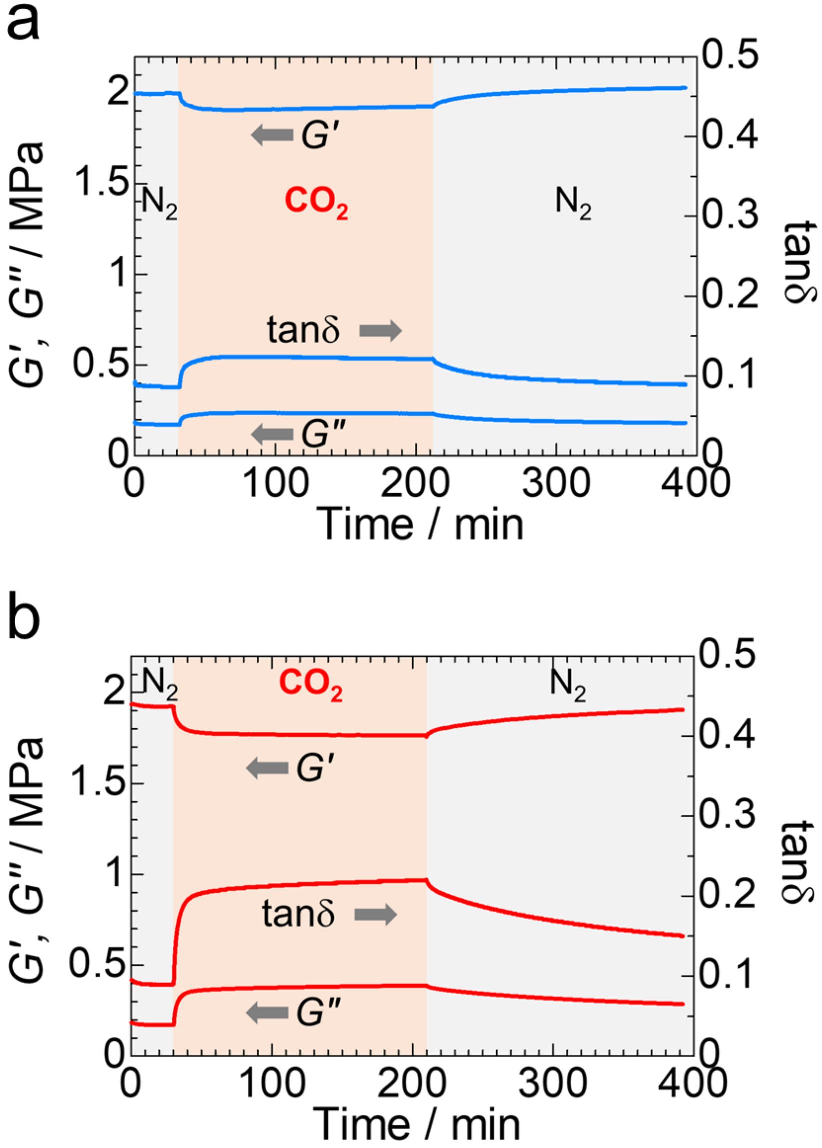


Fig. S3. Effect of CO_2 gas on viscoelastic property of (a) PDMS-Li and (b) PDMS-Na. Temperature and frequency are 25 °C and 1 Hz, respectively.

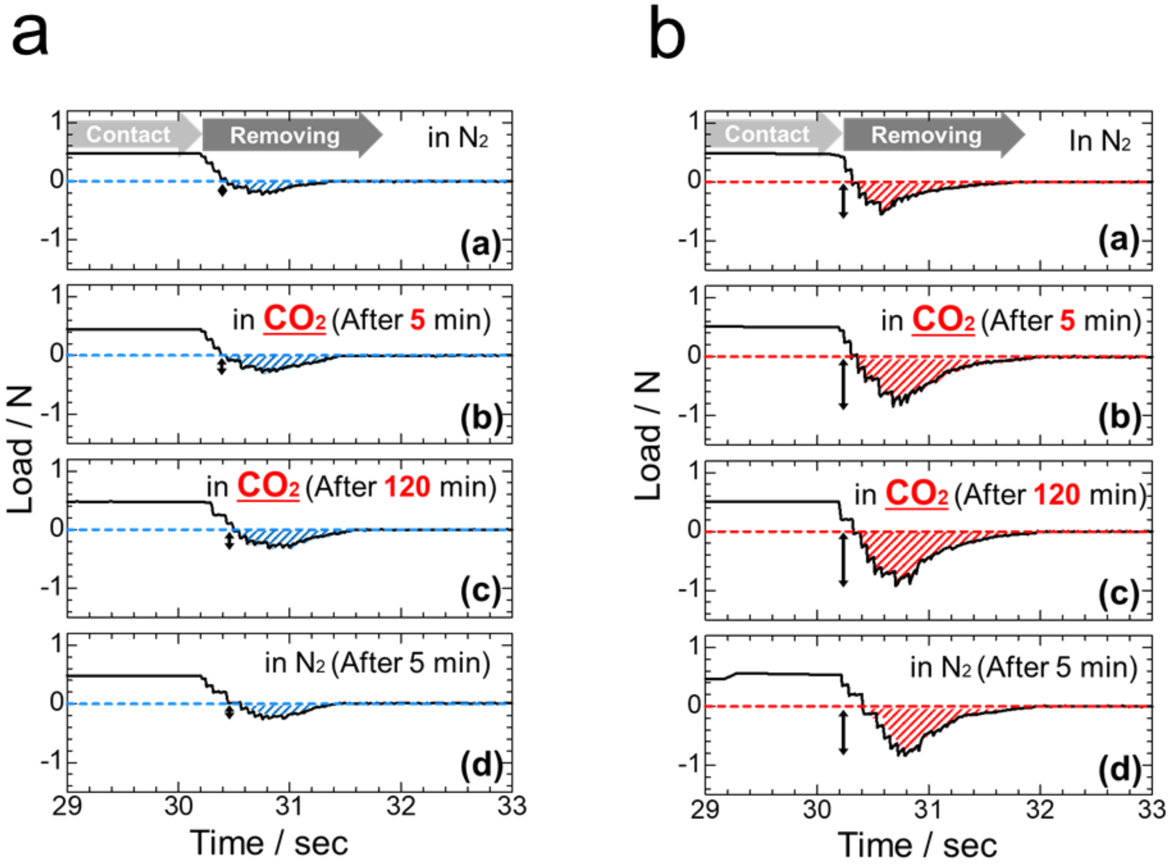


Fig. S4. Selected force vs time curves of (a) PDMS-Li and (b) PDMS-Na at 25 °C in different gases.

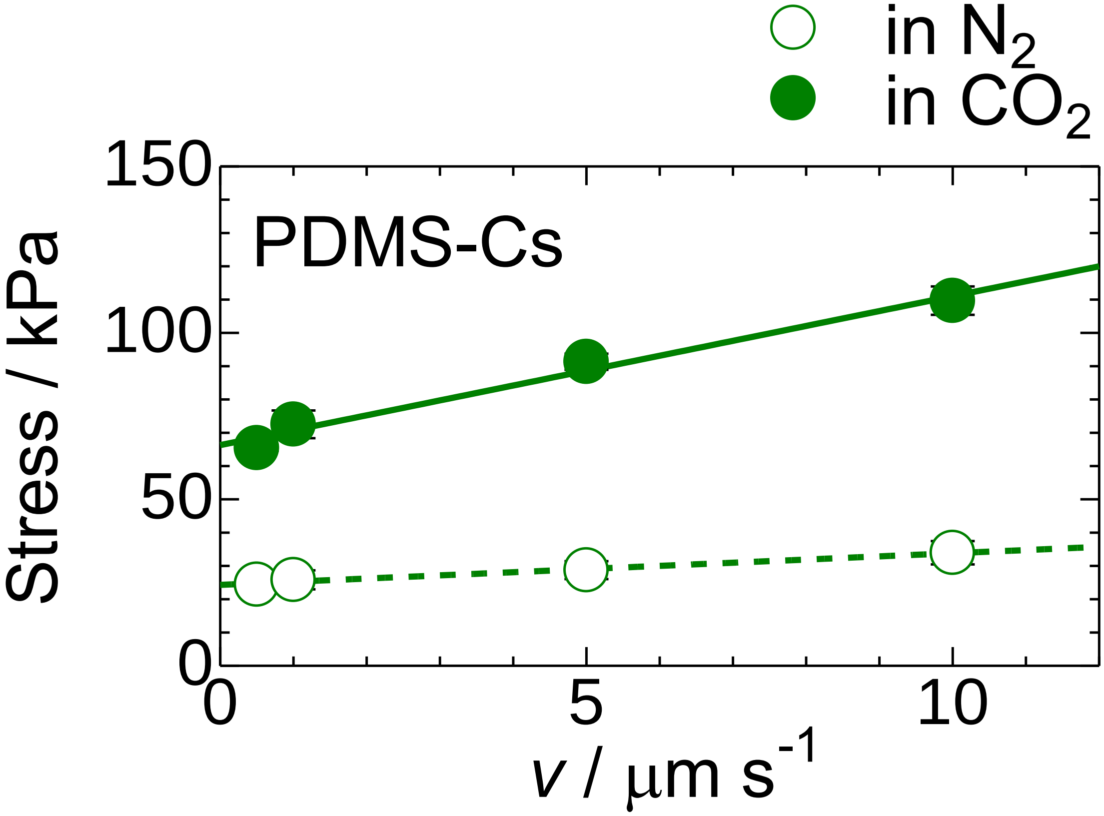


Fig. S5. Effect of velocity of the probe at removing on the adhesion of PDMS-Cs.