

**Supplementary Information for**

**Elastomers mechanically reinforced and toughened with CO<sub>2</sub> gas**

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## Supplementary Methods

**Materials.** Diethoxydimethylsilane (DEMS, >98%), Dimethoxydimethylsilane (DMMS, >98%), 3-aminopropyldiethoxymethylsilane (ADEMS, >97%), 3-aminopropyldimethoxymethylsilane (ADMMS, >97%), tris(2-aminoethyl)amine (TAEA, >98.0%), octamethylcyclotetrasiloxane (D4, >98.0%), bromophenol blue, 1,4-butanediol diglycidyl ether (BDE), and butyl isocyanate (>98.0%) were purchased from Tokyo Chemical Industry Co., Ltd. Poly(ethylene-co-glycidyl methacrylate) (PEGMA) was obtained from Sigma-Aldrich Co. LLC. Hexamethyldisiloxane (HMDS, >98.0%) and 1,3-bis(3-aminopropyl)tetramethyldisiloxane (APMDS, 97%), polydimethylsiloxane (PDMS, KF-96H-50000CS), PDMS modified with diamine group (KF-861), and PDMS modified with epoxy group (KF-1001) were purchased from Shin-Etsu Chemical Co., Ltd. Hydrochloric acid (HCl, 35%), sodium carbonate (>99.0%), molecular sieves (3A 1/16), and  $\text{CDCl}_3$  (99.8%) were purchased from Nacalai Tesuque, Inc. Tetramethylammonium hydroxide pentahydrate (TMAHP, >99%), tetrahydrofuran (THF, >99.5%), chloroform (>99.0%), ethanol (>99.5%), and methanol (>99.8%) were obtained from Kanto Chemical Co., Inc.

**Polymerization of PDMS–M5 (Supplementary Fig. 1a).** A mixture of DEMS (655.1 g, 4.42 mol), ADEMS (93.9 g, 575 mmol), ethanol (200 mL), and water (353 mL, 19.6 mol) was stirred in a glass beaker at room temperature for 6 h. The reaction mixture was further stirred at 80°C for 112 h and then 110°C for 45 h to remove the solvents. The resulting oily sample was heated at 110°C for 28 h in a vacuum. The resultant polymer (114 g), D4 (134 g, 452 mmol), APMDS (0.58 g, 2.32 mmol), and TMAHP (85.4 mg, 0.471 mmol) were stirred at 90°C for 48 h in a three-neck flask under  $\text{N}_2$  flow. The reaction mixture was further heated at 130°C for 1 h to terminate the polymerization. The resultant PDMS–M5 was heated at 100°C for 24 h in a vacuum. The weight-average molecular weight ( $M_w$ ) and the polydispersity index (PDI,  $M_w/M_n$ ) of PDMS–M5, determined by gel permeation chromatography (GPC) calibrated with PDMS standards (Scientific Polymer Products Inc.), were 61,200 and 1.81, respectively. PDMS–M5 was reacted with excess butyl isocyanate in a THF solution to prevent the adsorption of amine groups to the GPC column. The amine concentrations in PDMS–M5 determined by neutralization titration is 5.2 mol% ( $6.8 \times 10^{-4} \text{ mol g}^{-1}$ ).  $^1\text{H-NMR}$  (400 MHz,  $\text{CDCl}_3$ ) (Supplementary Fig. 2a):  $\delta$  (ppm) = 0.07 (6H),  $\delta$  = 0.44 (2H),  $\delta$  = 1.47 (2H),  $\delta$  = 2.65 (2H).

**Polymerization of PDMS–M10 (Supplementary Fig. 1a).** A mixture of DEMS (596.7 g, 4.02 mol), ADEMS (192.5 g, 1.01 mol), ethanol (250 mL), and water (362.1 mL, 20.1 mol) was stirred in a glass beaker at room temperature for 5 h. The reaction mixture was further stirred at 80°C for 85 h and then 110°C for 25 h to remove the solvents. The resulting oily sample was heated at 110°C for 42 h in a vacuum. The resultant polymer (95.3 g), D4 (113.8 g, 147 mmol), APMDS (0.0732 g, 0.295 mmol), and TMAHP (73.2 mg, 0.404 mmol) were stirred at 90°C for 48 h in a three-neck flask under N<sub>2</sub> flow. And then, the reaction mixture was further heated at 130°C for 1h to terminate the polymerization. The resultant PDMS–M10 was heated at 100°C for 24 h in a vacuum. The  $M_w$  and PDI of PDMS–M10, determined by GPC calibrated with PDMS standards, were 98,200 and 2.14, respectively. PDMS–M10 was reacted with excess butyl isocyanate in a THF solution to prevent the adsorption of amine groups to the GPC column. The amine concentrations in PDMS–M10 determine by neutralization titration is 10 mol% ( $1.3 \times 10^{-3} \text{ mol g}^{-1}$ ).

**PDMS–D5.** Commercially available KF-861 was used as PDMS–D5. The  $M_w$  and PDI of PDMS–D5, determined by GPC calibrated with PDMS standards, were 43,000 and 1.59, respectively. PDMS–D5 was reacted with excess butyl isocyanate in a THF solution to prevent the adsorption of amine groups to the GPC column. The amine concentrations in PDMS–D5 determine by neutralization titration is 4.7 mol% ( $6.2 \times 10^{-4} \text{ mol g}^{-1}$ ). Namely, the concentration of diamine group in PDMS–D5 is  $3.1 \times 10^{-4} \text{ mol g}^{-1}$ .

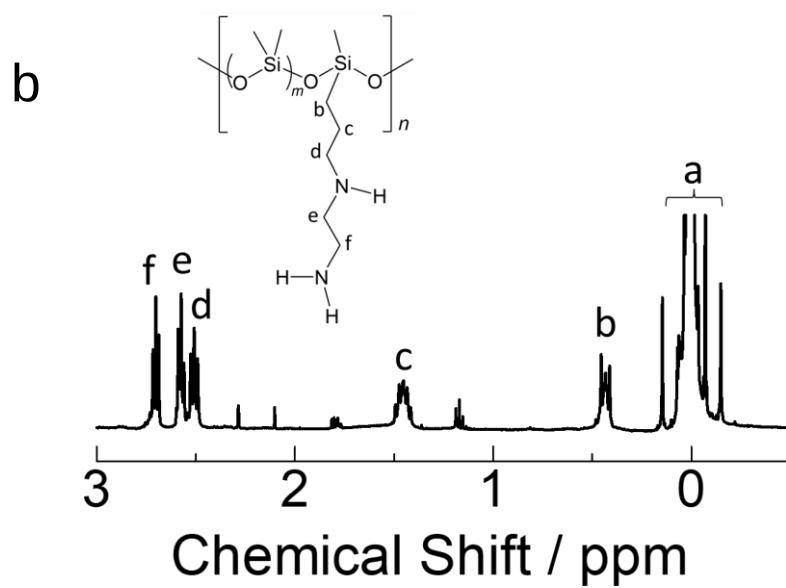
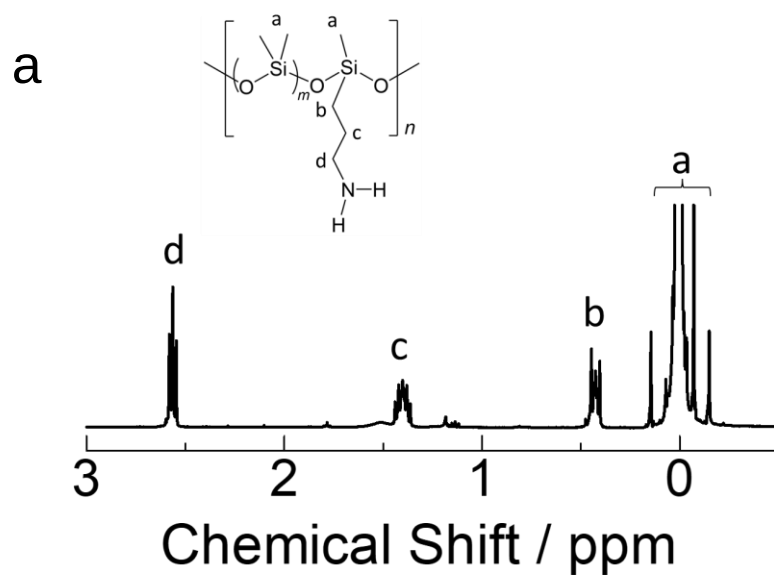
**Polymerization of PDMS–D9 (Supplementary Fig. 1b).** A mixture of DMMS (325.5 g, 2.71 mol), ADMMS (62.1 g, 301 mmol), ethanol (200 mL), and water (216 mL, 12.0 mol) was stirred in a glass beaker at room temperature for 9 h. The reaction mixture was further stirred at 70°C for 21 h and then 100°C for 18 h to remove the solvents. The resulting oily sample was heated at 35°C for 29 h in a vacuum. The resultant polymer (122 g), D4 (256 g, 863 mmol), HMDS (0.613 g, 3.78 mmol), and TMAHP (139 mg, 0.764 mmol) were stirred at 90°C for 45.5 h in a three-neck flask under N<sub>2</sub> flow. And then, the reaction mixture was further heated at 130°C for 1h to terminate the polymerization. The resultant PDMS–D9 was vacuum dried at room temperature for 38.5 h, and then heated at 90°C for 28.5 h in a vacuum. The  $M_w$  and the PDI of PDMS–D, determined GPC, were 68,200 and 2.64, respectively. The amine concentrations in PDMS–D9 determine by neutralization titration is 9.2 mol% ( $1.1 \times 10^{-3} \text{ mol g}^{-1}$ ). Namely, the concentration of diamine group in PDMS–D9 is  $5.5 \times 10^{-4} \text{ mol g}^{-1}$ . <sup>1</sup>H-NMR (400

MHz, CDCl<sub>3</sub>) (Supplementary Fig. 2b):  $\delta$  (ppm) = 0.07 (6H),  $\delta$  = 0.44 (2H),  $\delta$  = 1.47 (2H),  $\delta$  = 2.51 (2H),  $\delta$  = 2.57 (2H),  $\delta$  = 2.70 (2H).

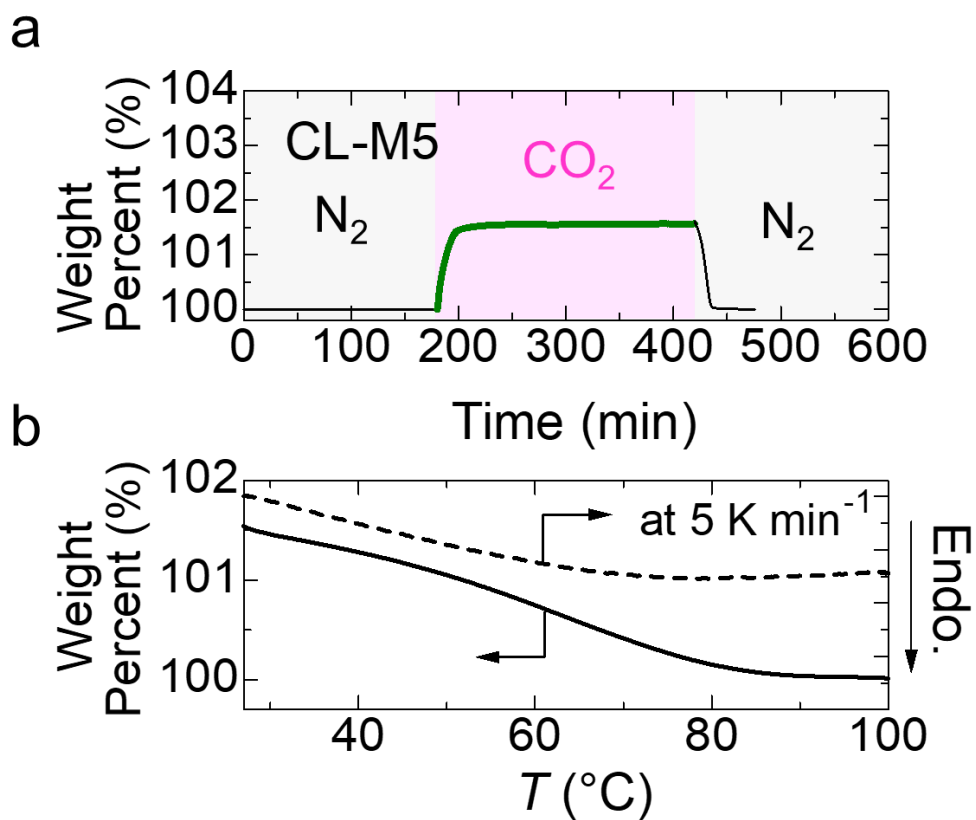
**Crosslinking with BDE (Supplementary Fig. 1c).** PDMS-Mx and PDMS-Dx were chemically crosslinked using 1,4-butanediol diglycidyl ether (BDE) with a concentration of  $8.5 \times 10^{-5}$  mol g<sup>-1</sup>. Each polymer (7.94 g) was dissolved in dry THF (10 mL) with BDE (0.138 g) and poured into a Teflon petri dish. The mixture with PDMS-Mx was dried at 50°C for 17 h. The obtained CL-Mx sheet was further dried at 90°C for 48 h in a vacuum. In the case of the mixture with PDMS-Dx, the mixture was dried at 35°C for 39 h and then at 60°C for 7 h. The mixture was further heated at 90°C for 14 h in a vacuum to obtain a CL-Dx sheet.

**Handling of sample sheets.** Sample sheets were stored in aluminium packages with molecular sieves to prevent moisture absorption. Before the measurements, the sample sheets were further vacuum-dried at room temperature for at least 24 h and were carefully set up into the instruments to avoid absorbing moisture.

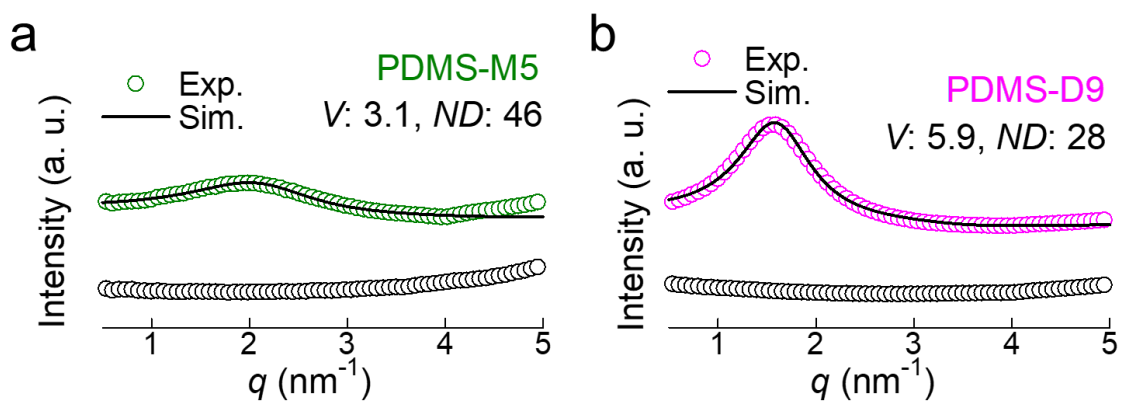




**Supplementary Fig. 2.**  $^1\text{H}$ -NMR spectra of PDMS-M5 **a** and PDMS-D9 **b**.



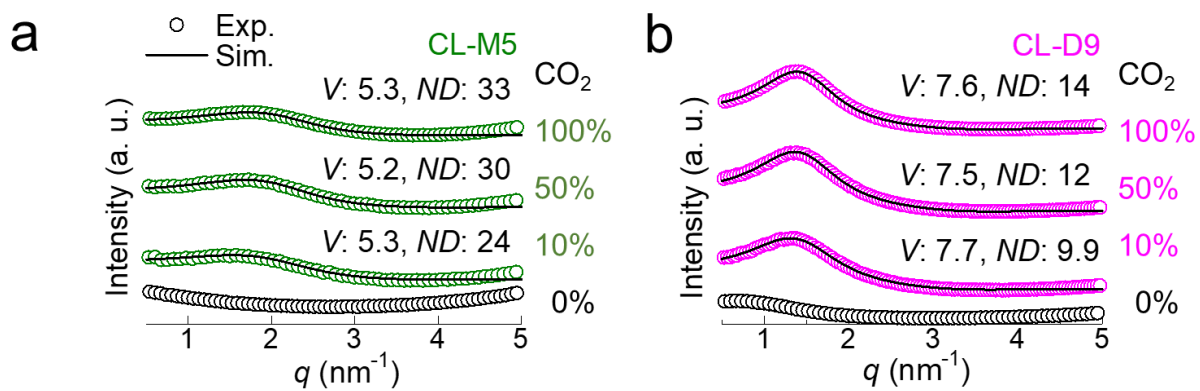
**Supplementary Fig. 3. a**, Weight changes of CL–M5 with different gases. At the first  $\text{N}_2$  and  $\text{CO}_2$  processes, measurements were conducted at  $25^{\circ}\text{C}$ . The sample was heated at  $5 \text{ K min}^{-1}$  in the second  $\text{N}_2$  process. **b**, Temperature dependence of weight and heat flow in the second  $\text{N}_2$  process.



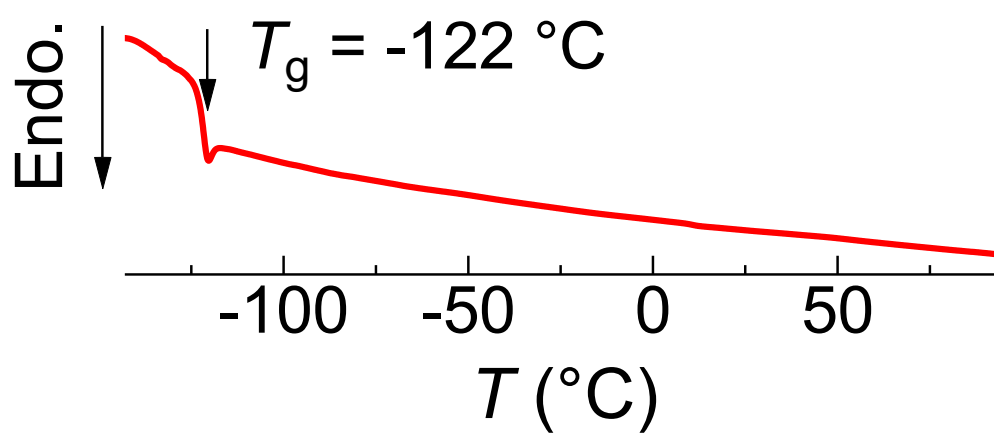
**Supplementary Fig. 4.** Experimental and simulated SAXS patterns of PDMS-M5 **a**

and PDMS-D9 **b**. The SAXS patterns with and without CO<sub>2</sub> are indicated using the

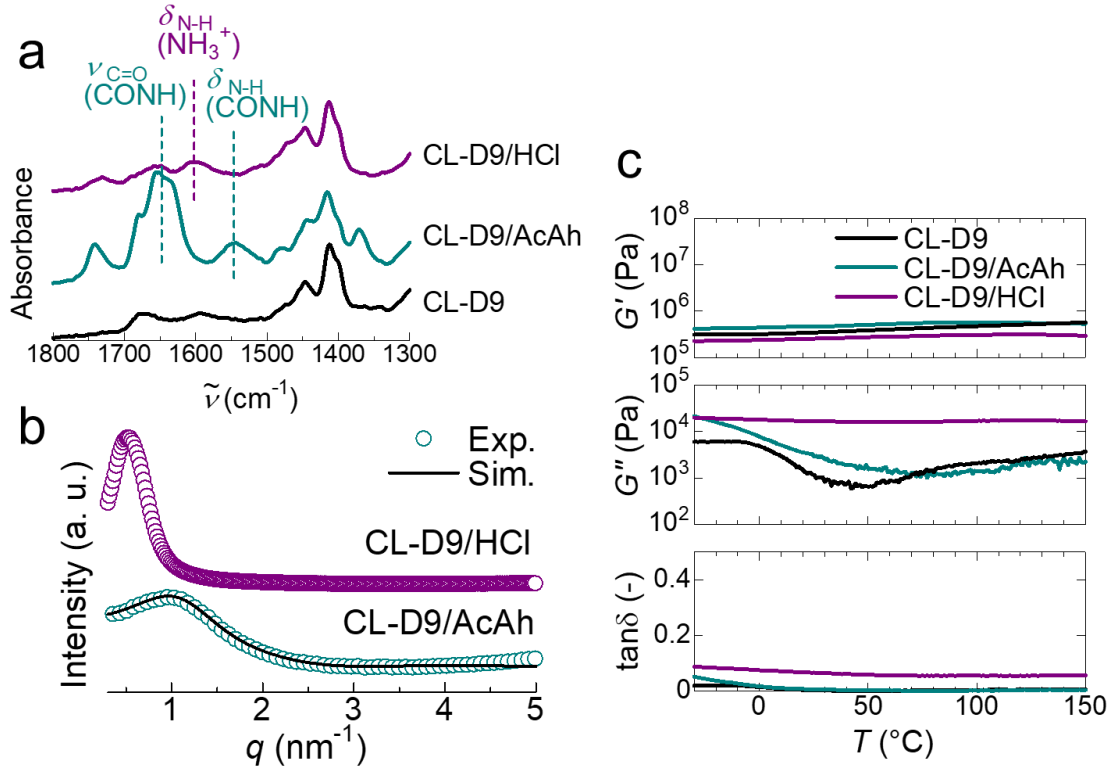
colored and black plots, respectively. The YC model was used for the simulations<sup>1</sup>.



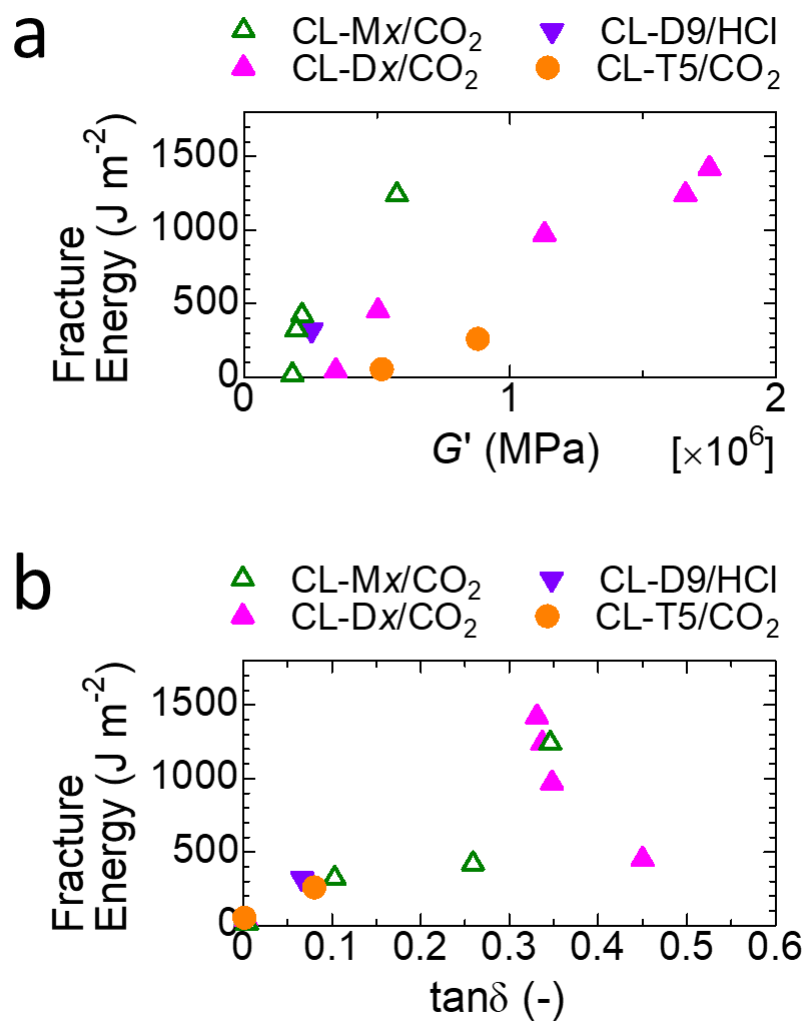
**Supplementary Fig. 5.** Experimental and simulated SAXS patterns of CL-M5 **a** and CL-D9 **b** exposed to  $\text{N}_2/\text{CO}_2$  mixed gases at various  $\text{CO}_2$  concentrations.



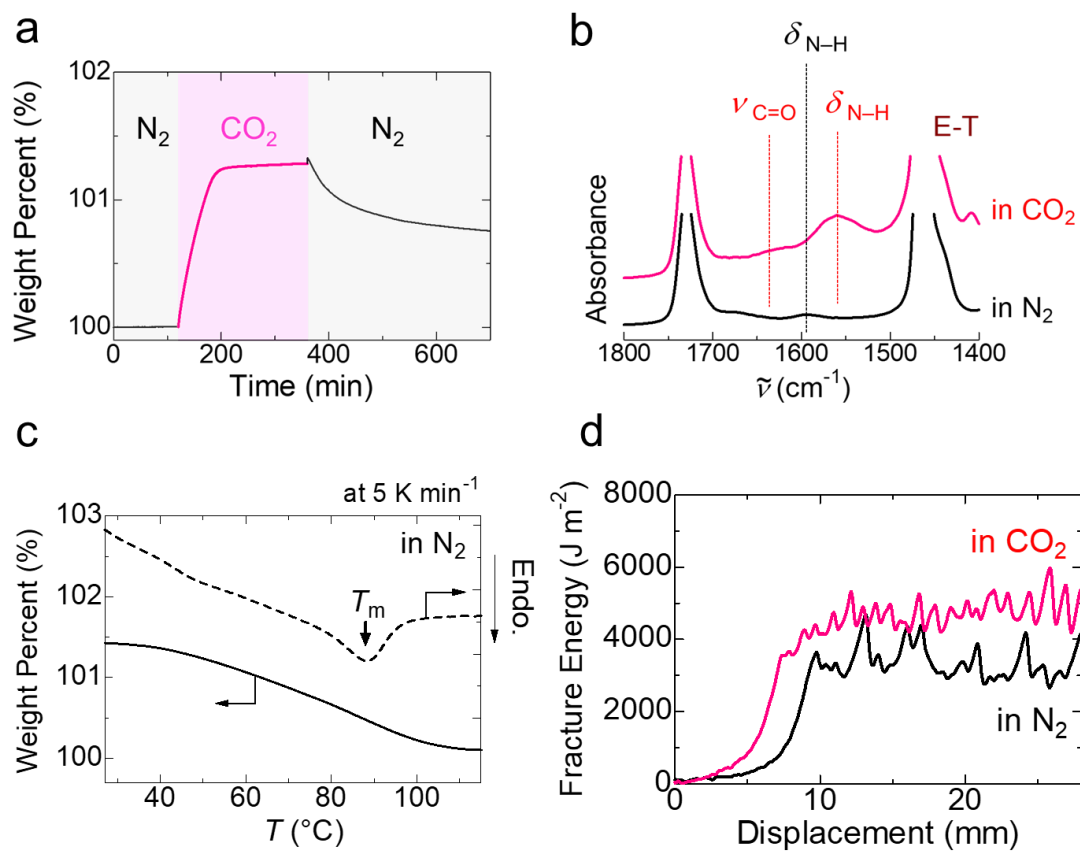
**Supplementary Fig. 6.** DSC trace of PDMS-M5. The specimen was heated at  $10 ^{\circ}\text{C min}^{-1}$ .



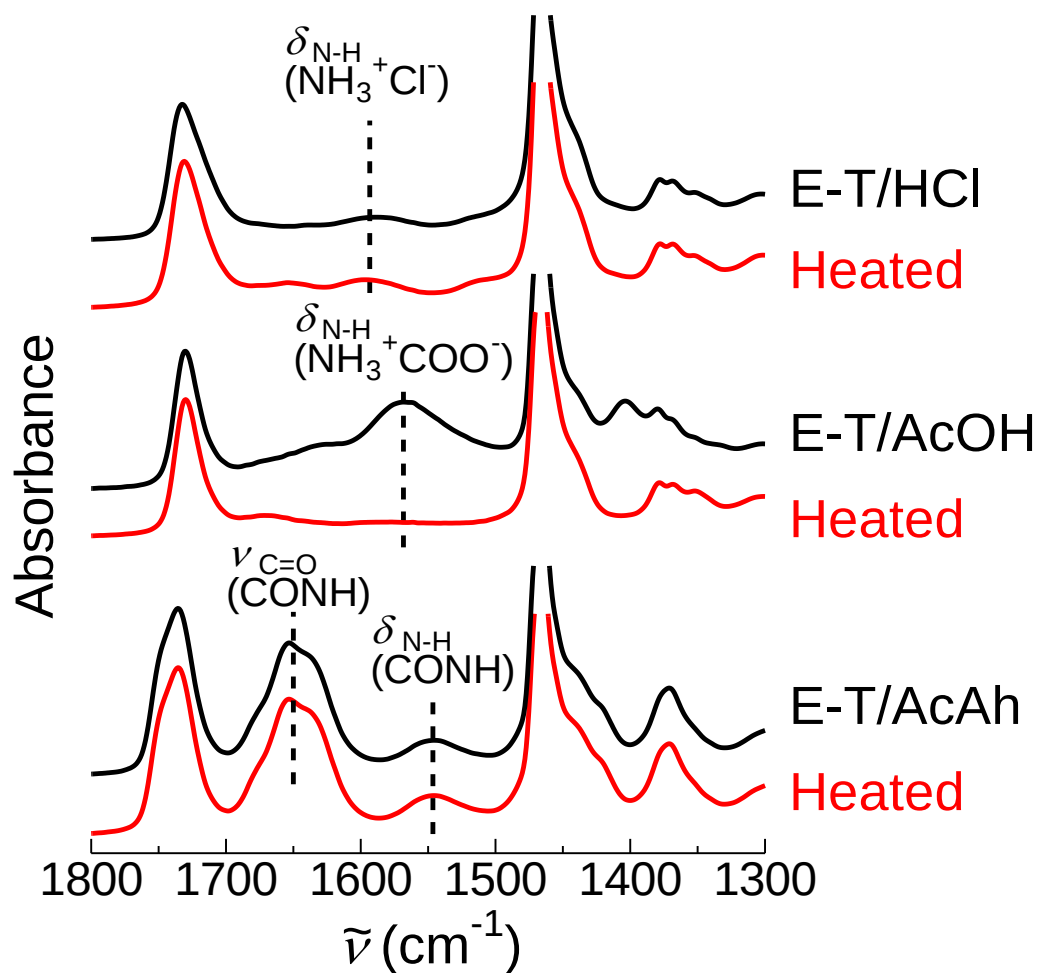
**Supplementary Fig. 7. a,** FT-IR spectra of CL-D9 with HCl and AcAh gases. The spectra indicate the neutralization of amines with HCl and AcAh.<sup>2</sup> **b,** Experimental and simulated SAXS patterns of CL-D9 with HCl and AcAh gases. The SAXS pattern for CL-D9/AcAh was simulated using the YC model<sup>1</sup>.  $V$  and  $ND$  are 12 nm<sup>3</sup> and 3.0 (10nm)<sup>-3</sup>, respectively. The YC model was found to be unsuitable for the simulation of CL-D9/HCl. **c,** Temperature dependence of shear storage modulus ( $G'$ ), shear loss modulus ( $G''$ ) and loss tangent ( $\tan\delta$ ) of CL-D9, CL-D9/HCl, and CL-D9/AcAh measured at 1 Hz in N<sub>2</sub> gas.



**Supplementary Fig. 8.** Plots of fracture energy values of indicated elastomers for shear storage modulus ( $G'$ ) **a** and loss tangent ( $\tan\delta$ ) **b**.



**Supplementary Fig. 9.** **a**, Weight changes of E-T at 25 °C with different gases at a flow rate of 100 mL min<sup>-1</sup>. **b**, FT-IR spectra of E-T measured in N<sub>2</sub> and CO<sub>2</sub> gases. Ammonium carbamates are formed with CO<sub>2</sub> gas<sup>3</sup>. **c**, Temperature dependence of weight and heat flow of E-T fully reacted with CO<sub>2</sub> on the heating process in N<sub>2</sub>. The heating rate is 5 K min<sup>-1</sup>. The melting of polyethylene is observed at 85 °C. **d**, Tearing test results of E-T sheets in N<sub>2</sub> and CO<sub>2</sub> gases.



**Supplementary Fig. 10.** FT-IR spectra of E-T exposed with HCl, acetic acid (AcOH), and AcAh gases. By heating at 110 °C for 30 min, AcOH molecules are released from the E-T while no change is observed for the other samples.

## Supplementary References

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- (2) Heacock, R. A., & Marion, L. The infrared spectra of secondary amines and their salts. *Can. J. Chem.* **34**, 1782–1795 (1956).
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