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Ultrafast Synthesis of Silicone Elastomers using Silsesquioxane Cages as Crosslinkers

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Chemicals and Instruments

Deionized (DI) water used in this work was obtained from Ultra Clear SIEMENS under ASTM type 2. The commercial grade of solvents (i.e., acetone, DCM) were further distilled. The analytical grade of THF, Toluene, DMF, DMSO and isopropanol were used without purification. Potassium carbonate anhydrous, octamethylcyclotetrasiloxane, hexamethyldisiloxane and 2,4,6,8- tetramethyl- 2,4,6,8- tetravinylcyclotetrasiloxane were purchased from Ajax Chemicals and TCI Chemicals. Octavinylsilsesquioxane (OVS) was prepared according to the literature report.[14] The NMR spectra were collected by solid-state nuclear magnetic resonance spectroscopy (Bruker ASCEND 400 MHz WB NMR/ DNP spectrometer. The FT-IR spectra were collected using the attenuated total reflectance (ATR) technique on a Bruker model Alpha spectrometer. SEM images along with elemental analysis were done by FEI Quanta 400 SEM. Thermal gravimetric analysis (TGA) were done by TA Instruments SDT 2690. X-ray diffraction experiment was performed by Bruker D8 Advance diffractometer with monochromatic CuKα radiation ($\lambda = 0.154$nm., Applied voltage = 40kV, current = 30 mA, $2\theta = 5.00\text{-}65.00^{o}$ and scan rate = $5^{o}s^{-1}$). Compressive test of the materials was measured using Universal testing machine (INSTRON 5569) with loading force 1 kN. The compression test was performed by using cylindrical shape of CSSEs and measured at crosshead speed of 12 mm. per min. N_2 adsorption−desorption analysis was performed with a Micromeritics apparatus (ASAP 2060) at 77.38 K. The sample of 0.1774 g of material was degassed at 80 °C for 24 h under vacuum prior to measurements.

Experiment Section

Synthesis of cross-linked siloxane/silsesquioxane elastomers (CSSEs)

OVS (3 g, 4.74 mmol), K_2CO_3 (40 mg, 0.29 mmol) and D_4 (octamethylcyclotetrasiloxane or 2,4,6,8- tetramethyl- 2,4,6,8- tetravinylcyclotetrasiloxane 7 mL, 20 mmol) were dissolved in DMF solvent (14 mL). Thereafter, the reaction was subsequently stirred and heated at 70^{o}C for 10 min. Then, cloudy solution was observed. After that, it was aged for 2 min. The white solid product was obtained. The products (7.92 g of methyl CSSE and 6.30 g of vinyl CSSE) were washed with DCM and DI to remove the excess of reagents and base. Afterward, the water exchange process was done by immersed in isopropanol for overnight. Samples were soaked in HMDSO (50 mL, 10%v/v) at 40^{o}C for 12 h. After the surface modification, wet samples were freeze-dried to remove solvent. Finally, methyl CSSE (8.05 g) and vinyl CSSE (7.97 g) were obtained after the treatment of HMDSO.

Absorption experiment

In absorption experiment, 2 mL of various solvents (water, DMF, MeOH, EtOH, THF, DCM, toluene and hexane) were mixed with 50 mg of product in vial. The vial was placed at room temperature for 1 h. The degree of swelling was calculated by the following equation.

Degree of swelling $= \frac{(W - W_0)}{W_0}$, where W is the weight of the swollen gel and W_0 is the weight of dry gel.

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Compressive test

In uniaxial compression tests, cylindrical CSSEs with a 3 mm diameter and 10 mm height was used. The experiment performed with loading force 1 kN. The speed of test as 12 mm/min. The %strain of CSSE was calculate by the following equation.

%strain = $\frac{\Delta L}{L} x 100$, where ΔL is the change in length and L is original length.

The stress of CSSE was given by the equation as below

Stress = $\frac{F}{A}$, where F is loading force (N) and A is cross-section area of material (m^2).

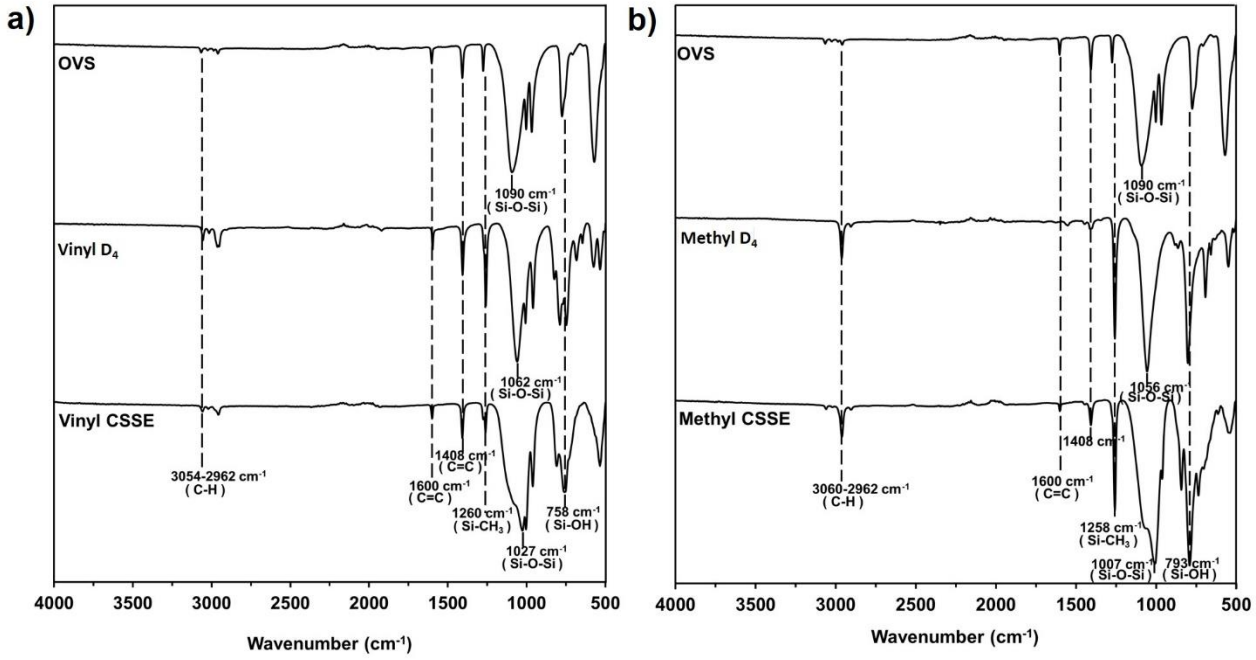

Fig. S1 FTIR spectra of a) OVS, vinyl D_4 and vinyl CSSE at solid-state and b) OVS, methyl D_4 and methyl CSSE at solid state

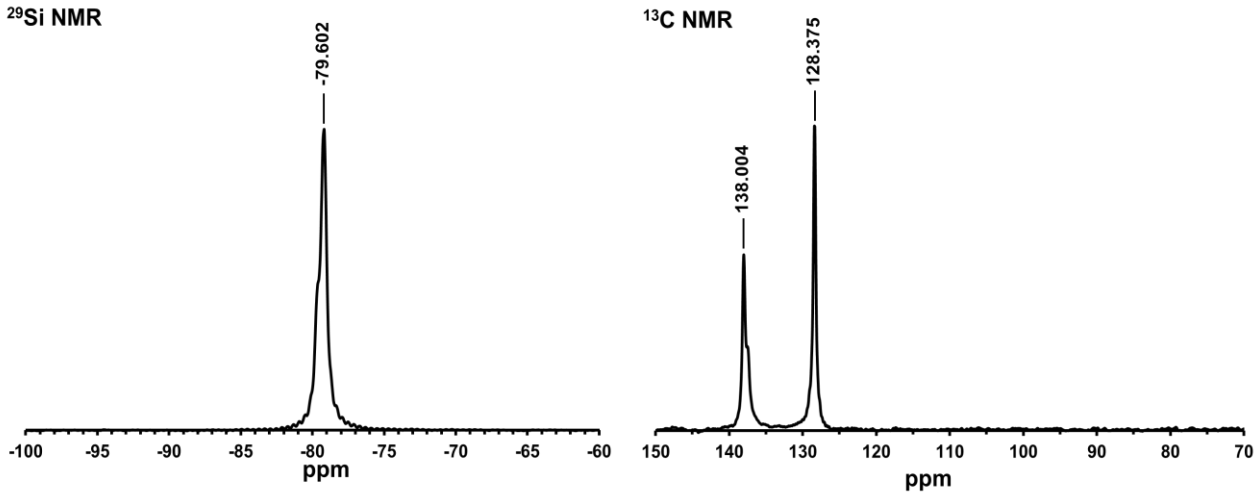

Fig. S2 ^{29}Si and ^{13}C NMR spectra of OVS in solid state

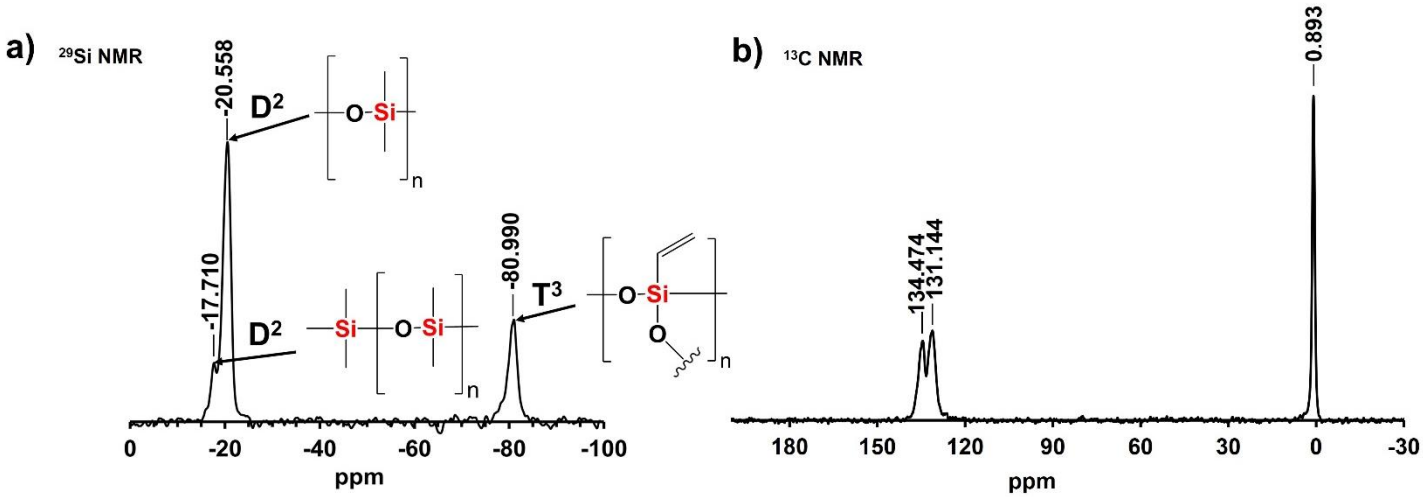

Fig. S3 ^{29}Si and ^{13}C NMR spectra of methyl CSSE in solid state

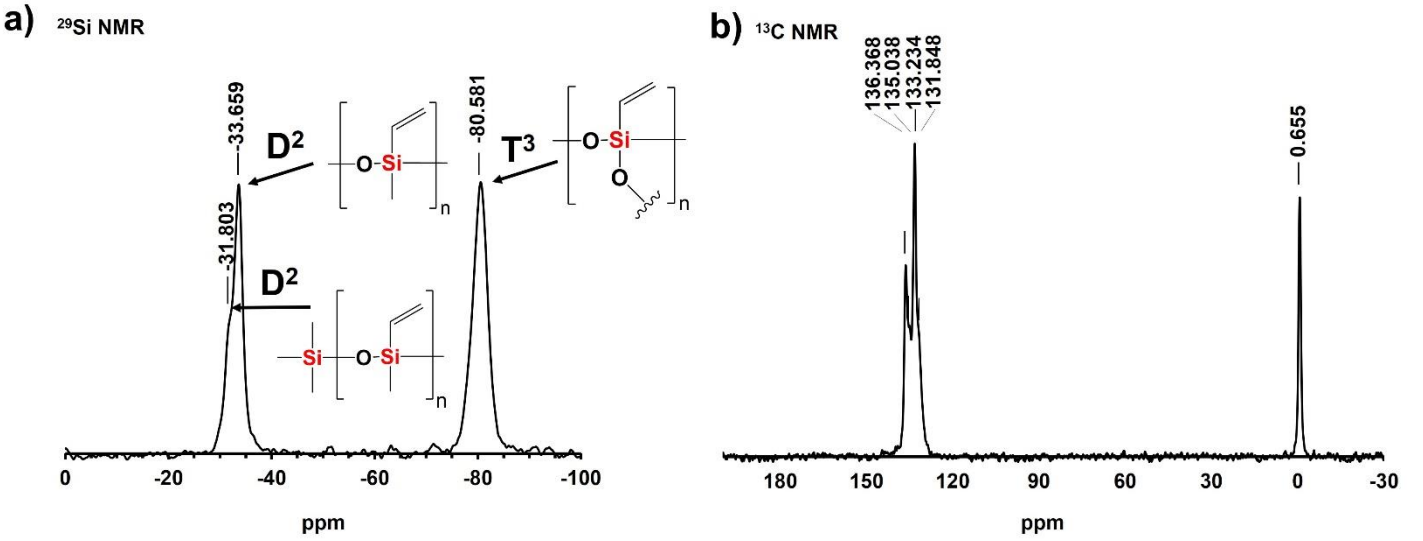

Fig. S4 ^{29}Si and ^{13}C NMR spectra of vinyl CSSE in solid state

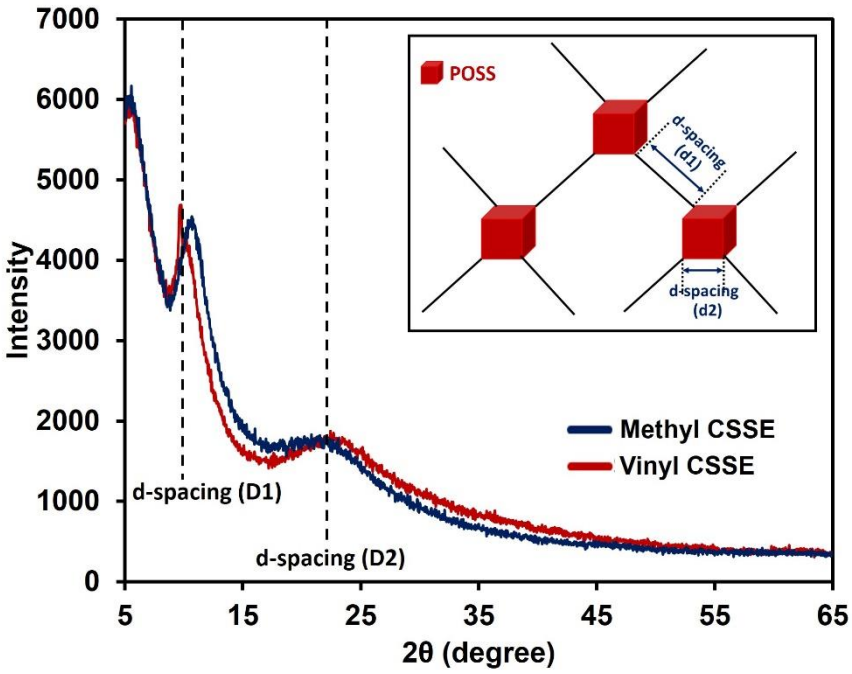

Fig. S5 XRD curves of vinyl CSSE (Black) and methyl CSSE (Red) samples

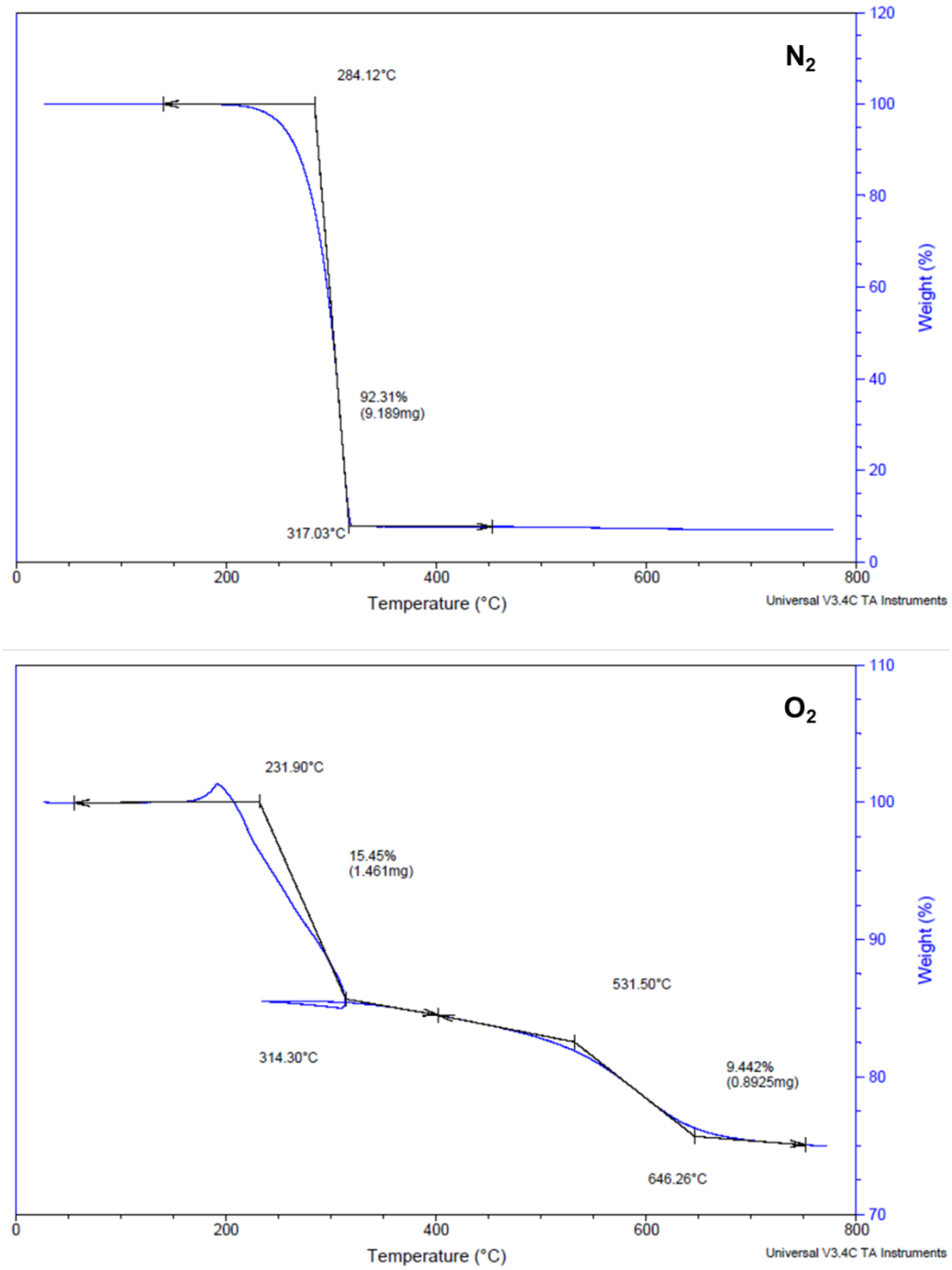

Fig. S6 Thermal gravimetric analysis (TGA) of octavinylsilsesquiloxane (OVS) under N_2 and O_2 atmosphere

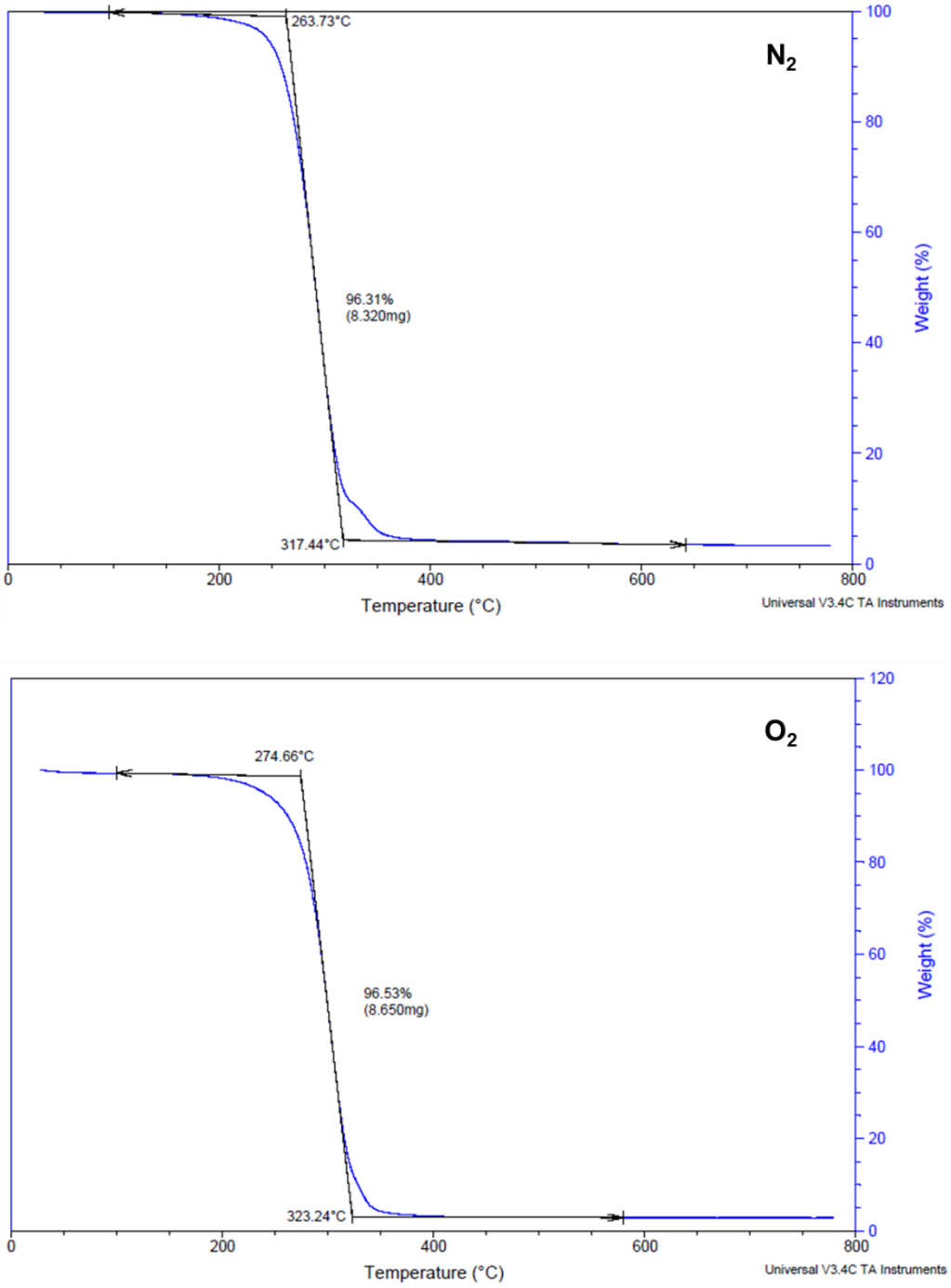

Fig. S7 Thermal gravimetric analysis (TGA) of methyl CSSE under N_2 and O_2 atmosphere

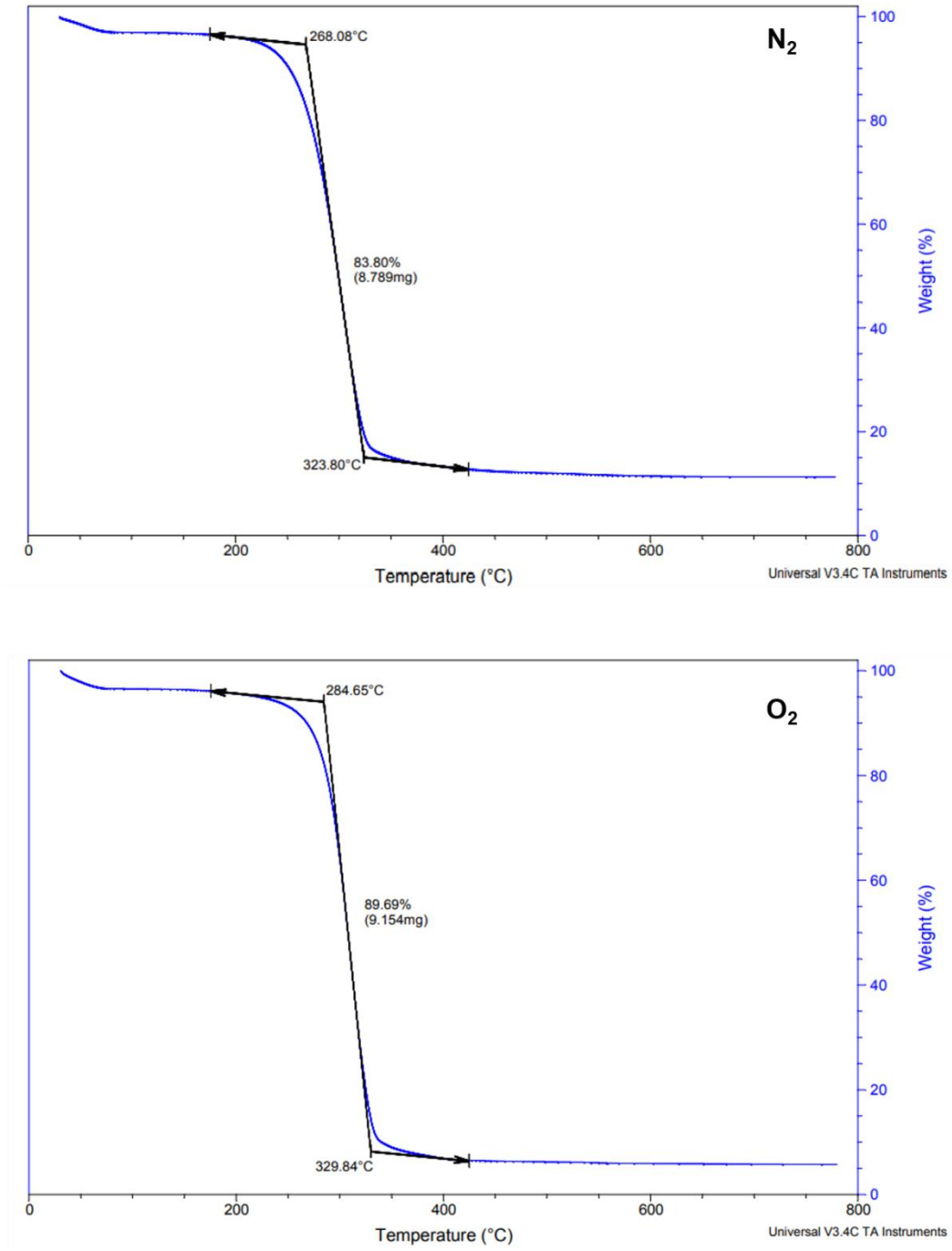

Fig. S8 Thermal gravimetric analysis (TGA) of vinyl CSSE under N_2 and O_2 atmosphere

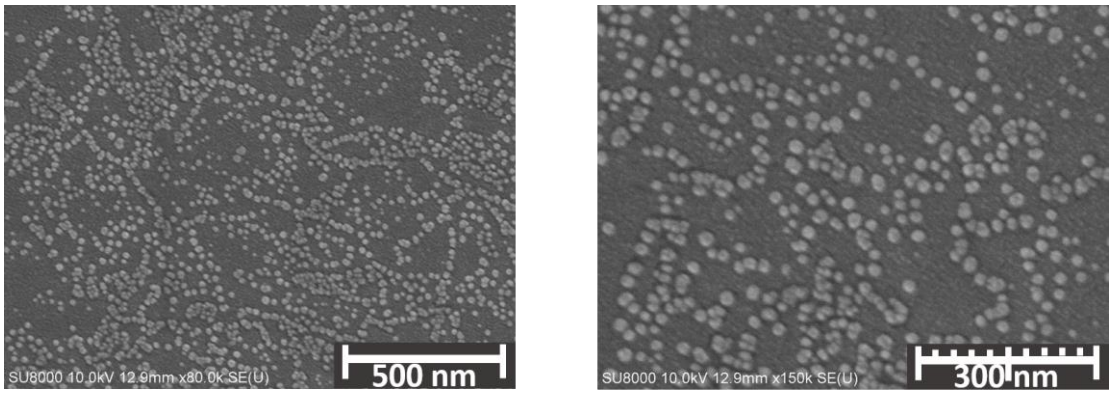

Fig. S9 SEM images of vinyl CSSE

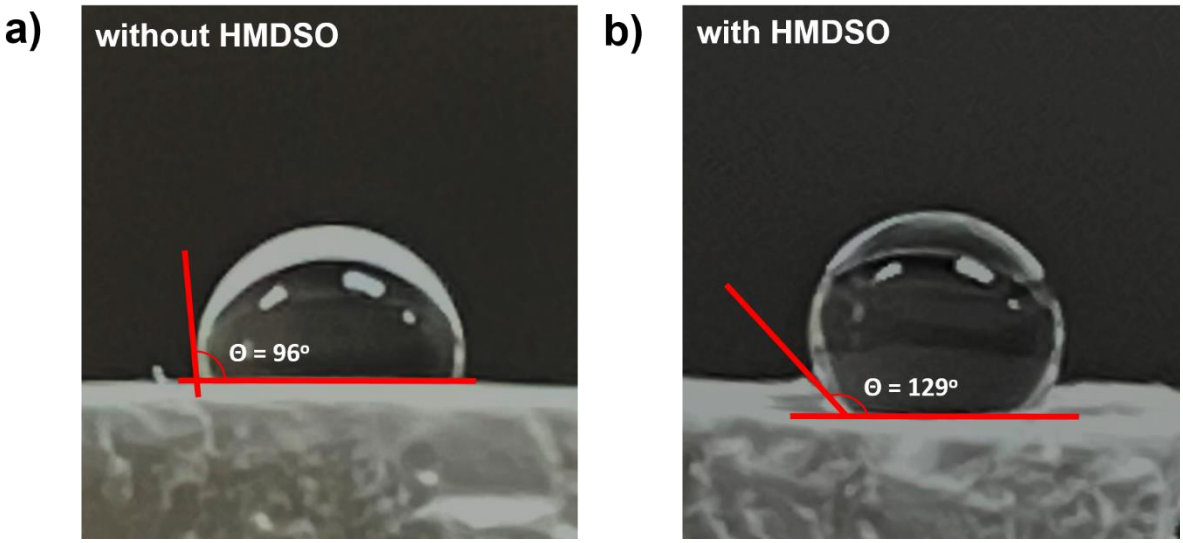

Fig. S10 Optical images of vinyl CSSE a) without and b) with HMDSO modification

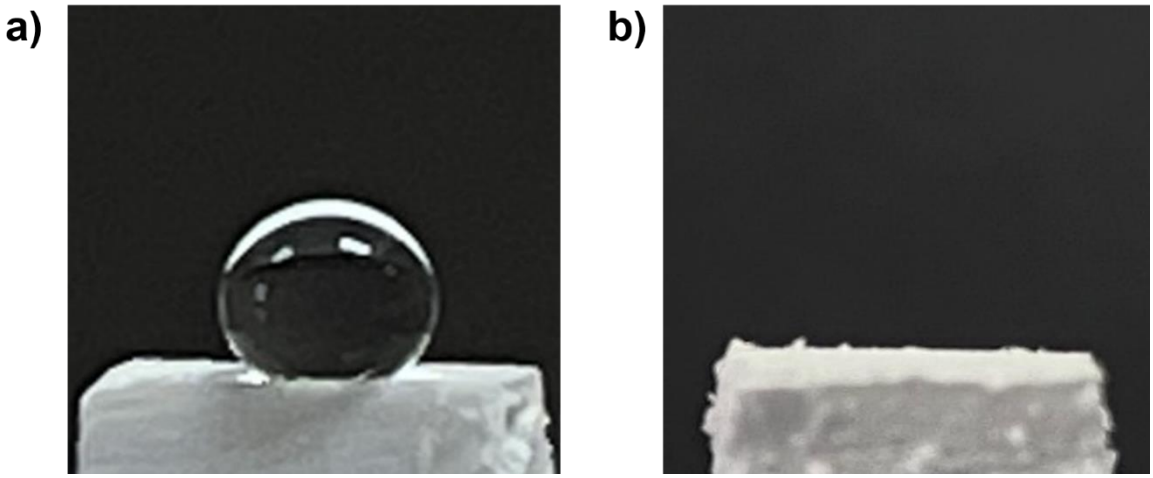

Fig. S11 Optical images of a) water and b) oil on the surface of methyl CSSE

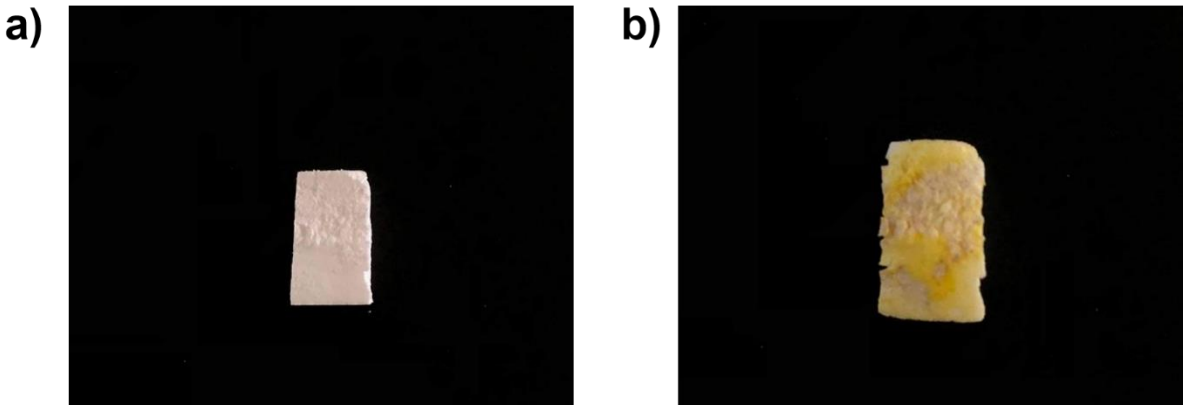

Fig. S12 Optical images of methyl CSSE a) before and b) after adsorption process in mixed solvent (water and ether stained with yellow dye)

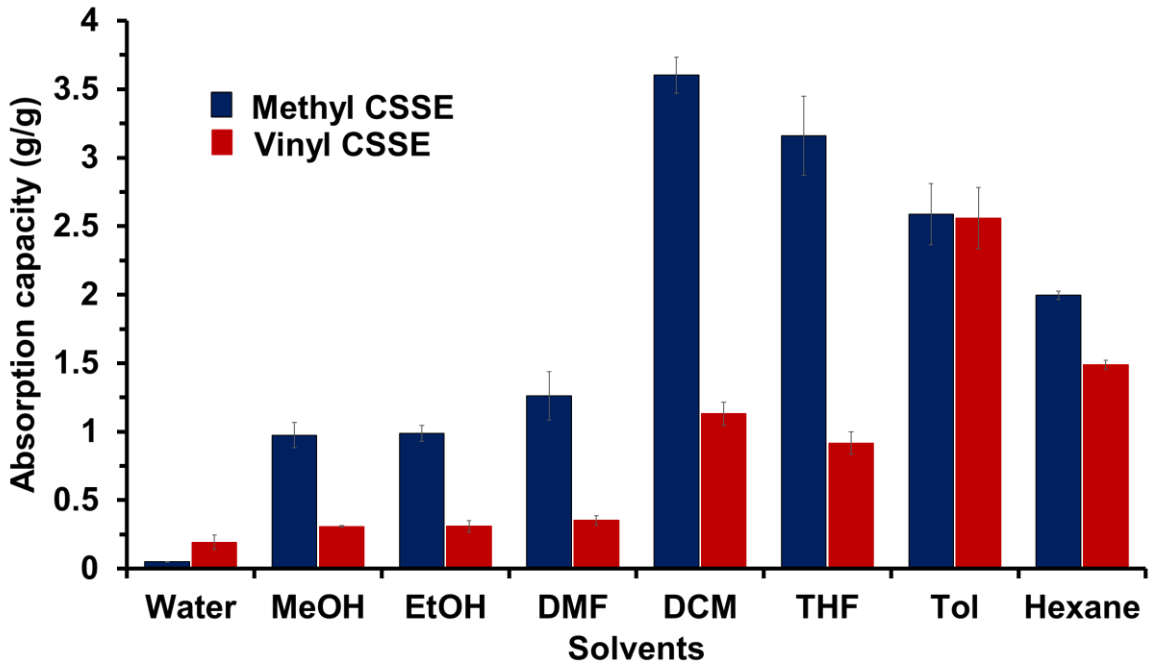

Fig. S13 Adsorption capacity of methyl CSSE and vinyl CSSE in various solvents

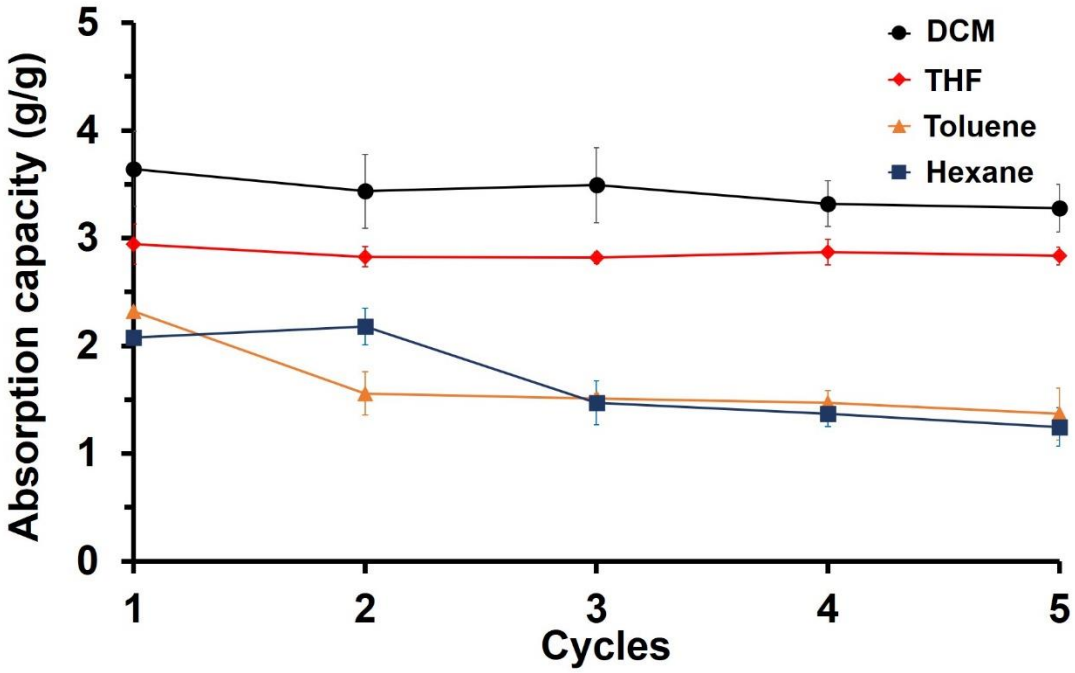

Fig. S14 Recyclability of methyl CSSE in various solvents

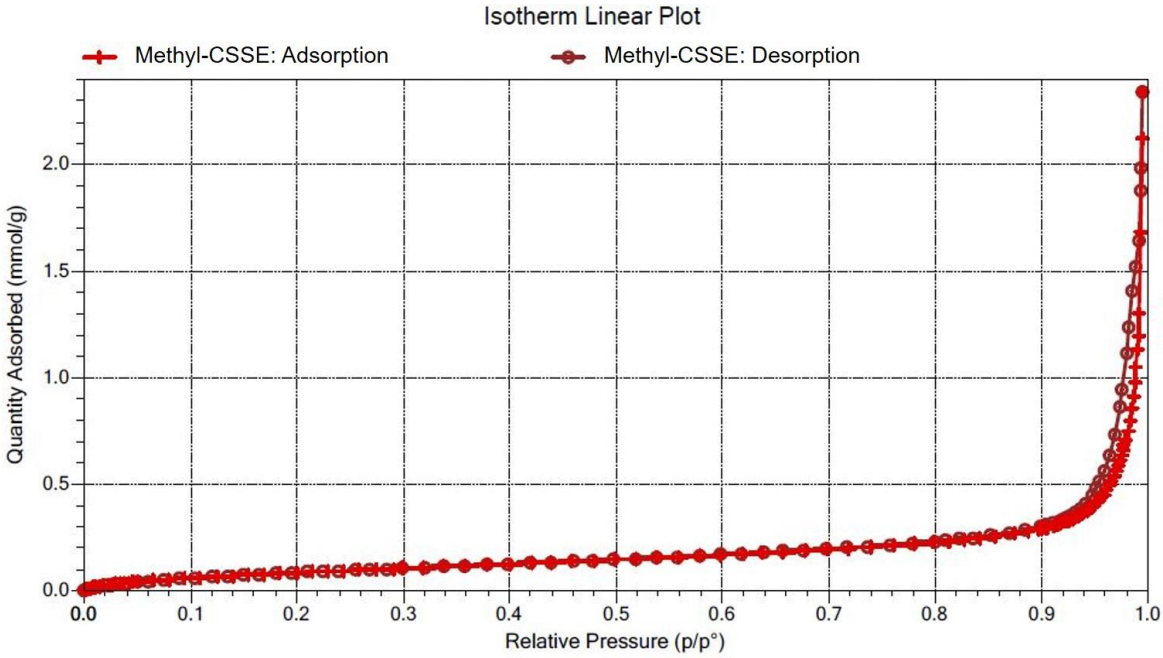

Fig. S15 The N_2 adsorption−desorption of methyl CSSE at 77 K

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Table S1 Experiment conditions of CSSEs with varying POSS reactants.

Reactants		Conditions				Results
POSS	**D_4**	**Catalyst**	**Solvent**	**Temperature (°C)**	**Time (mins)**	
T_8 (0.2g)	-	K_2CO_3 (15 mg)	DMF (1mL)	60	300	Brittle solid gel
T_{10} (0.2g)	-	K_2CO_3 (15 mg)	DMF (1mL)	60	1440	N/A
T_{12} (0.2g)	-	K_2CO_3 (15 mg)	DMF (1mL)	60	1440	N/A
-	Vinyl D_4 (0.2mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	300	Liq. gel
T_8 (0.2g)	Vinyl D_4 (0.2mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	45	Solid gel (+)
T_8 (0.2g)	Methyl D_4 (0.2mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	45	Solid gel (+)

N/A No reaction occurred.

(+) Elasticity rating

Table S2 Experiment conditions of CSSEs with varying volumes of D_4 and DMF.

Reactants		Conditions				Results
POSS	**D_4**	**Catalyst**	**Solvent**	**Temperature (°C)**	**Time (mins)**	
T_8 (0.2g)	Methyl D_4 (0.2mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	45	Solid gel(+)
T_8 (0.2g)	Methyl D_4 (0.4mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	45	Solid gel (++)
T_8 (0.2g)	Methyl D_4 (0.5mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	45	Solid gel (+++)
T_8 (0.2g)	Methyl D_4 (1 mL)	K_2CO_3 (15 mg)	DMF (1mL)	60	150	Solid gel (+++)
T_8 (0.2g)	Methyl D_4 (0.5 mL)	K_2CO_3 (15 mg)	DMF (0.5 mL)	60	20	Solid gel (+++)
T_8 (0.2g)	Methyl D_4 (0.5 mL)	K_2CO_3 (15 mg)	THF (0.5 mL)	60	300	N/A

N/A No reaction occurred.

(+) Elasticity rating

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Table S3 Experiment conditions of CSSEs with varying types of catalyst.

Reactants		Conditions				Results
POSS	**D_4**	**Catalyst**	**Solvent**	**Temperature (°C)**	**Time (mins)**	
T_8 (0.2g)	Methyl D_4 (0.5 mL)	K_2CO_3 (15 mg)	DMF (0.5 mL)	60	20	Solid gel (+++)
T_8 (0.2g)	Methyl D_4 (0.5 mL)	Na_2CO_3 (15 mg)	DMF (0.5 mL)	60	300	N/A
T_8 (0.2g)	Methyl D_4 (0.5 mL)	KOH (15 mg)	DMF (0.5 mL)	60	300	N/A
T_8 (0.2g)	Methyl D_4 (0.5 mL)	LiOH(15 mg)	DMF (0.5 mL)	60	300	N/A
T_8 (0.2g)	Methyl D_4 (0.5 mL)	NaOH(15 mg)	DMF (0.5 mL)	60	300	N/A

N/A No reaction occurred.

(+) Elasticity rating

Table S4 Experiment conditions of CSSEs after upscale of reaction.

Reactants		Conditions				Results
POSS	**D_4**	**Catalyst**	**Solvent**	**Temperature (°C)**	**Time (mins)**	
T_8 (3 g)	Methyl D_4 (7.5 mL)	K_2CO_3 (15 mg)	DMF (7.5 mL)	60	300	Solid gel (+++)
T_8 (3 g)	Methyl D_4 (7.5 mL)	K_2CO_3 (50 mg)	DMF (7.5 mL)	60	60	Solid gel (+++)
T_8 (3 g)	Methyl D_4 (7.5 mL)	K_2CO_3 (50 mg)	DMF (7mL)	Room temperature	1440	N/A
T_8 (3 g)	Methyl D_4 (7.5 mL)	K_2CO_3 (50 mg)	DMF (7mL)	60	45	Solid gel (+++)
T_8 (3 g)	Methyl D_4 (7.5 mL)	K_2CO_3 (50 mg)	DMF (7mL)	75	15	Solid gel (+++)

N/A No reaction occurred.

(+) Elasticity rating

Table S5 Adsorption capacity values of CSSEs in different solvents

Solvents	Methyl CSSE		Vinyl CSSE	
	Average	SD	Average	SD
Water	0.051	0.00157	0.193	0.05178
MeOH	0.975	0.09305	0.309	0.00654
EtOH	0.987	0.05728	0.310	0.04057
DMF	1.261	0.17668	0.352	0.03430
DCM	3.603	0.13229	1.131	0.08411
THF	3.160	0.28766	0.917	0.08187
Tol	2.588	0.22384	2.560	0.22340
Hexane	1.996	0.02987	1.847	0.03257

Table S6 Adsorption capacity values of methyl CSSE in different solvents

Cycles	DCM		THF		Tol		Hexane	
	Average	SD	Average	SD	Average	SD	Average	SD
1	3.642	0.34782	2.944	0.18820	2.319	0.04478	2.075	0.03459
2	3.435	0.34134	2.828	0.09194	1.559	0.17027	2.179	0.20115
3	3.493	0.34816	2.818	0.05428	1.513	0.20329	1.471	0.04228
4	3.321	0.21226	2.871	0.11936	1.474	0.11815	1.371	0.11212
5	3.280	0.22064	2.834	0.08447	1.367	0.17768	1.247	0.24221

Table S7 The condition comparison of synthesized elastomer

Elastomers	Reactions	Conditions	Ref.
UHMW-PDMS-based elastomer	Crosslinking polydimethylsiloxane-α,ω-diols	TMAH catalyst, Toluene, 48 h at room temperature	1.
Multifunctional silicone elastomer	Ring-opening copolymerization of D_4 and Dual-D_4^{Vi}	Trific acid 0.3%, 10 h at 45 °C	2.
Epoxidized Natural Rubber	ENR/AT-PDMS curing reaction	Hydroquinone, 60 °C for 10 min with a rotor speed of 60 rpm using a laboratory-sized two-roll mill	3.
Thermoplastic elastomer of poly(styrene-*b*-(ethylene-*co*-butylene)-*b*-styrene) (SEBS)	Click coupling reaction	CuI catalyst, DMF, 24 h at room temperature under N_2 atmosphere	4.
PUrea-DDSQ	polycondensation of diamines	NaH, DMF, 24 h, heating the mixture up to 180 °C under CO_2 atmosphere	5.
Poly(acrylate amide) Elastomers	Reversible addition-fragmentation chain transfer (RAFT) polymerizations	DMF, 72 h at 80 °C	6.
Cross-linked siloxane/silsesquioxane-based elastomer	Anionic ring-opening polymerization	K_2CO_3, DMF, 15 min at 70°C	Our work

Ref.

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Supplementary Movies

Video S1. This video shows the synthesis of CSSE.

Video S2. This video shows the selective absorption of ether-water mixture by using methyl CSSE.

Video S3. This video shows CSSEs at a strain of 45% and after compressive test.