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Supporting Information

TEMPO driven thiol-ene reaction for the preparation of polymer functionalized silicon wafers

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Experimental Section

Characterization technique

Nuclear magnetic resonance (NMR) spectroscopy

Bruker DPX-400 spectrometer was utilized to collect the ^{1}H NMR and ^{13}C NMR spectra using deuterated chloroform and water solvent at 25°C.

Atomic force microscopy (AFM)

AFM studies were conducted using a Dimension Icon Model in tapping mode.

X-ray photoelectron spectroscopy (XPS)

The Al-K-Alpha+ XPS spectrometer (Thermo Fisher Scientific) was used for XPS analysis of treated or modified silicon wafer. The Thermo Avantage software was utilized for the result collection as well as analysis. All Silicon wafer surfaces have been investigated with a micro-focused, monochromated Al Kα X-ray source (400 μm spot size). The kinetic energy of the electrons has been calculated by a hemispherical energy analyzer running at 23.5 eV pass energy for elementary spectra in constant analyzer energy mode at 180°. The K-Alpha+charge compensation method used 8 eV energy electrons and low-energy argon ions in the study to prevent any build-up of spatial charge. In addition, the pass settings of 23.5, 0.025 eV stage, 50 ms time/stage and 10 cycles have been applied.

Contact angle measurement

The water contact angles were calculated using Drop Shape Analyzer-DSA100 (Krüss) on Si wafers.

Fluorescence microscopy

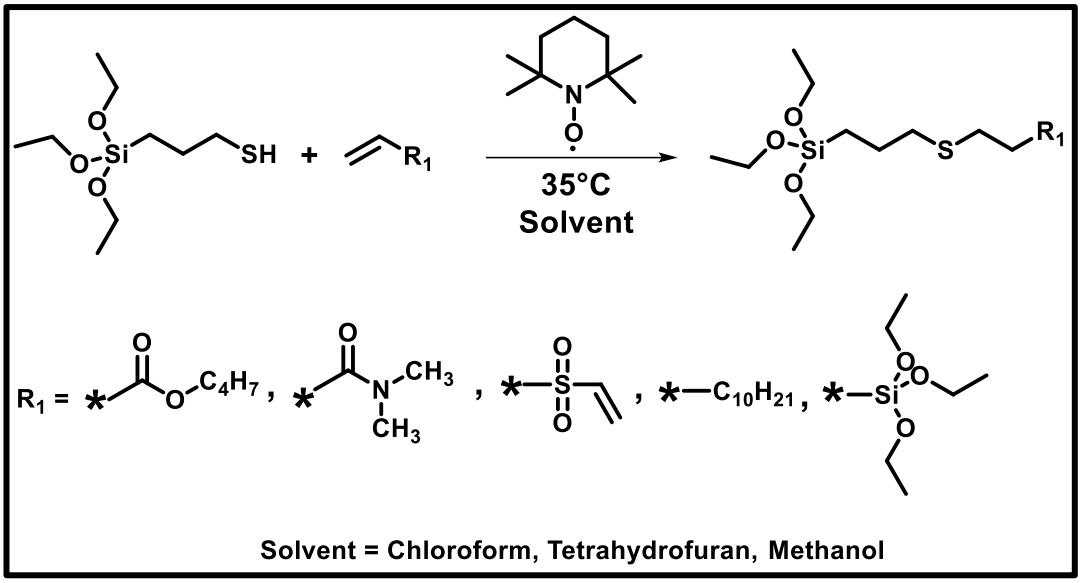
The albumin–fluorescein isothiocyanate conjugate (FTIC-Albumin) treated silicon wafers were analyzed using Leica DM2500.

Materials

Si wafers [p-type, boron doped (100)] and (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO, 98%) were procured from Sigma Aldrich. Divinyl sulfone (>96%, DVS), vinyltriethoxysilane (>98%, VTS), 1-dodecene (>99.5%, DD), *N,N'*-dimethylacrylamide (>99%, DMA), 3-mercaptopropyltriethoxysilane (>96%, MPTES), trifluoroacetic acid (99%, TFA) and triphenylphosphine (95%) were procured from TCI India and used without purification. L-Cysteine (>99%) was purchased from Sisco Research Laboratories Pvt. Ltd., India and used without purification. The *n*-butyl acrylate (>99%, *n*-BA) has been procured from Fisher Scientific, India. Triethylamine, carbon disulphide, and magnesium sulphate has been purchased from Merck, India. Piranha solution has been prepared using 98 wt.% concentrated sulphuric acid and hydrogen peroxide. Albumin–fluorescein isothiocyanate conjugate (FTIC-Albumin, Sigma) was used without purification. Methanol, chloroform, ethanol, ethyl acetate, hexane, diethyl ether, dichloromethane and tetrahydrofuran have been procured from Merck, India, and used without further purification.

General method for model reactions

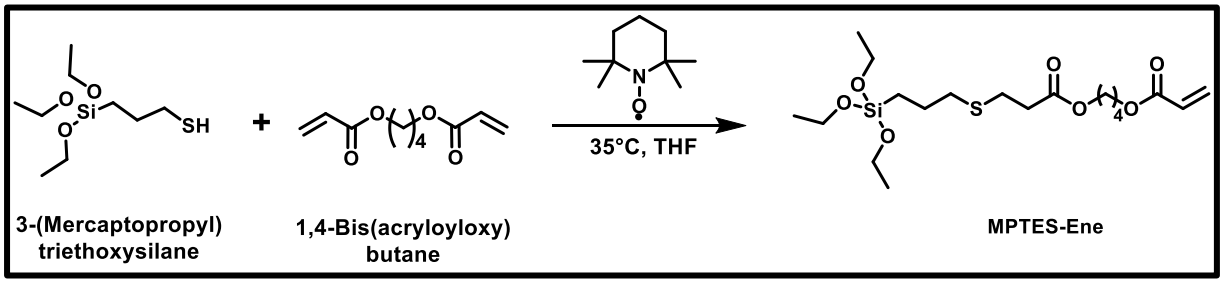
The model reactions were performed in between thiol (3-mercaptopropyltriethoxy silane) and variable enes (*n*-butyl acrylate, *N,N'*-dimethyl acrylamide, divinyl sulfone, 1-dodecene and vinyltriethoxysilane) under different reaction medium such as methanol, tetrahydrofuran or chloroform at 35 °C as represented in **Scheme S1**. The equimolar ratio of thiol/ene was used in all model reactions. The model reaction was monitored using ^{1}H NMR spectroscopy in deuterated chloroform.



Scheme S1. Scheme for the model reaction between 3-mercaptopropyltriethoxysilane and variables enes using TEMPO initiated thiol-ene chemistry at 35 °C in the different reaction medium.

Method for preparation of ene functionalized silanizing agent (MPTES-Ene)

3-Mercaptopropyltriethoxysilane (10 mmol) and 1,4-bis(acryloyloxy)butane (15 mmol) were dissolved in 10 mL tetrahydrofuran and subsequently, TEMPO (1 mmol) was added followed by stirring at 35°C for 16 h, as represented in **Scheme S2**. After 16 h, the solvent was evaporated under a vacuum. The ^{1}H and ^{13}C NMR spectroscopy was performed to characterize the MPTES-Ene.



Scheme S2. Synthesis of 3-mercaptopropyltriethoxysilane functionalized with Ene (MPTES-Ene) using the 1,4-bis(acryloyloxy)butane and 3-mercaptopropyltriethoxysilane in the presence of TEMPO initiator at 35 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ0.71(t, 2H, -Si-**CH_2**-CH_2-); δ1.22(t, 9H, -(**CH_3**-CH_2-O-Si-CH_2)$_3$-); δ1.73(m, 8H, -O-Si-CH_2-**CH_2**-, -COO-CH_2-**CH_2**-**CH_2**-CH_2-COO-); δ2.56(m, 4H, -**CH_2**-S-CH_2-**CH_2**-COO-); δ2.75(t, -CH_2-S-**CH_2**-CH_2-); δ3.81(q, 6H, (-CH_3-**CH_2**-O-Si-CH_2-

CH_2-)$_3$;); δ4.11-4.19(m, 4H, -COO-**CH_2**-CH_2-CH_2-**CH_2**-COO-); δ5.80(d, 1H, vinyl); δ6.05(dd, 1H, vinyl); δ6.05(d, 1H, vinyl).

^{13}C NMR (100 MHz, $CDCl_3$): δ11.37(-O-Si-**CH_2**-CH_2-); 19.8(-**CH_3**-CH_2-O-Si-); 24.65, 28.33(-COO-CH_2-**CH_2**-**CH_2**-CH_2-COO-,-CH_2-S-**CH_2**-CH_2-); 36.4, 36.6(-**CH_2**-S-CH_2-**CH_2**-); 59.7(-CH_3-**CH_2**-O-Si-CH_2-); 65.4, 65.5 (-COO-**CH_2**-CH_2-CH_2-**CH_2**-COO-); 129.9, 132.2 (-**CH=CH_2**); 167.67 (-**COO**-CH_2-CH_2-)173.46 (-CH_2-**COO**-CH=CH_2).

Method for preparation of ene functionalized cysteine (Cys-Ene)

The preparation of Ene functionalized cysteine (Cys-Ene) has been discussed in our previous manuscript.[1]

Treatment of Si wafers with piranha solution

The Si wafers were washed three times with ethanol, chloroform, and acetone and subsequently treated with piranha solution for 1 h at 90 °C. The treated wafers (Si-OH) have been washed with water many times and dried under nitrogen. The pre-treated Si wafers were characterized using XPS, contact angle and AFM analysis.

Procedure for the preparation of ene functionalized Si wafers via silanization (Si-Ene)

The silanization was accomplished using 10 mL of a dried toluene solution of MPTES-Ene (100 mg) in the presence of triethylamine (0.1 mL) as shown in **Scheme S3**. The Si wafers were dipped in the above solution for 24 h under reflux condition. After 24 h, washing with tetrahydrofuran, water, and acetone was performed and samples were dried in a stream of nitrogen. The resulting Si wafers were characterized using XPS, contact angle and AFM analysis.

Procedure for the preparation of thiol functionalized Si wafers via silanization (Si-SH)

The silanization was accomplished using 10 mL of a dried toluene solution of 3-mercaptopropyltriethoxysilane (100 mg), triethylamine (0.1 mL), and PPh_3(5 mg) to yield Si wafers modified with thiol functionality as shown in **Scheme S4.** The Si wafers were dipped in the above solution for 24 h under reflux condition. After 24 h, washing with tetrahydrofuran, water, and acetone was performed and samples were dried under a nitrogen stream.

Method for the preparation of thiol and ene functionalized polymers

The preparation of thiol functionalized polymer (Polymer-SH) such as poly(*N*-isopropylacrylamide) and polystyrene and Ene functionalized polymer (Polymer-Ene) such as poly(isobornylacrylate) and poly(acrylic acid) has been discussed in our previous manuscript.[2]

Conjugation of polymer functionalized with thiol or ene and Cys-Ene with Si wafer functionalized with thiol or ene using thiol-ene chemistry initiated by TEMPO (Si-Polymer)

The modification of the Si-SH/Ene wafer was performed using a 10 mL THF solution of polymer-SH (PNIPAM-SH/PS-SH)/polymer-Ene (PiBoA-Ene/PAA-Ene)/Cys-Ene (300 mg) using TEMPO (0.015 mmol) initiated thiol-ene chemistry. The reaction time was 16 h as shown in **Scheme 1 and 2**. After 16 h, Si-Polymer (Si-PNIPAM/Si-PS/Si-PiBoA/Si-PAA/Si-Cys) was washed three times with tetrahydrofuran, chloroform, or water. The wafers were dried under vacuum. The resulting Si-polymer has been characterized using XPS, AFM, and contact angle measurement.

General procedure for performing antifouling study

The albumin–fluorescein isothiocyanate conjugate (FTIC-albumin) (3 mg) was dissolved in a 3 mL PBS buffer solution. Si-Cys and Si-SH were immersed in the FITC-albumin solution for 3h. After 3h, Si wafers were washed thoroughly with PBS solution three times. The resulting Si wafers were characterized using fluorescence microscopy.

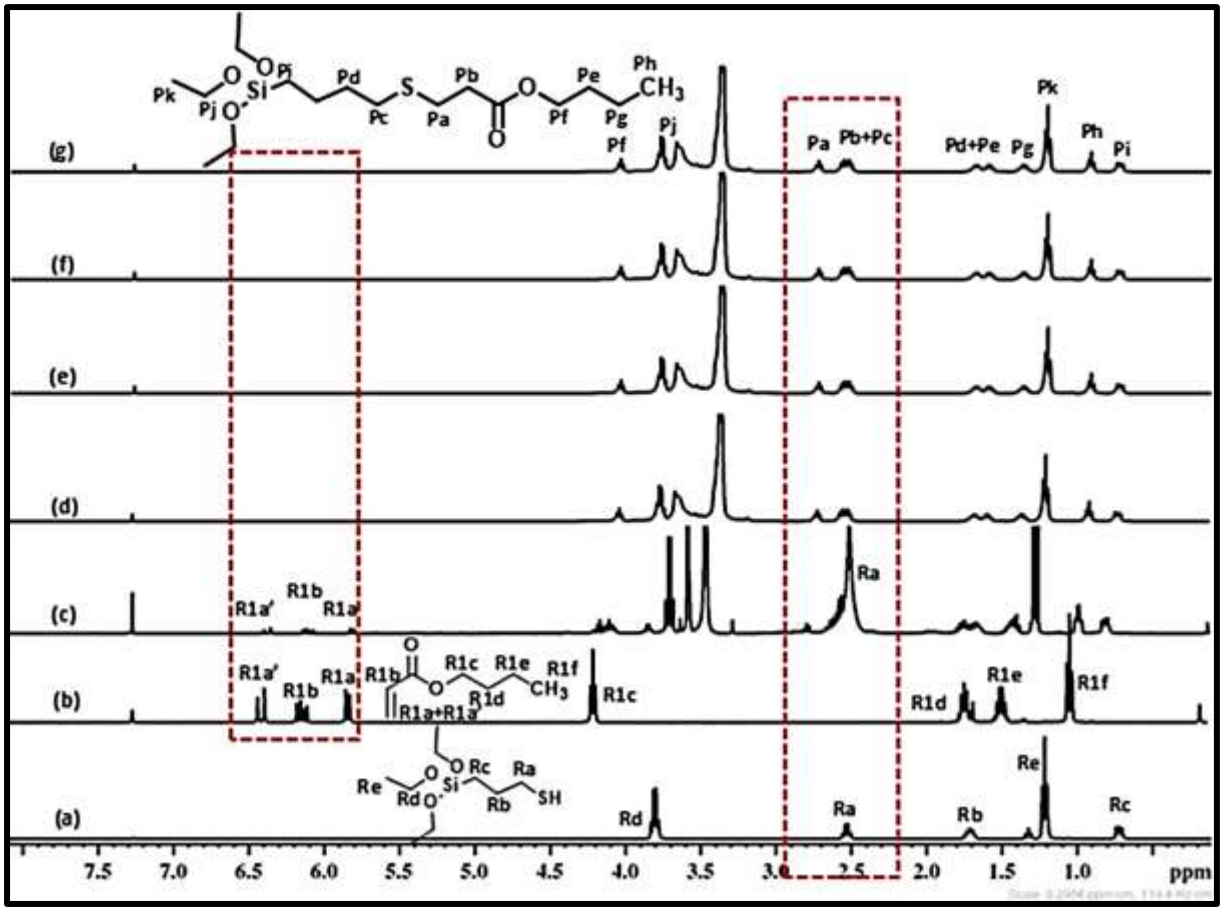


Figure S1. ^{1}H NMR spectra for reaction between 3-mercaptopropyltriethoxysilane and *n*-butyl acrylate at 35 °C for 16 h using methanol as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) *n*-butyl acrylate (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

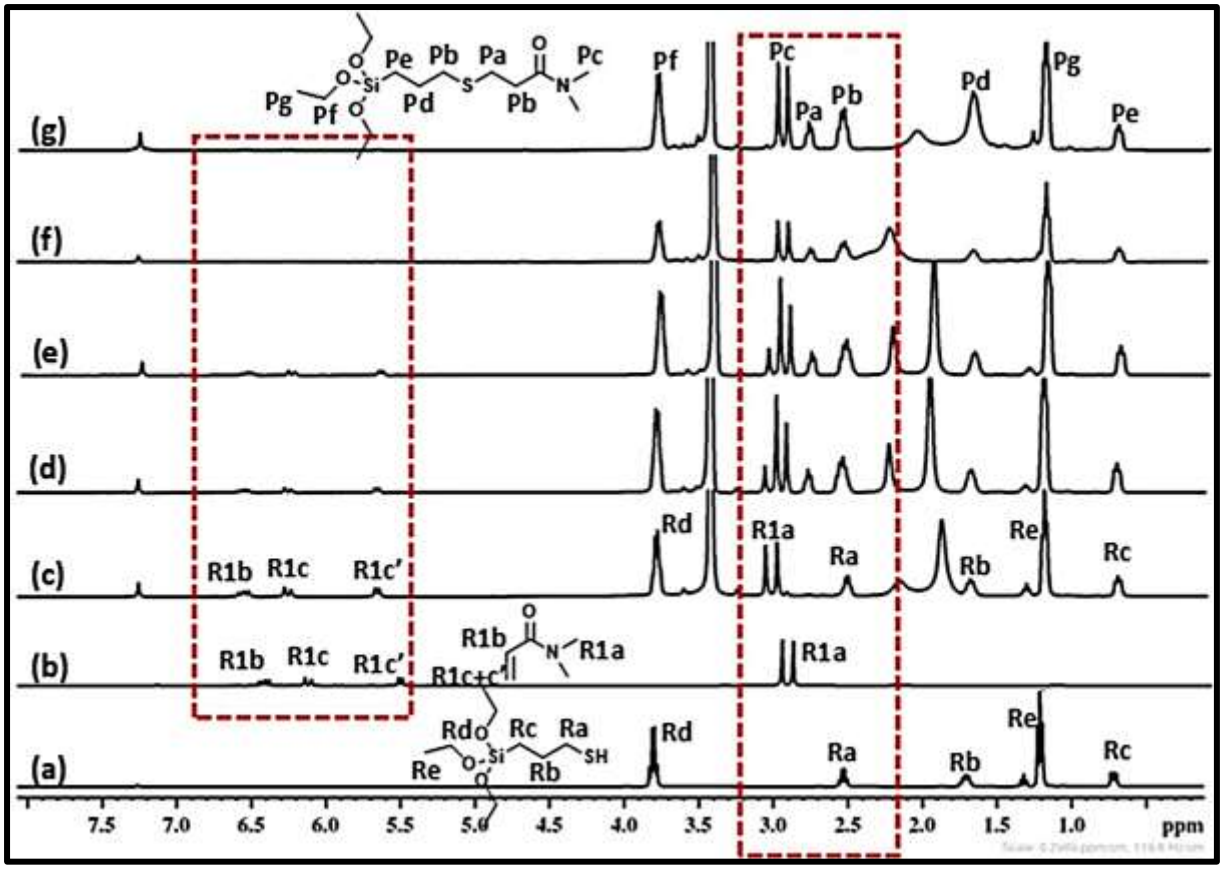


Figure S2. ^{1}H NMR spectra for reaction between 3-mercaptopropyltriethoxysilane and *N*,*N*-dimethylacrylamide at 35 °C for 16 h using methanol as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) *N*,*N*-dimethyl acrylamide (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

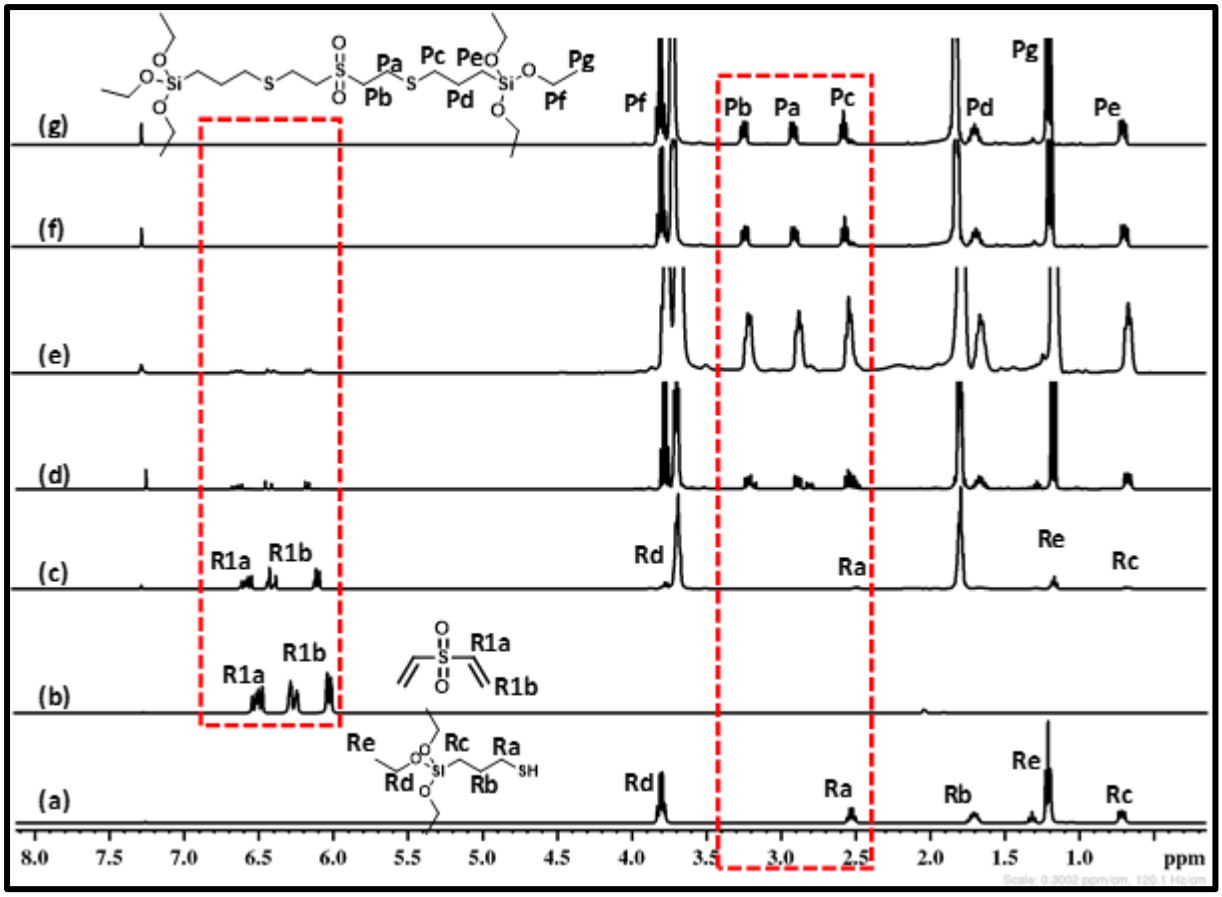


Figure S3. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and divinylsulfone at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) divinylsulfone (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

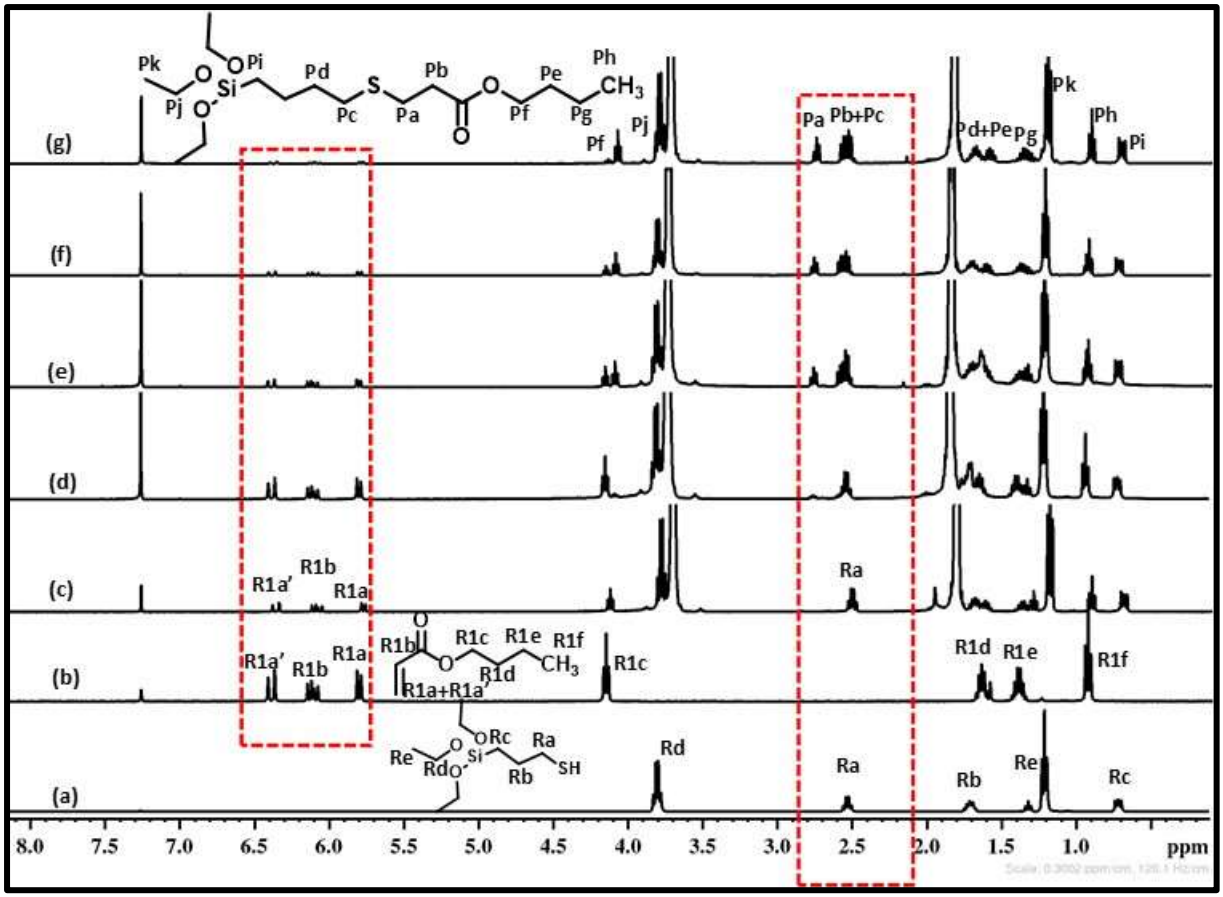


Figure S4. ^{1}H NMR spectra for reaction between 3-mercaptopropyltriethoxysilane and *n*-butyl acrylate at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) *n*-butyl acrylate (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

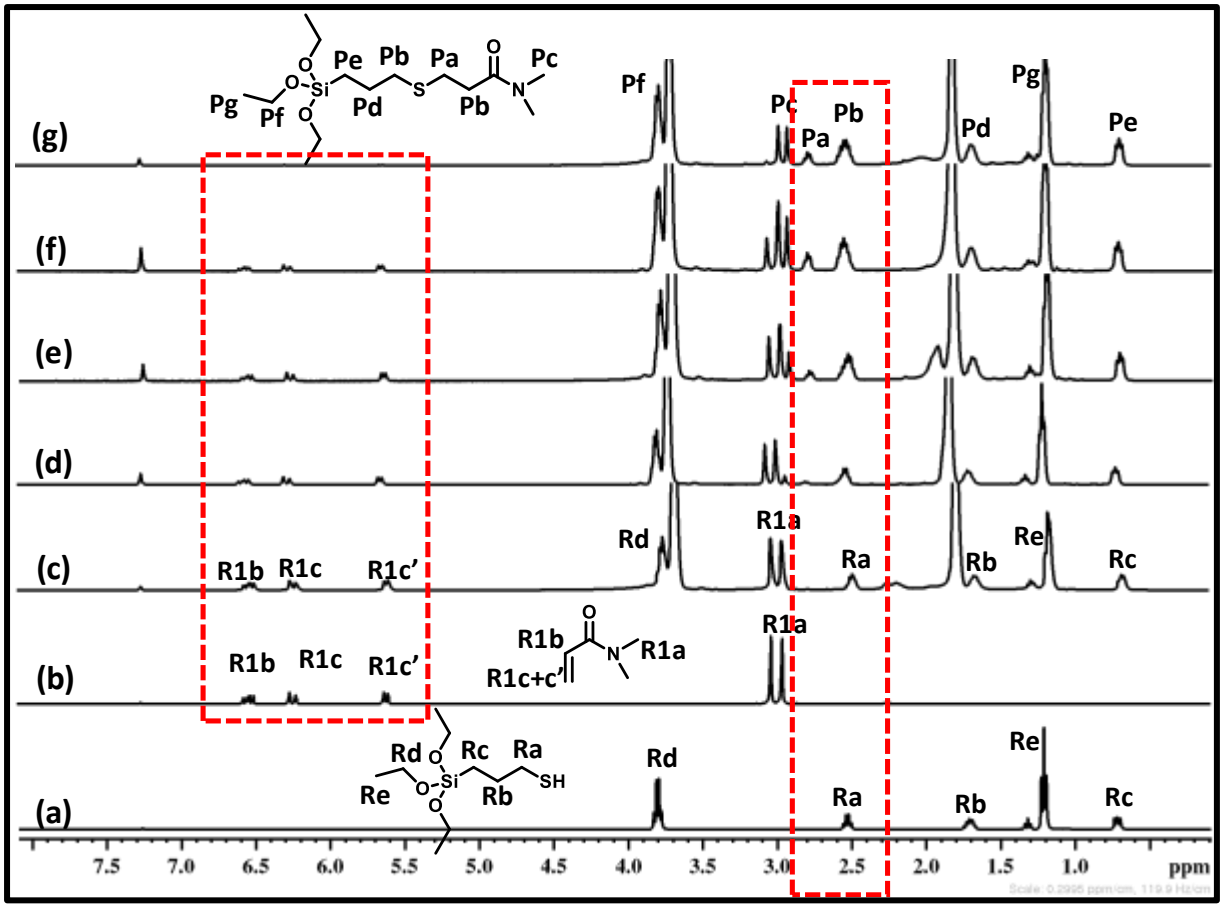


Figure S5. ^{1}H NMR spectra for reaction between 3-mercaptopropyltriethoxysilane and *N*,*N*-dimethyl acrylamide at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) *N*,*N*-dimethyl acrylamide (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

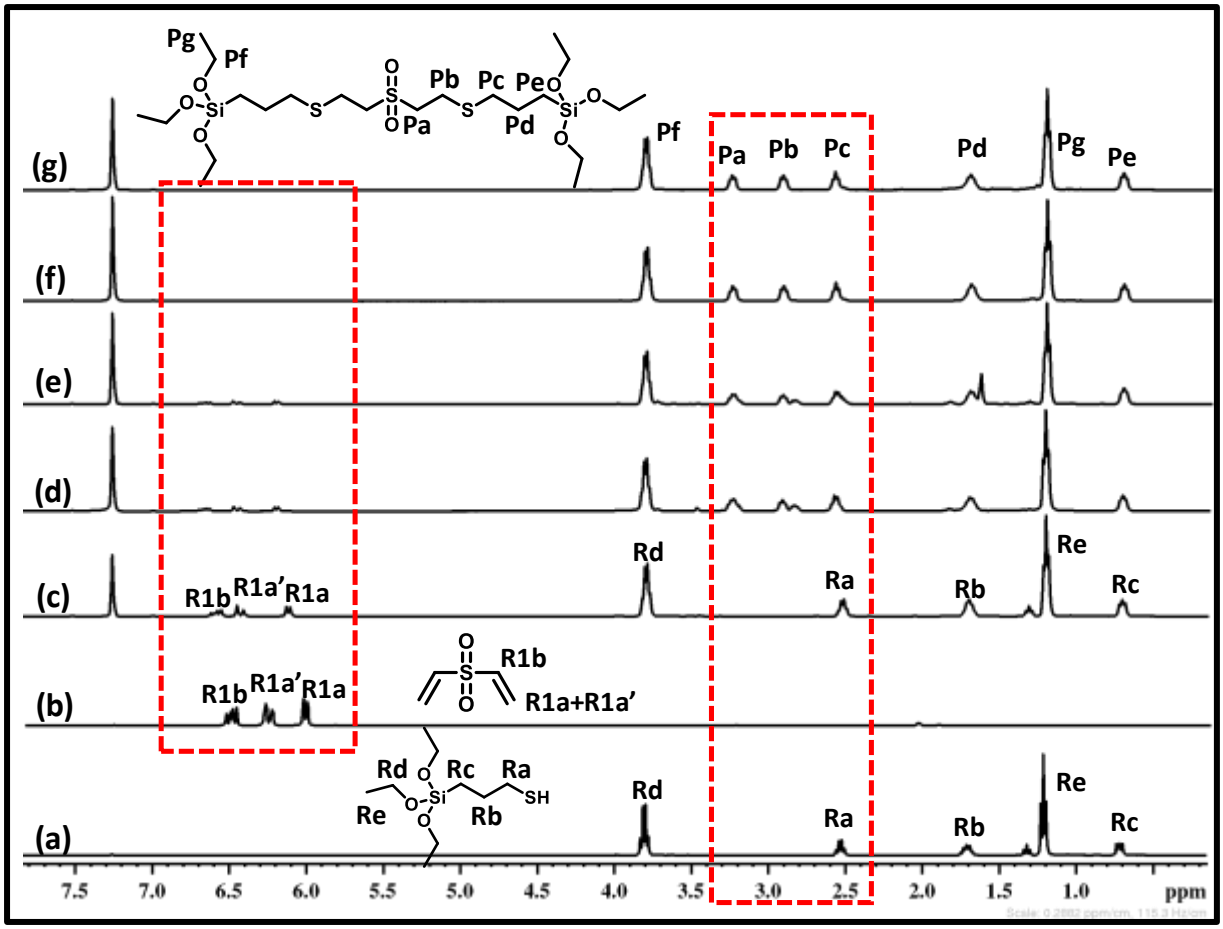


Figure S6. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and divinylsulfone at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) divinylsulfone (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

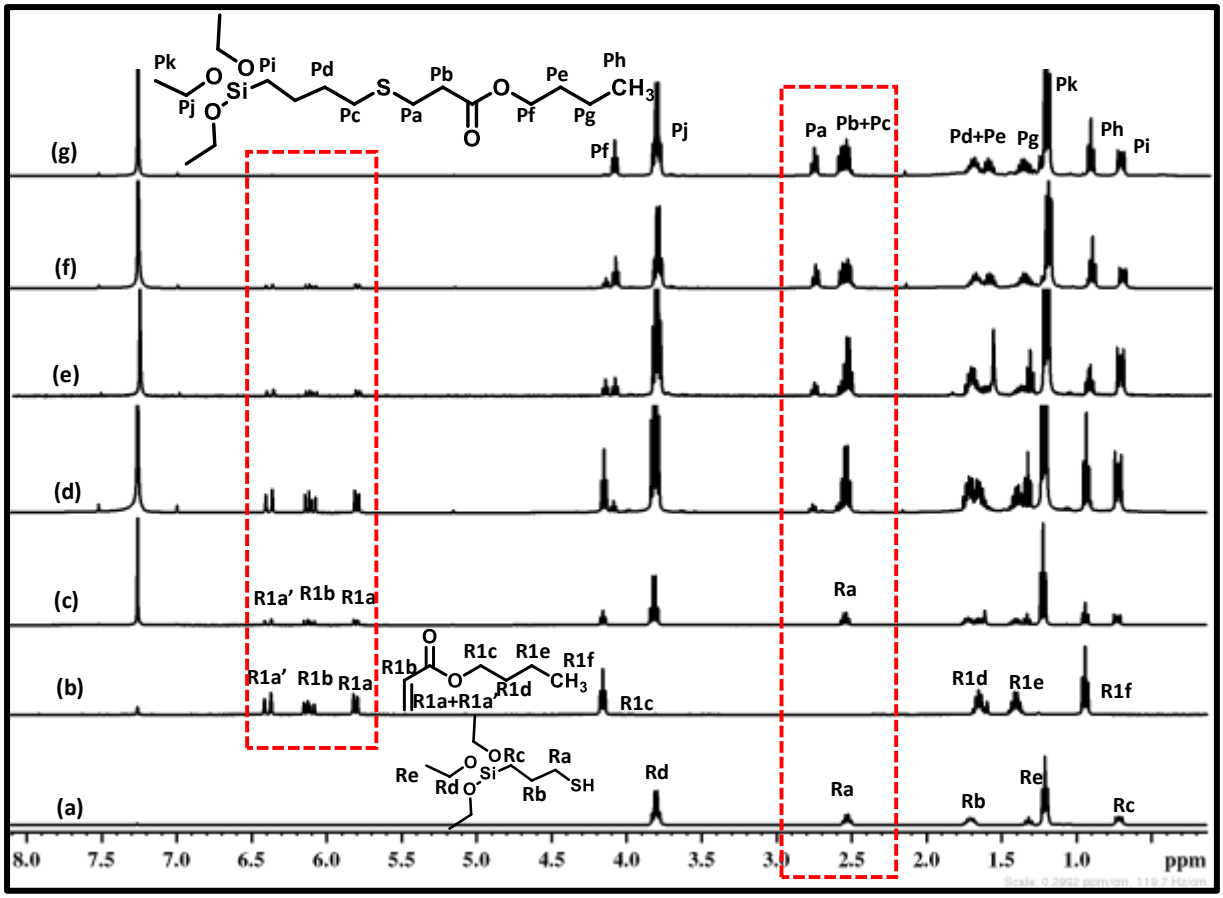


Figure S7. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and *n*-butyl acrylate at 35 °C using chloroform as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) *n*-butyl acrylate (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

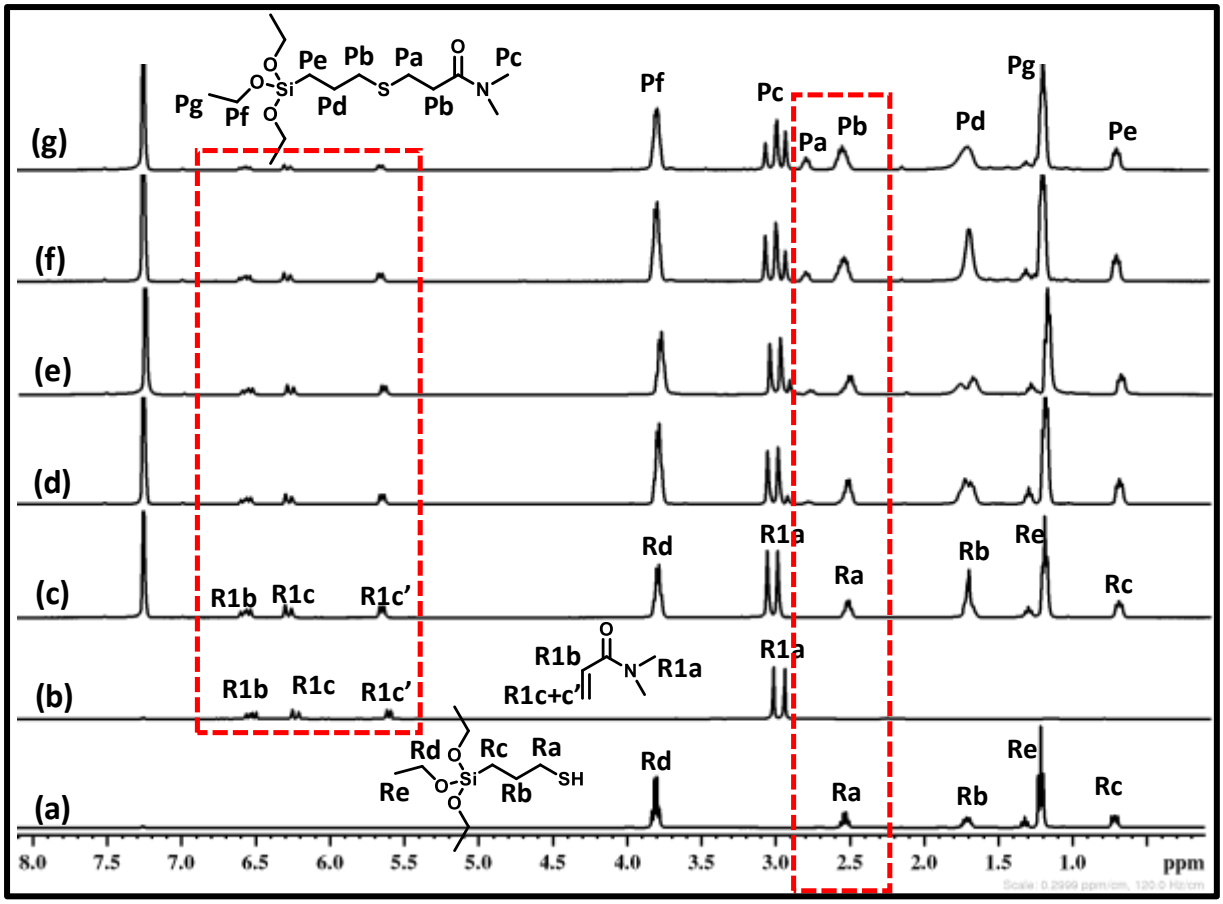


Figure S8. ^{1}H NMR spectra for reaction between 3-mercaptopropyltriethoxysilane and *N*,*N*-dimethyl acrylamide at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) *N*,*N*-dimethyl acrylamide (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

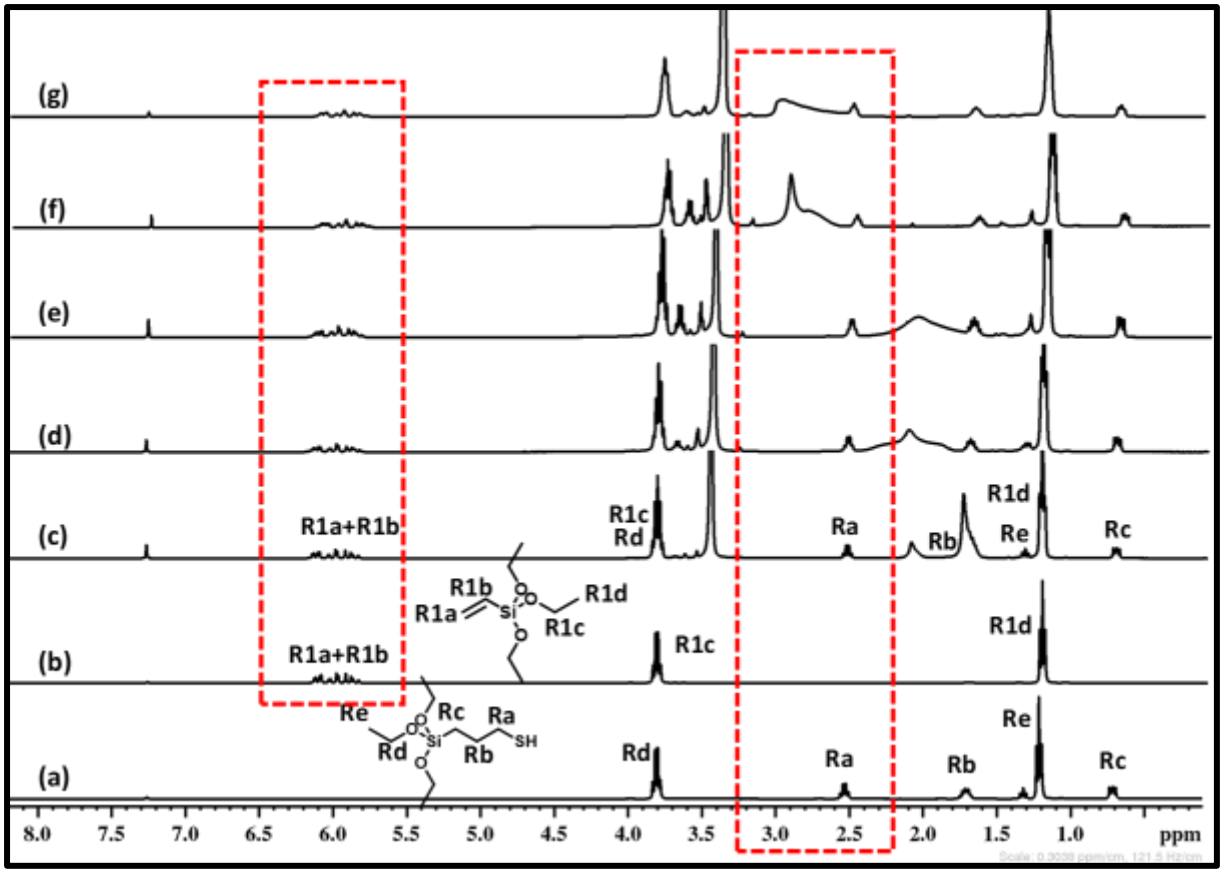


Figure S9. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and vinyltriethoxysilane at 35 °C for 16 h using methanol as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) vinyltriethoxysilane (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

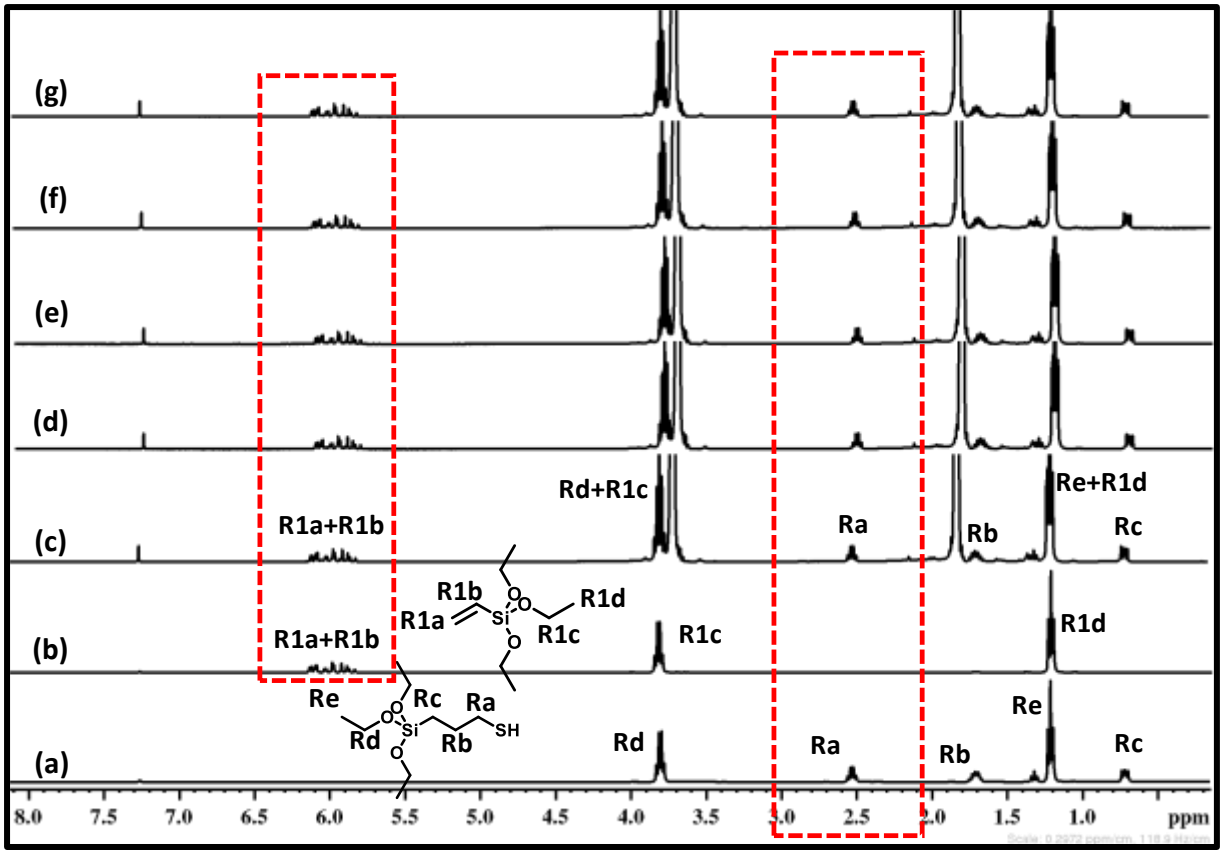


Figure S10. [1]H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and vinyltriethoxysilane at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) vinyltriethoxysilane (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

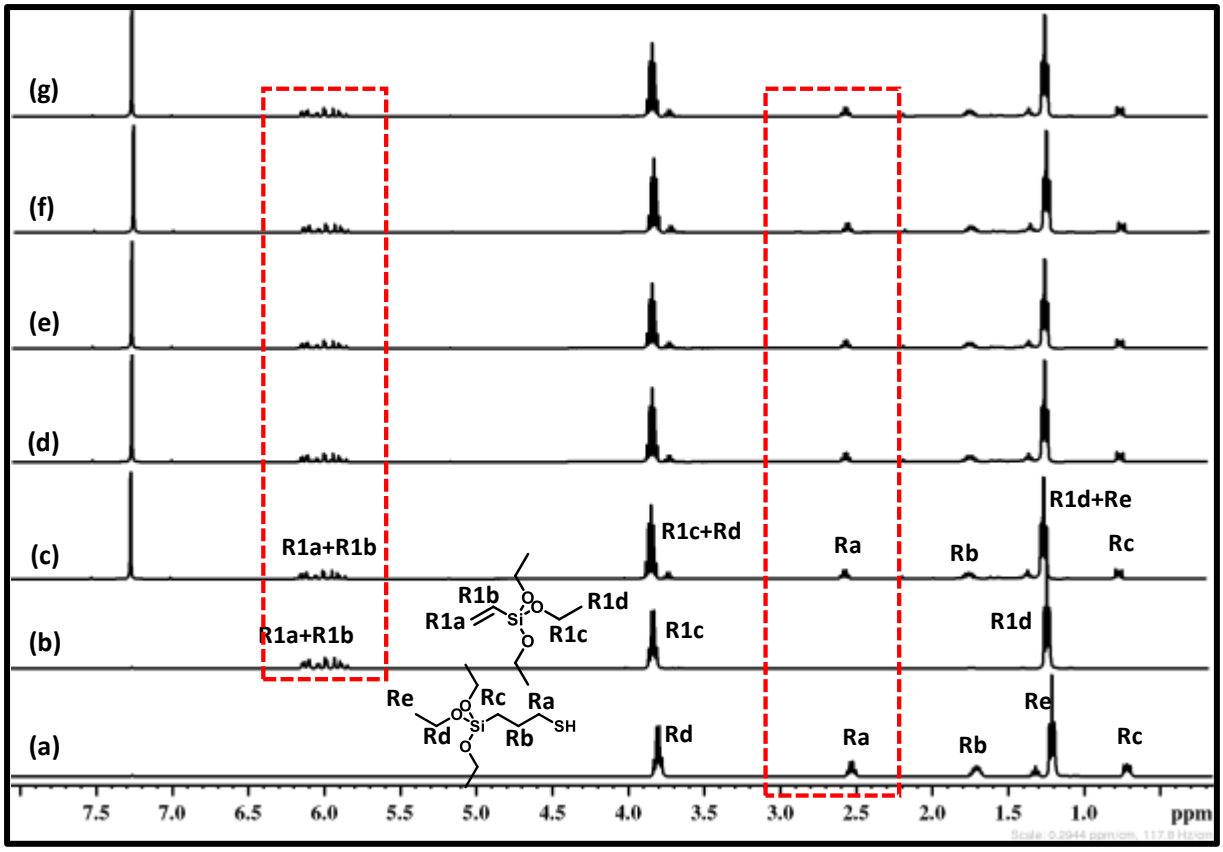


Figure S11. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and vinyltriethoxysilane at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) vinyltriethoxysilane (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

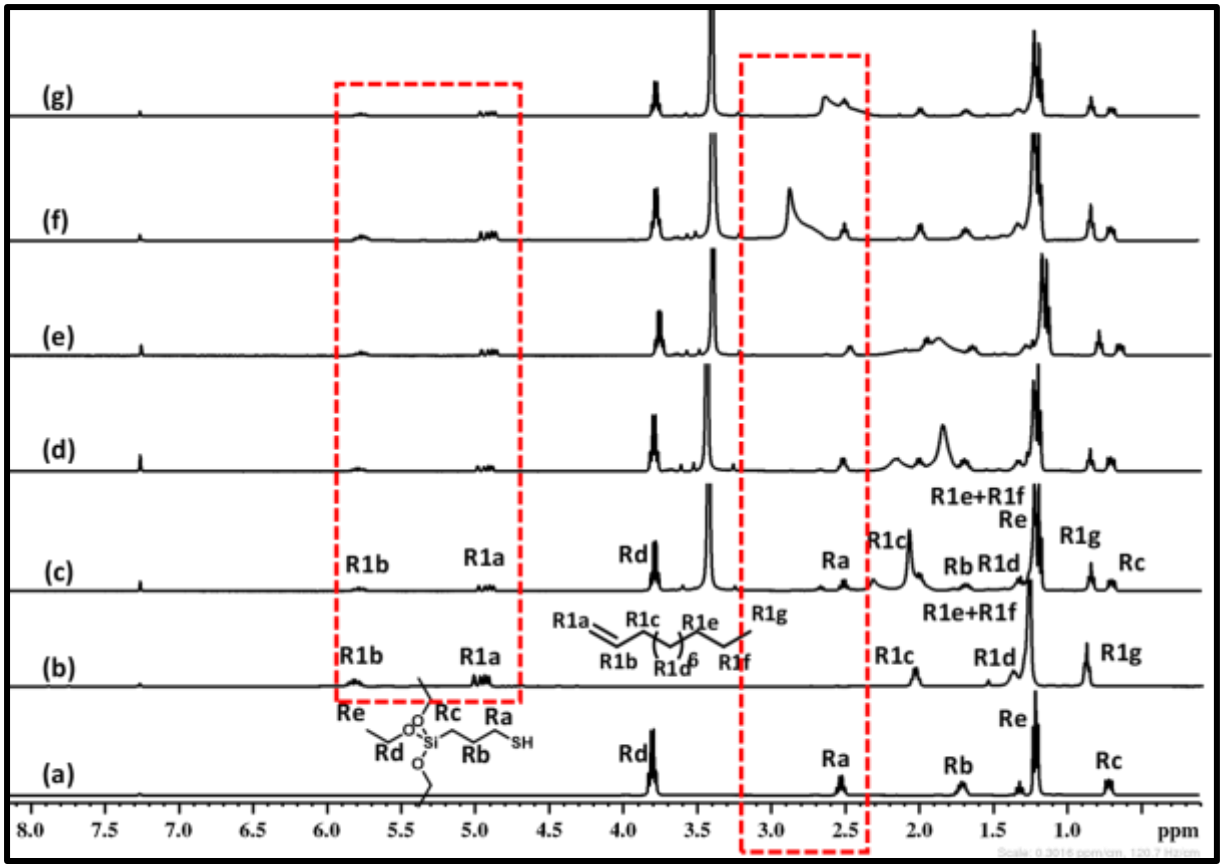


Figure S12. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and 1-dodecene at 35 °C for 16 h using methanol as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) 1-dodecene (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

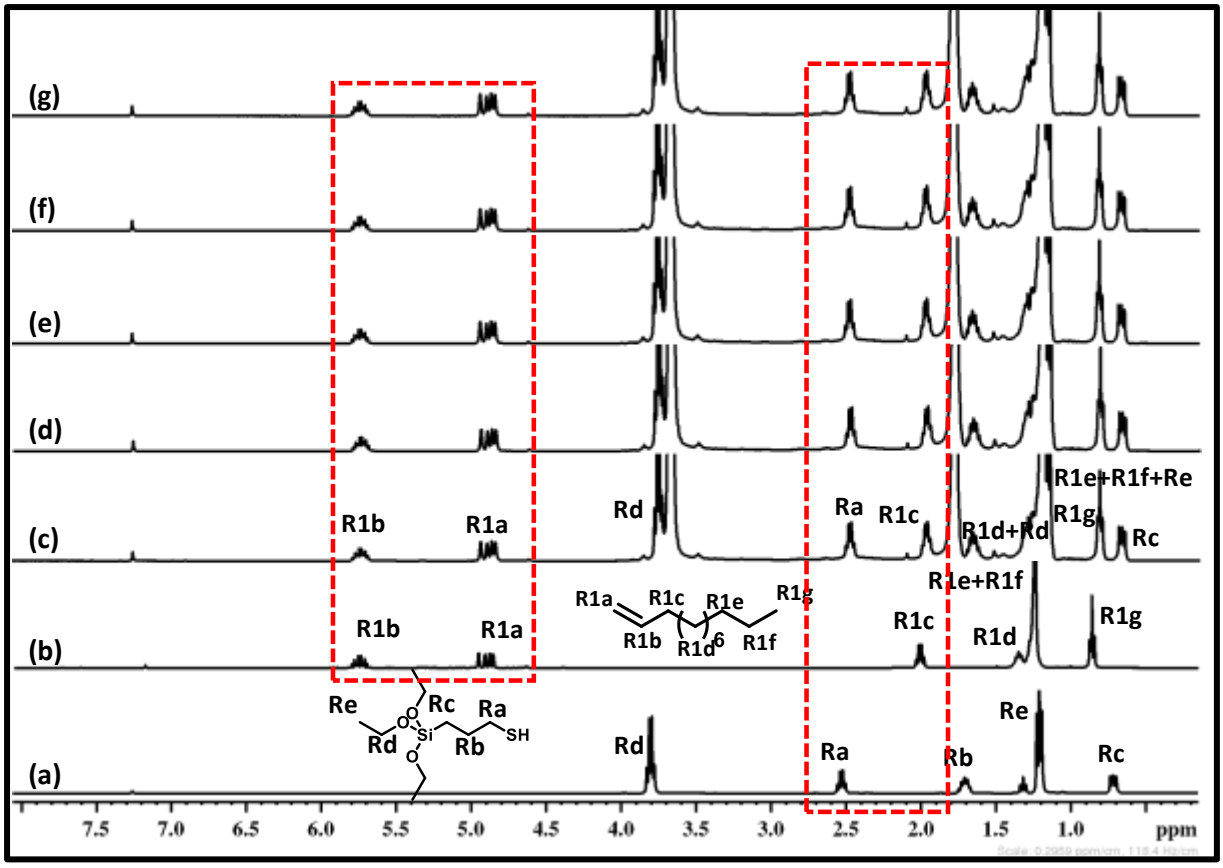


Figure S13. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and 1-dodecene at 35 °C for 16 h using tetrahydrofuran as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) 1-dodecene (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

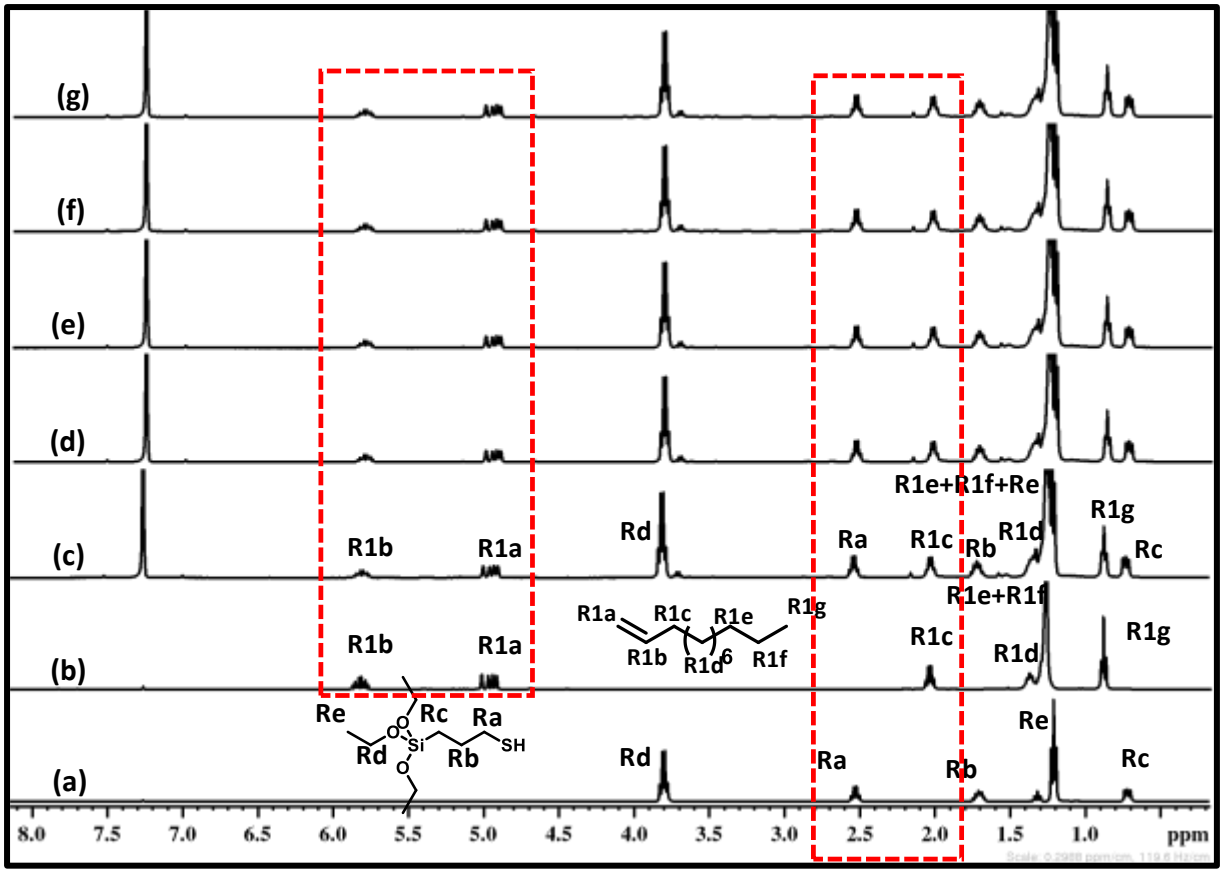


Figure S14. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and 1-dodecene at 35 °C for 16 h using chloroform as a solvent and with varying initiator (TEMPO) loading (a) 3-mercaptopropyltriethoxysilane, (b) 1-dodecene (c) 0 mmol TEMPO, (d) 0.01 mmol TEMPO (e) 0.05 mmol TEMPO, (f) 0.08 mmol TEMPO and (g) 0.1 mmol TEMPO.

Table S1. Thioether formation *vs.* variable times for the reaction of 3-mercaptopropyltriethoxysilane with variables enes (divinyl sulfone, *N,N'*-dimethyl acrylamide, *n*-butyl acrylate, 1-dodecene and vinyltriethoxysilane) in methanol at 35 °C.

	Thioether Formed (%)		
Time (h)	**3-mercapto propyltriethoxysilane + Divinyl sulfone**	**3-mercapto propyltriethoxysilane + *n*-butyl acrylate**	**3-mercapto propyltriethoxysilane + *N,N'*-dimethylacrylamide**
0	0	0	0

4	71	100	82
8	98	100	86
12	99	100	90
16	100	100	100

The reaction of 3-mercaptopropyltriethoxysilane with variable enes were accomplished at 1:1 thiol/ene ratio and 0.1 mmol TEMPO concentration under methanol at 35 °C to observe the thioether formation ^{1}H NMR spectroscopy was utilized. The reaction between 3-mercaptopropyltriethoxysilane and *n*-butyl acrylate showed 100 % thioether formation at 4 h, however, the reaction between 3-mercaptopropyltriethoxysilane and divinyl sulfone displayed nearly quantitative conversion at 8 h, while reaction between 3-mercaptopropyltriethoxysilane and *N,N'*-dimethyl acrylamide displayed 100 % conversion under methanol at 16 h as mentioned in **Table S1**.

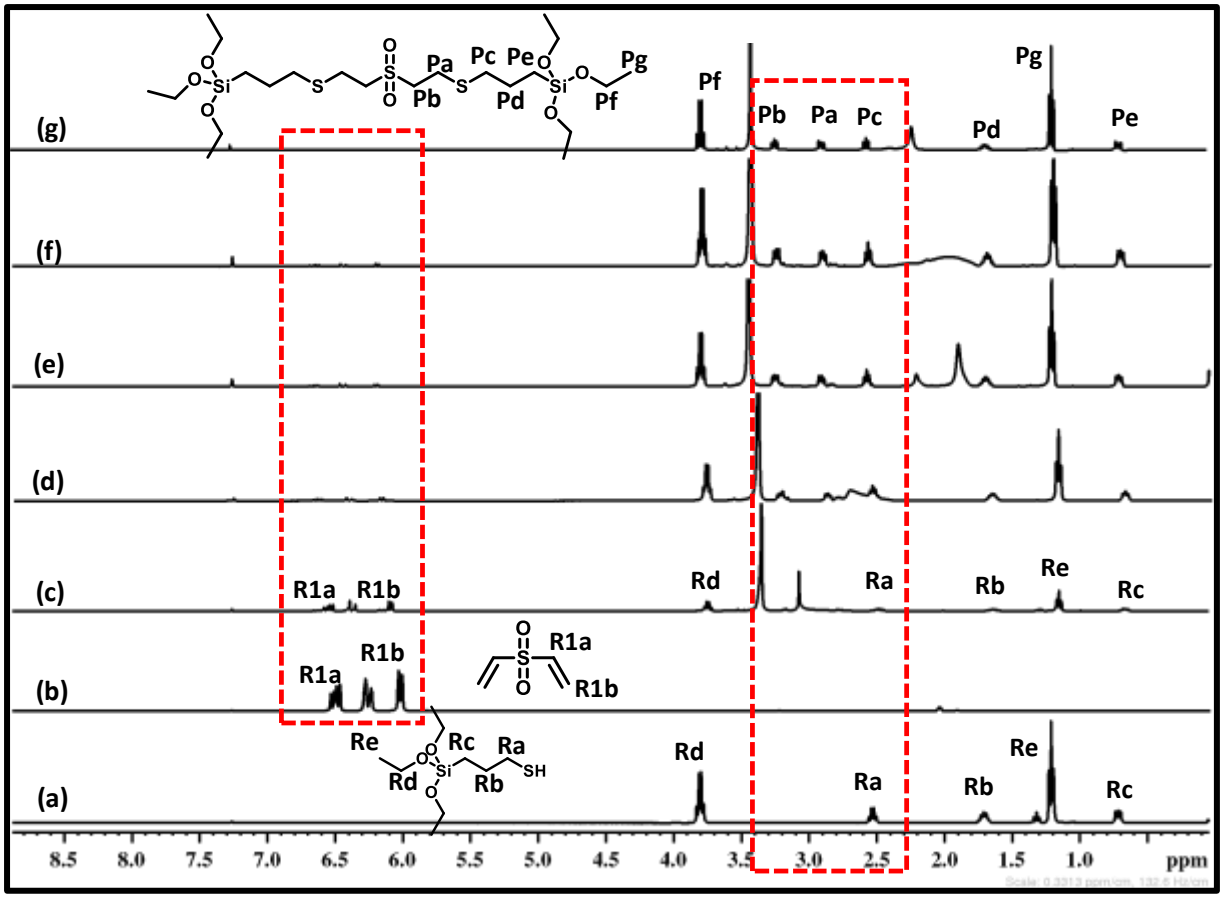


Figure S15. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and divinylsulfone at 35 °C using methanol as solvent and varying time (a) 3-mercaptopropyltriethoxysilane, (b) divinylsulfone, (c) 0 h , (d) 4 h (e) 8 h (f) 12 h and (g) 16 h.

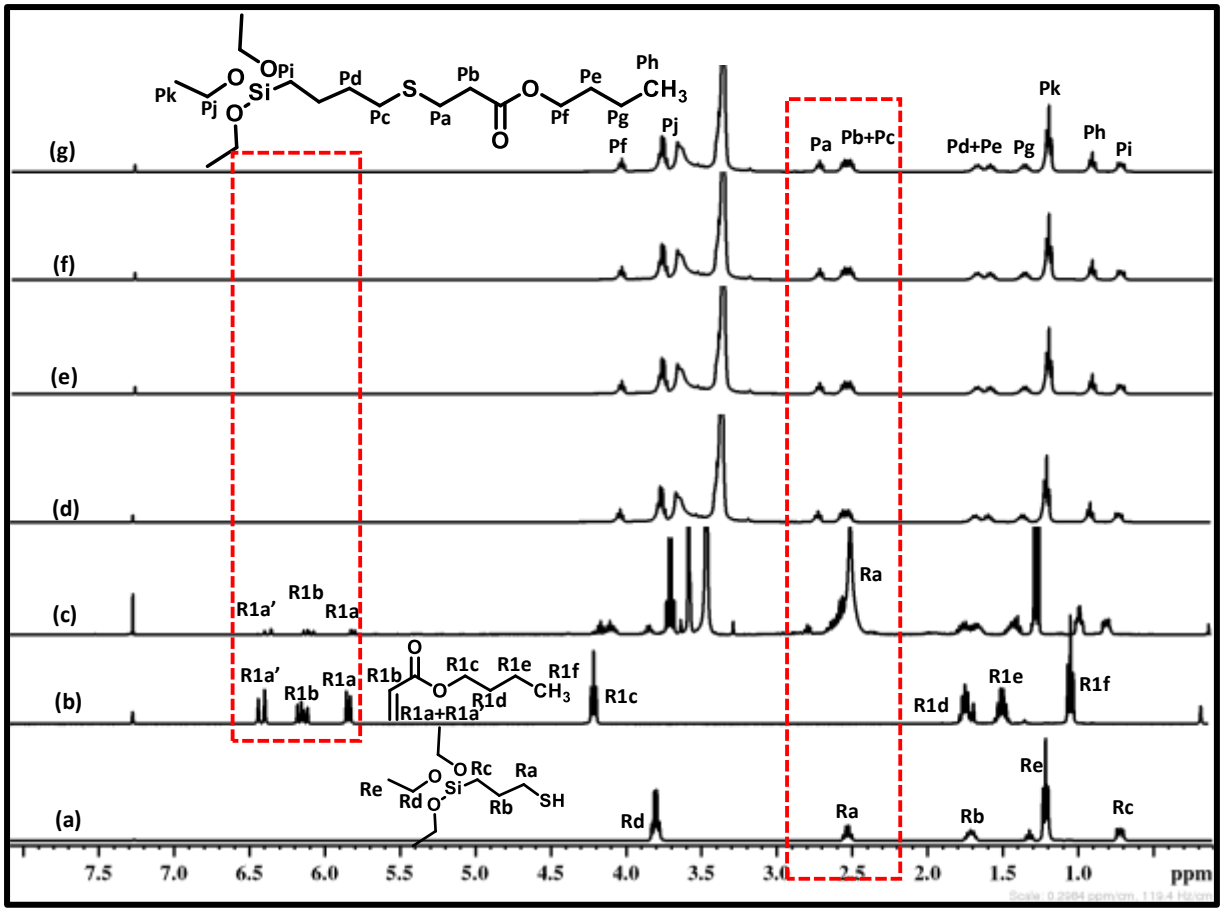


Figure S16. ^{1}H NMR spectra for the reaction between 3-mercaptopropyltriethoxysilane and *n*-butyl acrylate at 35 °C using methanol as solvent and varying time (a) 3-mercaptopropyltriethoxysilane, (b) *n*-butylacrylate, (c) 0 h , (d) 4 h (e) 8 h (f) 12 h and (g) 16 h.

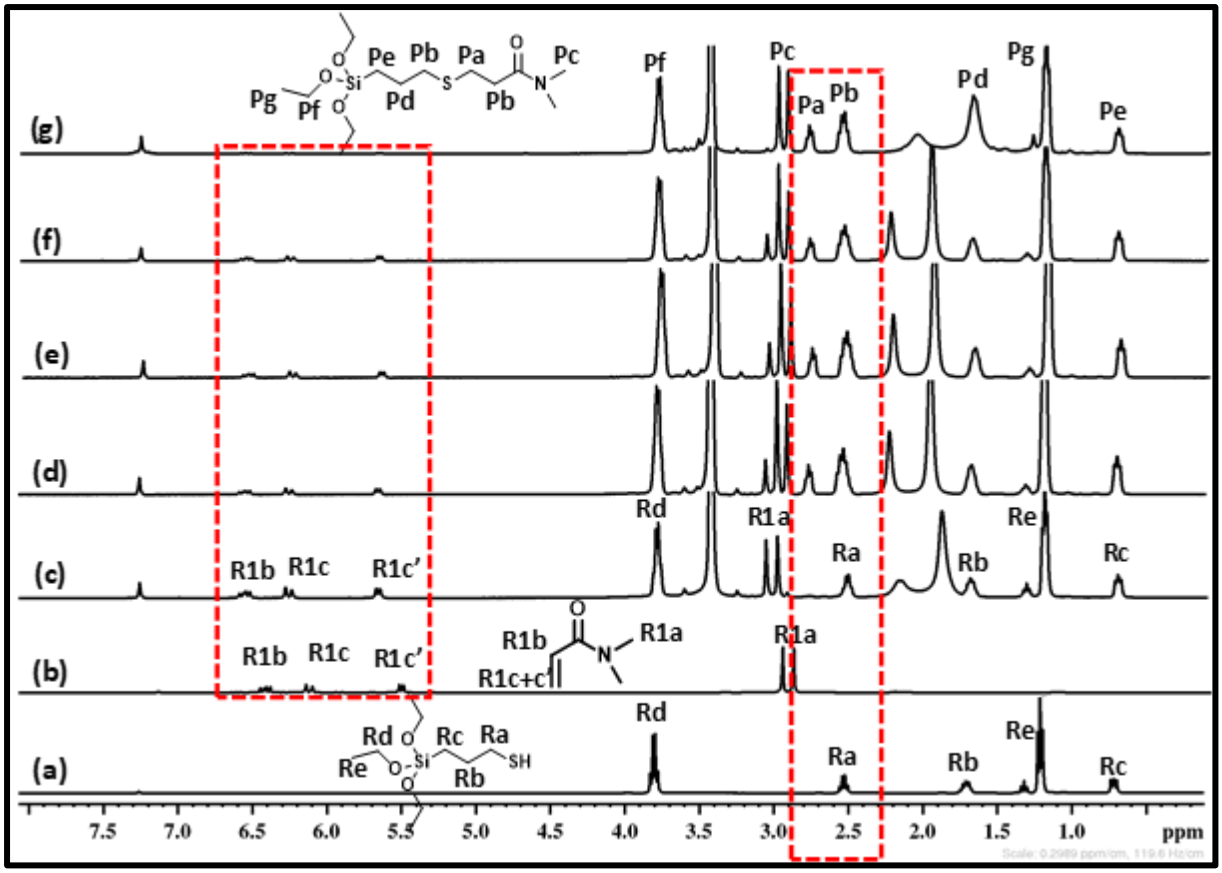


Figure S17. ^{1}H NMR spectra for reaction between 3-mercaptopropyltriethoxysilane and *N*,*N*-dimethyl acrylamide at 35 °C using methanol as solvent and varying time (a) 3-mercaptopropyltriethoxysilane, (b) *N*,*N*-dimethyl acrylamide, (c) 0 h (d) 4 h (e) 8 h (f) 12 h and (g) 16 h.

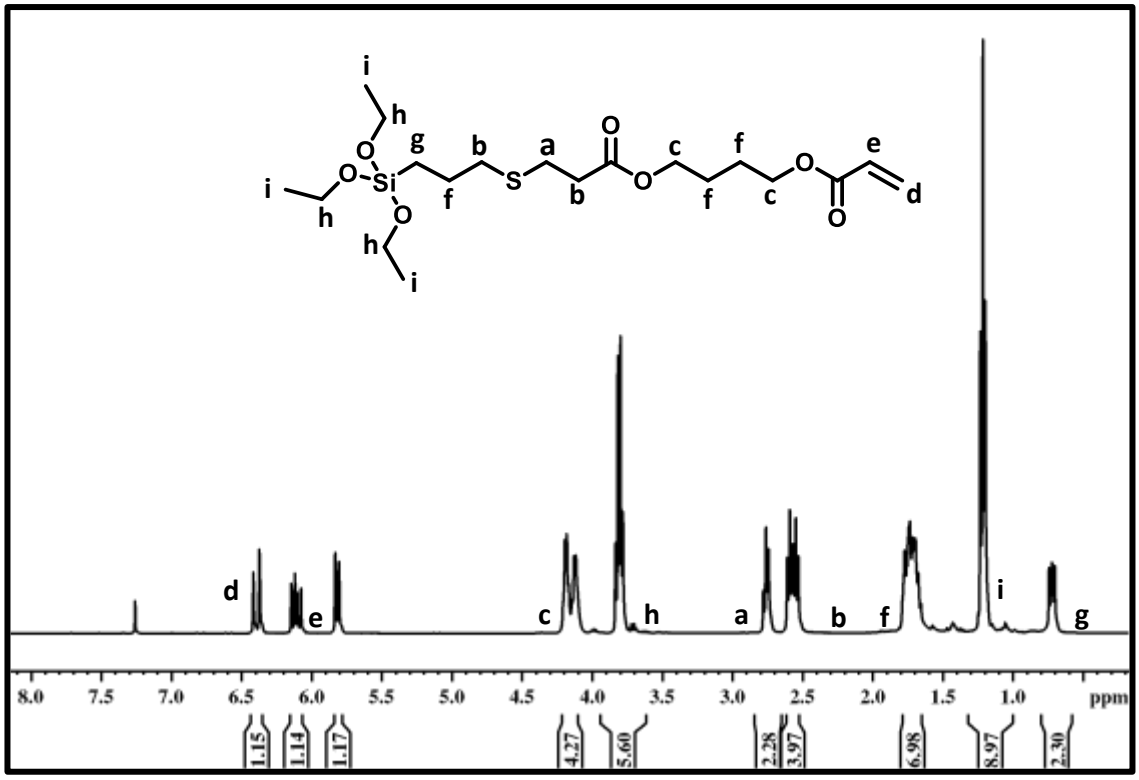


Figure S18. ^{1}H NMR spectrum of MPTES-Ene prepared by reaction of 3-mercaptopropyltriethoxysilane and 1,4-bis(acryloyloxy)butane through thiol-ene chemistry initiated by TEMPO at ambient temperature.

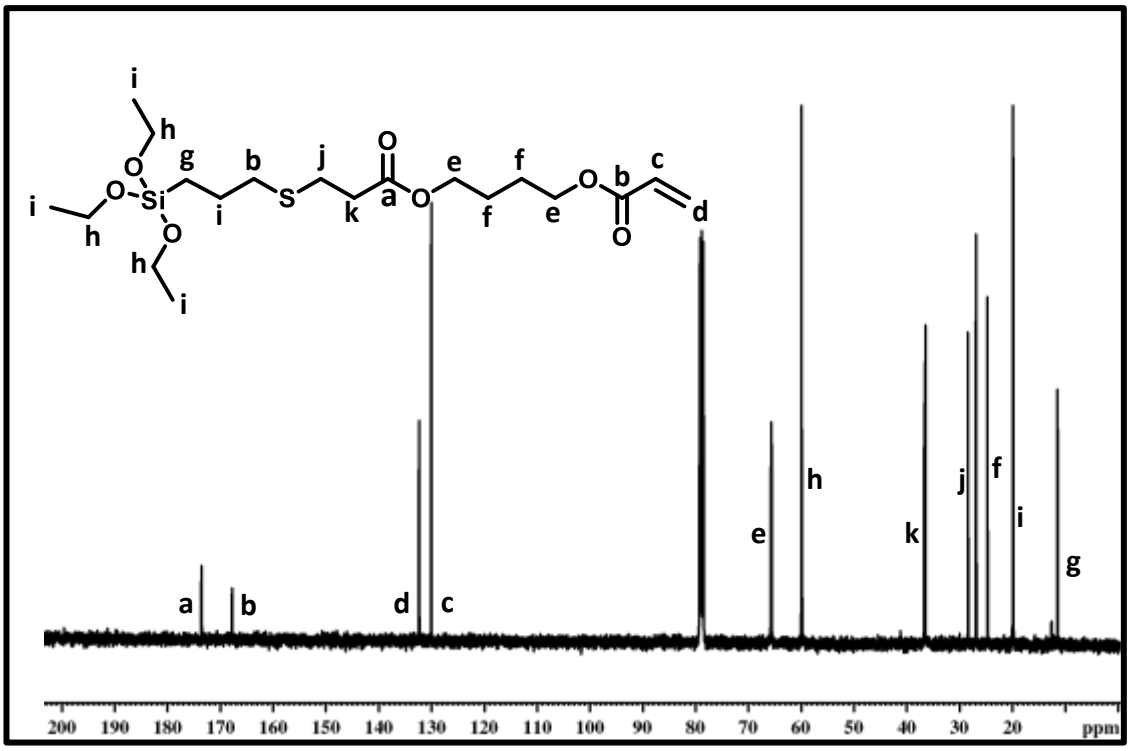


Figure S19. ^{13}C NMR spectrum of MPTES-Ene prepared by reaction of 3-mercaptopropyltriethoxysilane and 1,4-bis(acryloyloxy)butane through thiol-ene chemistry initiated by TEMPO at ambient temperature.

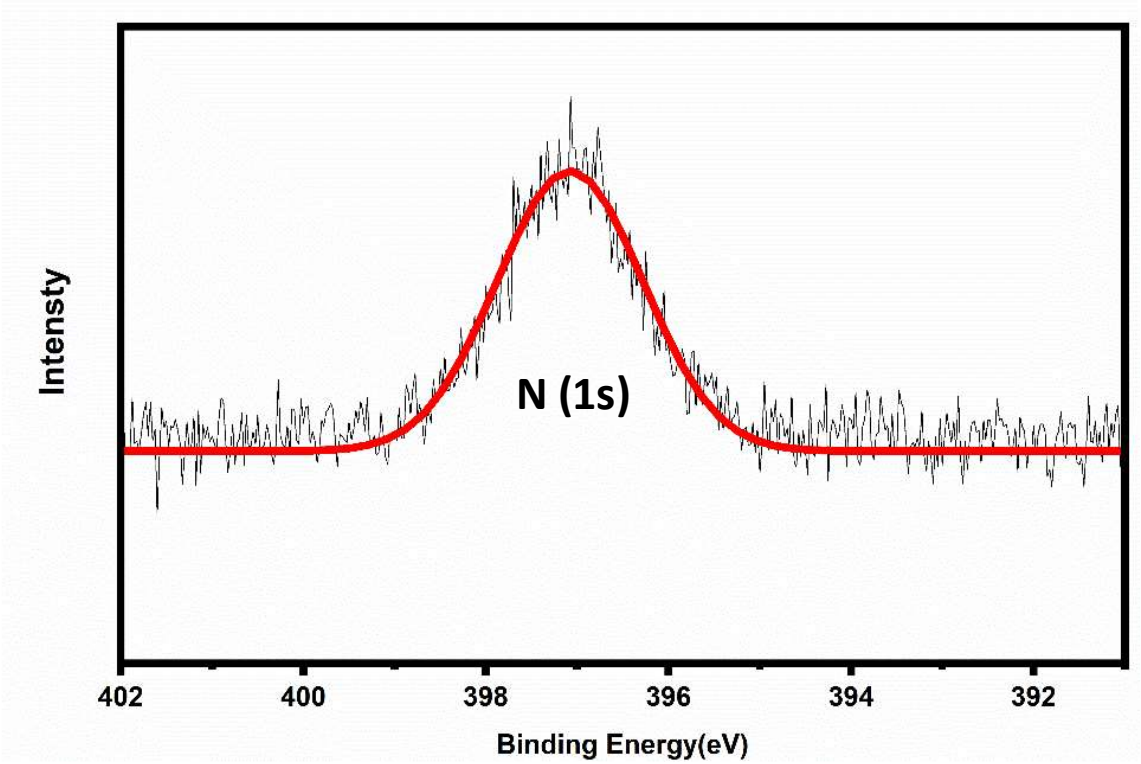


Figure S20. Deconvolution of N 1s element for Si wafers conjugated with PNIPAM-SH (Si-PNIPAM) using TEMPO initiated thiol-ene chemistry under ambient reaction condition.

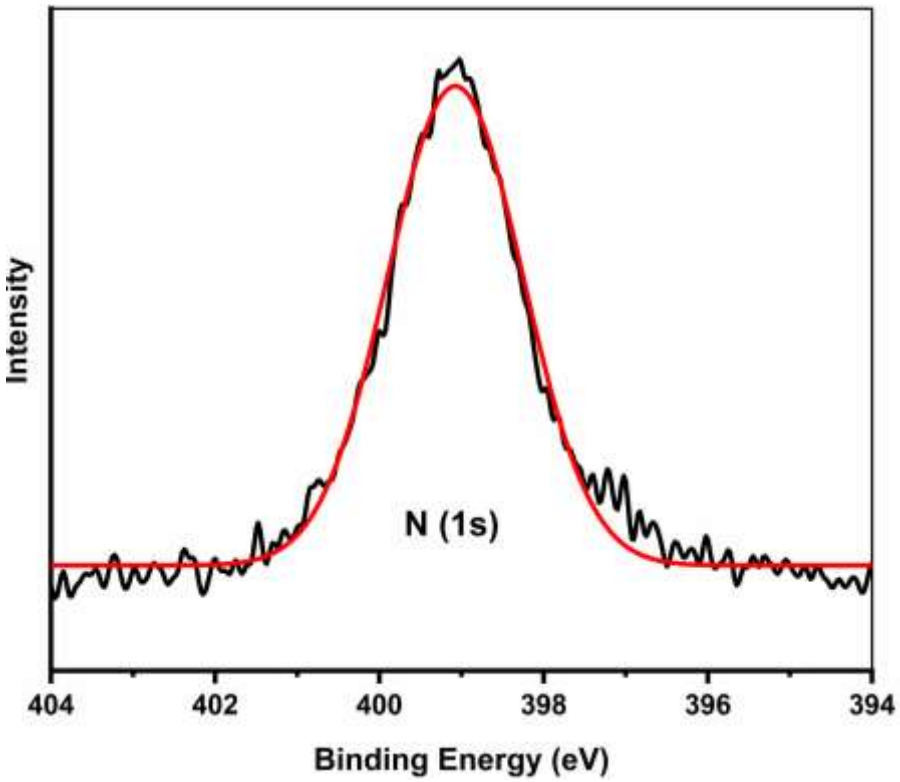


Figure S21. Deconvolution of N 1s element for Si wafers conjugated with Cys-Ene (Si-Cys) using TEMPO initiated thiol-ene chemistry under ambient reaction condition.

References

1 S. Hafeez, J. Jaishankar, P. Srivastava and L. Nebhani, *Mater. Today Commun.*, 2020, 27–31.

2 S. Hafeez and L. Nebhani, *Mater. Today Commun.*, 2019, **21**, 1–13.