Multifunctional Monomers based on Vinyl Sulfonates and Vinyl Sulfonamides for Crosslinking Thiol-Michael Polymerizations: Monomer Reactivity and Mechanical Behavior

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Supplementary Information

Contents

1. Materials

1-Hexanol, Ethylene glycol, Triethylene glycol, and Glycerol was purchased from Acros. 1,6-Hexanediol, 1,1,1-Tris(hydroxymethyl)propane, Acryloyl chloride, Pentaerythritol tetrakis(3-mercaptopropionate)(PETMP), 1-Hexyl acrylate, Ethylene glycol diacrylate, 1,6-Hexanediol diacrylate, Trimethylolpropane triacrylate, Tricyclo[5.2.1.$0^{2,6}$]decanedimethanol diacrylate, 1-Hexylamine, Hexamethylenediamine, *N*,*N*′-Dimethyl-1,6-diaminohexane, *N*,*N*′-Dimethyl-1,3-propanediamine, Homopiperazine, 2,3,6,6-Tetramethylpiperidine 1-oxyl (TEMPO), 2,2-Dimethoxy-2-phenylacetophenone (DMPA), anhydrous Dichloromethane, anhydrous Tetrahydrofuran, Ethylene glycol diethyl ether were purchased from Sigma Aldrich. 2-Chloroethane sulfonyl chloride and Tricyclo[5.2.1.$0^{2,6}$]decane-4,8-dimethanol was purchased from TCI chemicals and Triethylamine was purchased from fisher scientific. NPPOC-TMG[1] and SiTSH[2] were synthesized according to previously reported procedures. All other chemicals were of reagent grade and used without further purification.

2. Instrumentation

2.1. NMR Spectroscopy, ESI-MS and CHNS analysis

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. Proton chemical shifts are expressed in parts per million (δ) using TMS as an internal standard. The δ scale was referenced to deuterated solvents, indicated in the respective measurement. ESI-MS analysis was carried out on a Waters Synapt G2 HDMS Q-TOF Mass Spectrometer. CHNS elemental analysis was carried out on LECO 932.

2.2. FTIR

Reaction kinetics was analyzed using a FTIR spectrometer (Nicolet 8700) to monitor the real-time functional group conversion in transmission mode. Samples were sandwiched between two NaCl windows with a spacer of 30 μm and placed into a horizontal transmission apparatus. Irradiation was performed using a mercury-lamp (Acticure 4000) with a 320-390 nm bandgap filter after 1min, and continued for 5 min. The light intensity was kept at 10 mW/cm^2, which was measured by an International Light. Inc., model IL 1400A radiometer. By measuring IR peak area decreasing at 3100 cm^{-1} and 2560 cm^{-1}, real-time functional group conversion of vinyl and thiol group was monitored, and the conversion was calculated by the ratio of peak area to the peak area of the initial spectra.

2.3. DMA

Polymer network properties were tested using a TA Instruments Q800 dynamic mechanical analyzer in multifrequency strain mode with a sinusoidal stress of 1 Hz frequency and a heating rate of 3 °C min^{-1}. The glass transition temperature(s) (T_g) were assigned as the temperature(s) at the maxima of the tan δ curve. The rubbery moduli were determined in the rubbery region at T_g + *30 °C*. T_g half widths were taken as the widths of the tan delta peaks at half maximum values. DMA samples were prepared by injecting between two glass sides with 0.25 mm thickness spacers. The mixtures of thiols and vinyl sulfonates and vinyl sulfones were cured by using thermal initiation for 1 hr (80 °C, TEMPO, 1-2 wt. %) whereas the mixtures incorporating other vinyls

were cured photochemically with NPPOC-TMG (2 wt. %). The photopolymerization driven by photobase (NPPOC-TMG) was carried out using an Acticure 4000 light source with 320-390 nm bandpass filter. The light intensity was 50 mW/cm^2 and the duration of the irradiation was 1 hr. All samples were postcured at 100 °C for over an hour to ensure the highest conversion attainable. The samples were cut into strips with dimensions that were approximately 11 mm x 6 mm x 0.25 mm (l × w × t).

2.4. MTS

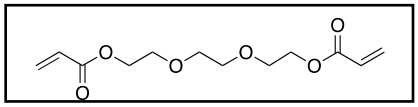
Flexural strength, Young's modulus and toughness were measured via a tensile test (MTS 858 Mini Bionix II) with a strain rate of 1 mm min^{-1} and a span of 20 mm. Samples were cured with 2 wt% TEMPO at 80^{o}C for 1 hour and postcured overnight before measurements. Dog-bone samples of the size 0.25 × 3.8 × 15 mm (t × w × l) were used. Flexural modulus was determined from the slope between 0.5 and 1% strain. Flexural strength, σ, was calculated from $\sigma = 3FL/2BH^2$, where F is the maximum load, and L, H, B are the sample dimensions. Four replicates were made for each sample.

2.5. Procedure for Hydrolytic Studies

For the evaluation of the hydrolytic degradation behavior the thiol-Michael network polymer films were prepared according to the procedure described for DMA sample preparation. Polymer films with the dimension of 11 mm x 6 mm x 0.25 mm (l × w × t) were immersed in freshly prepared 5wt% HCl or 5wt% NaOH, respectively, at room temperature. Before immersing the sample into acidic or basic conditions, the sample initial mass (M_i) was measured. Sample mass was then recorded in every 24 hr period after wiping dry the surface water by paper towel and then placing it back in the 5wt% HCl or 5wt% NaOH containing vials, respectively, for 1 week. After 7 days, the final sample mass was recorded and the change in the mass was calculated.

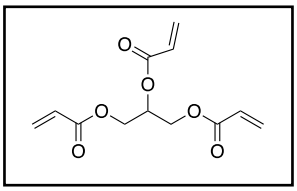
3. Synthesis of Acrylate derivatives

Triethylene glycol diacrylate (TEGDA, 2d)



To the solution of 3g (19.9 mmol) triethylene glycol in 60 mL of anhydrous DCM was added 6.1g (59.9 mmol) of Et_3N at 0^oC under nitrogen atmosphere. To the resulting solution, 2g (21.9 mmol) of acryloyl chloride in 10 mL of anhydrous DCM was added dropwise at 0^oC. After the completion of the addition, the reaction mixture was then stirred for 1 hr at room temperature under nitrogen atmosphere. The organic layer was then washed with $NaHCO_3$ followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get brown viscous liquid. The crude residue was purified by column chromatography (silica gel, Hexane/EtOAc 55:45) to obtain colorless liquid. Yield: 57%; ^1H NMR ($CDCl_3$, δppm): 6.41 (dd, J_1 = 17.33, J_2 = 1.46 Hz, 2H), 6.13 (dd, J_1 = 17.34 Hz, J_2 = 10.42 Hz, 2H), 5.82 (dd, J_1 = 1.47 Hz, J_2 = 10.41 Hz, 2H), 4.29 (t, J = 6.53 Hz, 4H), 3.72 (t, J = 6.28 Hz, 4H), 3.65 (s, 4H); ^{13}C NMR ($CDCl_3$): 63.61, 69.13, 70.57, 128.19, 130.92, 166.07; HRMS (ESI^+) m/z calcd for $C_{12}H_{18}O_6Li$ $[M+Li]^+$: 265.1264, found: 265.1264.

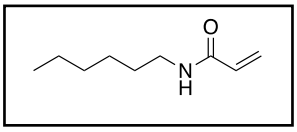
Glycerol triacrylate (GTA, 2g)



To the solution of 3g (32.5 mmol) glycerol in 60 mL of anhydrous THF was added 9.9g (97.7 mmol) of Et_3N at 0°C under nitrogen atmosphere. To the resulting solution, 3.2g (35.8 mmol) of acryloyl chloride in 10 mL of anhydrous THF was added dropwise at 0°C. After the completion of the addition, the reaction mixture was then stirred for 1 hr at room temperature under nitrogen atmosphere. The organic layer was then washed with $NaHCO_3$ followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get brown viscous liquid. The crude residue was purified by column chromatography (silica gel, Hexane/EtOAc 70:30) to obtain colorless liquid. Yield: 39.4%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.47-6.39 (m, 3H), 6.18-6.08 (m, 3H), 5.91-5.85 (m, 3H), 5.43 (m, 1H), 4.44 (dd, J_1 = 12.00 Hz, J_2 = 4.36 Hz, 2H), 4.34 (dd, J_1 = 11.99 Hz, J_2 = 5.88 Hz, 2H); ^{13}C NMR ($CDCl_3$): 62.31, 69.14, 127.66, 127.73, 131.71, 131.91, 165.09, 165.51; HRMS (ESI$^+$) m/z calcd for $C_{12}H_{14}O_6Li$ $[M+Li]^+$: 261.0951, found: 261.0953.

4. Synthesis of Acrylamide derivative

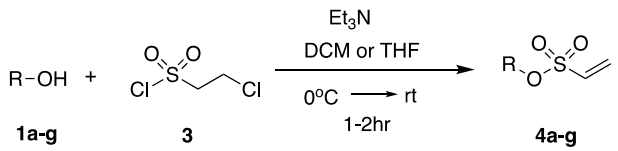
N-Hexyl-2-propenamide (HAA, 6a)



To the solution of 2g (19.7 mmol) 1-hexylamine in 60 mL of anhydrous DCM was added 6g (59.3 mmol) of Et_3N at 0°C under nitrogen atmosphere. To the resulting solution, 1.96 g (21.7 mmol) of acryloyl chloride in 10 mL of anhydrous DCM was added dropwise at 0°C. After the completion of the addition, the reaction mixture was then stirred for 1 hr at room temperature under nitrogen atmosphere. The organic layer was then washed with 1M HCl solution, followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get brown viscous liquid. The crude residue was purified by column chromatography (silica gel, Hexane/EtOAc 1:1) to obtain pale yellow liquid. Yield: 84%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.29 (dd, J_1 = 16.95 Hz, J_2 = 1.5 Hz, 1H), 6.09 (dd, J_1 = 16.51 Hz, J_2 = 10.25 Hz, 1H), 5.65 (dd, J_1 = 10.26, J_2 = 1.49 Hz, 1H), 3.35 (m, 2H), 1.55(m, 2H), 1.40-1.27(m, 6H), 0.91(t, J = 6.84, 3H);^{13}C NMR ($CDCl_3$): 13.96, 22.51, 26.62, 29.45, 31.47, 39.63, 125.69, 131.20, 165.79; HRMS (ESI$^-$) m/z calcd for $C_9H_{16}NO$ $[M-H]^{-\cdot}$: 154.1232, found: 154.1232.

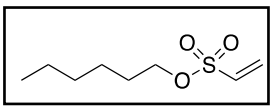
5. Synthesis of Multifunctional Vinyl Sulfonates

General Procedure for the Synthesis of Vinyl Sulfonate derivatives[3] (4a-4f):



To the solution of 1 mmol alcohol (1a-f) in 40 mL of anhydrous DCM was added Et_3N (3 mmol) at 0°C under nitrogen atmosphere. To the resulting solution, 2-chloroethane sulfonyl chloride (1.1 mmol) in 10 mL of anhydrous DCM was added dropwise at 0°C. After the completion of the addition, the reaction mixture was then stirred for 1 hr at room temperature under nitrogen atmosphere. The organic layer was then washed with $NaHCO_3$ followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get brown viscous liquid. The crude residue was purified by column chromatography to afford the corresponding vinyl sulfonate derivatives 4a-4f.

N-Hexyl vinyl sulfonate (HVS, 4a)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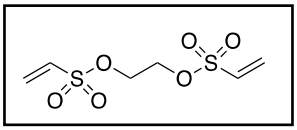
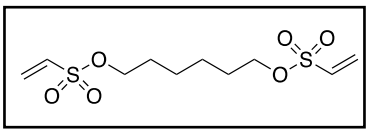
Obtained according to the general procedure from 1-Hexanol as a pale-yellow liquid after column chromatography (silica gel, Hexane/EtOAc 55:45); Yield: 49%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.53 (dd, J_1 = 16.66 Hz, J_2 = 9.83 Hz, 1H), 6.40 (d, J = 16.68, Hz, 1H), 6.11 (d, J = 9.84 Hz, 1H), 4.10 (t, J = 6.78 Hz, 2H), 1.71 (m, 2H), 1.42-1.24(m, 6H), 0.88 (t, J = 7.28 Hz, 3H); ^{13}C NMR ($CDCl_3$): 13.91, 22.40, 25.04, 28.89, 31.14, 71.10, 130.02, 132.49; Elemental analysis calcd (%) for $C_8H_{16}O_3S$: calcd(%): C, 49.97; H, 8.39; S, 16.67; found: C, 50.24; H, 8.52; S, 16.70.

Ethylene glycol di(vinyl sulfonate) (EGDVS, 4b)



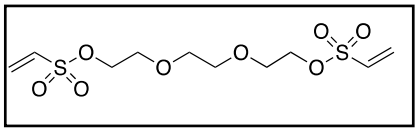
Obtained according to the general procedure from ethylene glycol as a pale-yellow liquid after column chromatography (silica gel, Hexane/EtOAc 85:15); Yield: 37%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.58 (dd, J_1 = 16.60 Hz, J_2 = 9.80 Hz, 2H), 6.44 (d, J = 16.61 Hz, 2H), 6.21 (d, J = 9.80 Hz, 2H), 4.34 (s, 4H); ^{13}C NMR ($CDCl_3$): 67.40, 131.42, 131.92; HRMS (ESI^+) m/z calcd for $C_6H_{11}O_6S_2$ $[M+H]^+$: 242.9997, found: 242.9998.

1,6-Hexanediol di(vinyl sulfonate) (HDDVS, 4c)



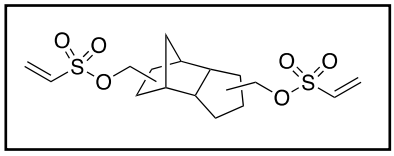
Obtained according to the general procedure from 1,6-Hexandiol as a pale-yellow liquid after column chromatography (silica gel, Hexane/EtOAc 50:50); Yield: 73%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.56 (dd, J_1 = 16.67 Hz, J_2 = 9.77 Hz, 2H), 6.44 (d, J = 16.67 Hz, 2H), 6.16 (d, J = 9.75 Hz, 2H), 4.14 (t, J = 6.78 Hz, 4H), 1.81-1.68 (m, 4H), 1.51-1.39 (m, 4H); ^{13}C NMR ($CDCl_3$): 24.88, 28.75, 70.64, 130.29, 132.40; Elemental analysis calcd (%) for $C_{10}H_{18}O_6S_2$: calcd(%): C, 40.26; H, 6.08; S, 21.49; found: C, 40.25; H, 5.95; S, 21.72.

Triethylene glycol di(vinyl sulfonate) (TEGDVS, 4d)



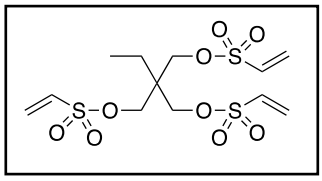
Obtained according to the general procedure from triethylene glycol as a pale-yellow liquid after column chromatography (silica gel, Hexane/EtOAc 40:60); Yield: 33%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.59 (dd, J_1 = 16.65 Hz, J_2 = 9.93 Hz, 2H), 6.39 (d, J = 16.65 Hz, 2H), 6.14 (d, J = 10.20 Hz, 2H), 4.24 (m, 4H), 3.74 (m, 4H), 3.65 (s, 4H); ^{13}C NMR ($CDCl_3$): 68.76, 69.71, 70.63, 130.37, 132.44; HRMS (ESI^+) m/z calcd for $C_{10}H_{18}O_8S_2Li$ $[M+Li]^+$: 337.0603, found: 337.0602.

Tricyclo[5.2.1.0^{2,6}]decane-4,8-dimethanol di(vinyl sulfonate) (TCDDVS, 4e)



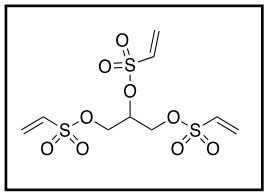
Obtained according to the general procedure from Tricyclo[5.2.1.$0^{2,6}$]decane-4,8-dimethanol, mixture of isomers as a pale-yellow viscous liquid after column chromatography (silica gel, Hexane/EtOAc 50:50); Yield: 49%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.59-6.48 (m), 6.44 (d, J = 16.67 Hz), 6.16 (d, J = 9.75 Hz), 4.14-3.76 (m), 2.59-2.04 (m), 1.86-1.36 (m), 0.94(m).

Trimethylolpropane tri(vinyl sulfonate) (TMPTVS, 4f)



Obtained according to the general procedure from 1,1,1-Tris(hydroxymethyl)propane as a pale-yellow liquid after column chromatography (silica gel, Hexane/EtOAc 35:65); Yield: 47%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.57 (dd, J_1 = 16.59 Hz, J_2 = 9.62 Hz, 3H), 6.46 (d, J = 16.62 Hz, 3H), 6.24 (d, J = 9.63 Hz, 3H), 4.02 (s, 6H), 1.56 (q, J_1 = 15.31 Hz, J_2 = 23.42 Hz, 2H), 0.94 (t, J = 8.66 Hz, 3H); ^{13}C NMR ($CDCl_3$): 6.90, 21.69, 42.07, 67.89, 131.52, 131.84; HRMS(ESI$^+$) m/z calcd for $C_{12}H_{20}O_9S_3Li$ $[M+Li]^+$: 411.0430, found: 411.0432.

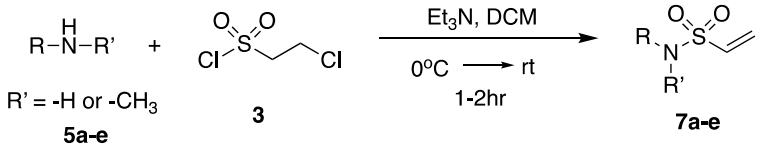
Glycerol tri(vinyl sulfonate) (GTVS, 4g)



To the solution of 3g (32.5 mmol) glycerol in 60 mL of anhydrous THF was added 9.8g (97.7 mmol) of Et_3N at 0°C under nitrogen atmosphere. To the resulting solution, 5.8g (35.8 mmol) of 2-chloroethane sulfonyl chloride in 10 mL of anhydrous THF was added dropwise at 0°C. After the completion of the addition, the reaction mixture was then stirred for 1 hr at room temperature under nitrogen atmosphere. The organic layer was then washed with $NaHCO_3$ followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get brown viscous liquid. The crude residue was purified by column chromatography (silica gel, Hexane/EtOAc 1:1) to obtain white solid. Yield: 47%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.68-6.54 (m, 3H), 6.48 (m, 3H), 6.25 (dd, J_1 = 14.66 Hz, J_2 = 9.83 Hz, 3H), 4.89 (m, 1H), 4.38-4.28 (m, 4H); ^{13}C NMR ($CDCl_3$): 67.05, 75.36, 131.50, 131.79, 132.14. Elemental analysis calcd (%) for $C_9H_{14}O_9S_3$: calcd(%): C, 29.83; H, 3.89; S, 26.54; found: C, 29.84; H, 3.92; S, 26.51.

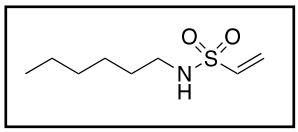
6. Synthesis of Multifunctional Vinyl Sulfonamides

General Procedure for the Synthesis of Vinyl Sulfonamide derivatives[4] (7a-7e):



To the solution of 1 mmol amine (5a-e) in 40 mL of anhydrous DCM was added Et_3N (2.1 mmol) at 0°C under nitrogen atmosphere. To the resulting solution, 2-chloroethane sulfonyl chloride (1.1 mmol) in 10 mL of anhydrous DCM was added dropwise at 0°C. After the completion of the addition, the reaction mixture was then stirred for 1 hr at room temperature under nitrogen atmosphere. The organic layer was then washed with 1M HCl solution, followed by washing with brine and water. The combined organic layer was then dried over Na_2SO_4 and concentrated at reduced pressure to get brown viscous liquid. The crude residue was purified by column chromatography to afford the corresponding vinyl sulfonamide derivatives 7a-7e.

N-Hexyl vinylsulfonamide (HVSA, 7a)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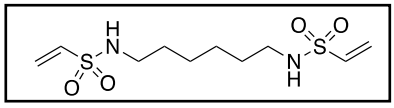
H

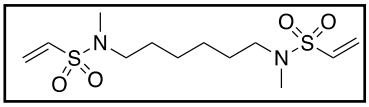
Obtained according to the general procedure from 1-Hexylamine as a pale-yellow liquid after column chromatography (silica gel, Hexane/EtOAc 40:60); Yield: 32%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.53 (dd, J_1 = 16.95 Hz, J_2 = 9.9 Hz, 1H), 6.24 (d, J = 16.56 Hz, 1H), 5.95 (d, J = 9.79 Hz, 1H), 3.01 (m, 2H), 1.55 (m, 2H), 1.40-1.21 (m, 6H), 0.88 (t, J = 6.15 Hz, 3H); ^{13}C NMR ($CDCl_3$): 13.76, 22.19, 26.11, 29.42, 31.00, 43.07, 126.31, 135.71. HRMS (ESI^+) m/z calcd for $C_8H_{18}NO_2S$ $[M + H]^+$: 192.1058, found: 192.1058.

N, N'-Hexamethylene bis(vinylsulfonamide) (HMDVSA, 7b)



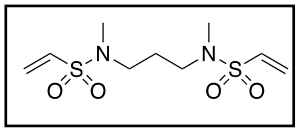
Obtained according to the general procedure from Hexamethylenediamine as a viscous pale-yellow liquid after column chromatography (silica gel, $CHCl_3$/MeOH 70:30); Yield: 38%; ^1H NMR ($CDCl_3$, δ ppm): 6.53 (dd, J_1 = 16.55 Hz, J_2 = 9.91 Hz, 2H), 6.23 (d, J = 16.57 Hz, 2H), 5.96 (d, J = 9.91 Hz, 2H), 4.85 (b, 2H), 2.99 (m, 4H), 1.64-1.48 (m, 4H), 1.44-1.30 (m, 4H); ^{13}C NMR ($CDCl_3$): 25.78, 29.56, 42.75, 126.66, 135.84; HRMS(ESI^+) m/z calcd for $C_{10}H_{20}N_2O_4S_2Li$ $[M+Li]^+$: 303.1025, found: 303.1026.

N, N'-Dimethyl-1,6-hexane di(vinyl sulfonamide) (DMHDVSA, 7c)



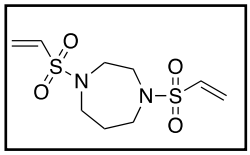
Obtained according to the general procedure from *N*,*N*′-Dimethyl-1,6-diaminohexane as a pale-yellow waxy solid after column chromatography (silica gel, Hexane/EtOAc 25:75); Yield: 51%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.40 (dd, J_1 = 16.57 Hz, J_2 = 9.94 Hz, 2H), 6.17 (d, J = 16.58 Hz, 2H), 5.96 (d, J = 9.96 Hz, 2H), 3.04 (t, J = 7.14 Hz, 4H), 2.74(s, 6H), 1.62-1.47 (m, 4H), 1.40-1.27 (m, 4H); ^{13}C NMR ($CDCl_3$): 25.93, 27.67, 34.36, 49.72, 127.42, 132.94; HRMS (ESI^+) m/z calcd for $C_{12}H_{25}N_2O_4S_2$ $[M+H]^+$: 325.1256, found: 325.1255.

N, N'-Dimethyl-1,3-propane di(vinyl sulfonamide) (DMPDVSA, 7d)



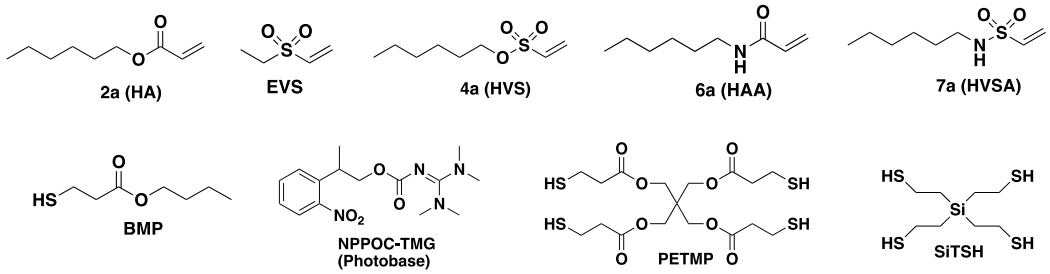
Obtained according to the general procedure from *N*,*N*′-Dimethyl-1,3-propanediamine as a pale-yellow solid after column chromatography (silica gel, Hexane/EtOAc 20:80); Yield: 42%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.43 (dd, J_1 = 16.57 Hz, J_2 = 9.93 Hz, 2H), 6.21 (d, J = 16.57 Hz, 2H), 6.01 (d, J = 9.94 Hz, 2H), 3.13 (t, J = 6.99 Hz, 4H), 2.80 (s, 6H), 1.90 (m, 2H); ^{13}C NMR ($CDCl_3$): 26.89, 34.98, 47.52, 128.01, 132.45; HRMS (ESI^+) m/z calcd for $C_9H_{19}N_2O_4S_2$ $[M + H]^+$: 283.0786, found: 283.0783.

Homopiperazine-1,4-bis(vinyl sulfonamide) (HPVSA, 7e)

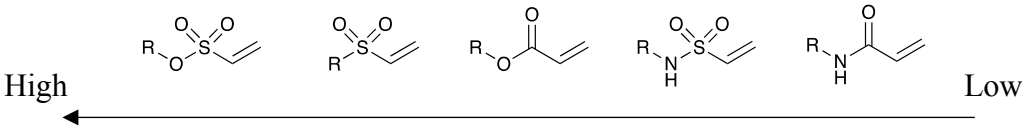


Obtained according to the general procedure from Homopiperazine as a pale-yellow solid after column chromatography (silica gel, Hexane/EtOAc 40:60); Yield: 18%; ^{1}H NMR ($CDCl_3$, δ ppm): 6.47 (dd, J_1 = 16.50 Hz, J_2 = 9.90 Hz, 2H), 6.21 (d, J = 16.51 Hz, 2H), 5.96 (d, J = 9.89 Hz, 2H), 3.44 (t, J = 6.22 Hz, 4H), 3.42 (s, 4H), 1.99 (m, 2H); ^{13}C NMR ($CDCl_3$): 29.63, 47.23, 50.92, 126.88, 134.17; HRMS (ESI$^+$) m/z calcd for $C_9H_{17}N_2O_4S_2$ $[M+H]^+$: 281.0630, found: 281.0624.

7. Model Compounds for Reactivity Study, Photobase and thiols used for network polymer



8. Relative Reactivity



9. Reaction Kinetics of Dimethyl Hexyl Vinyl Sulfonamide

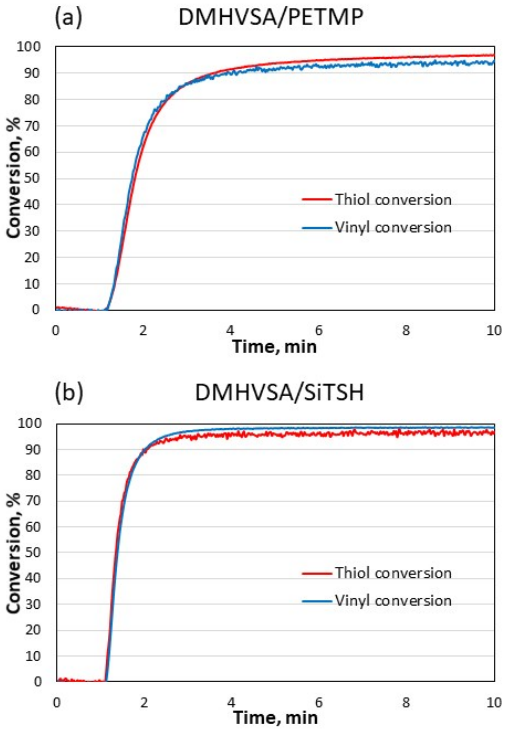


Fig. S1 Reaction kinetics of dimethyl hexyl vinyl sulfonamide (DMHVSA) with (a) PETMP and (b) SiTSH. Curing conditions: 50 mW/cm^2 UV light in the range of 320-390 nm with 1 wt. % of NPPOC-TMG as photobase catalyst.

10. Reaction Kinetics of Crosslinking Polymerization

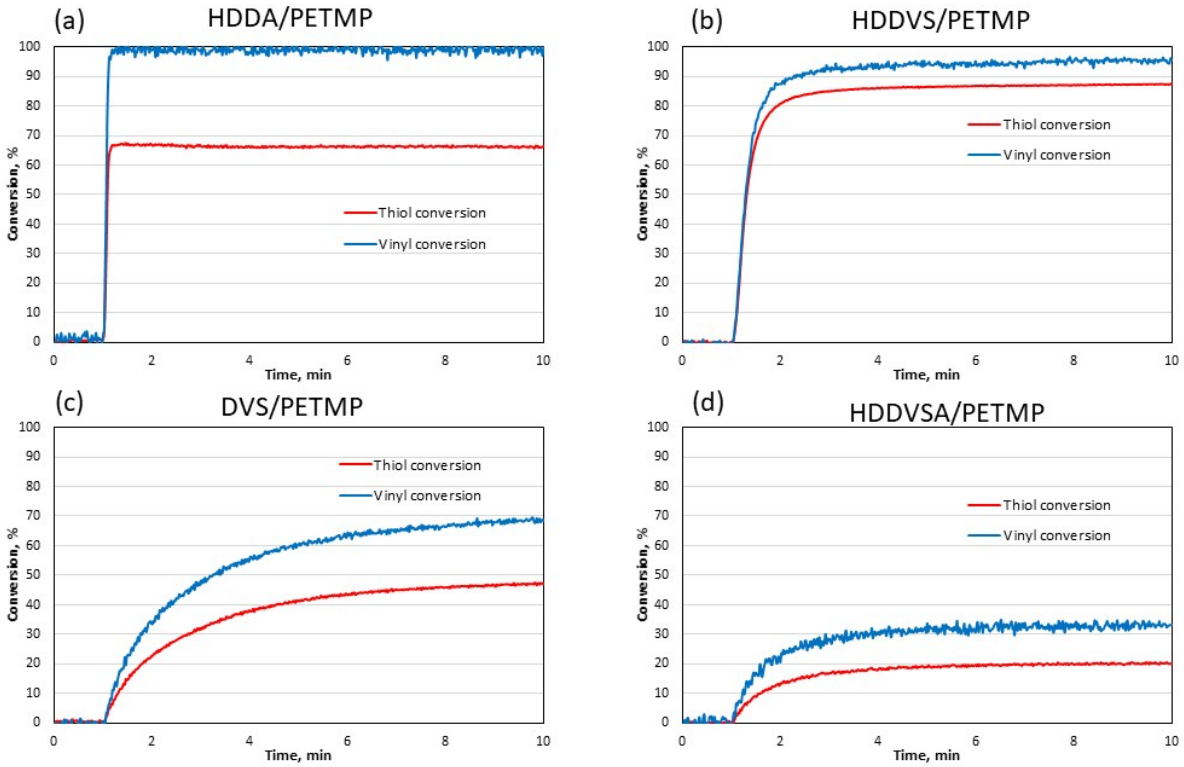
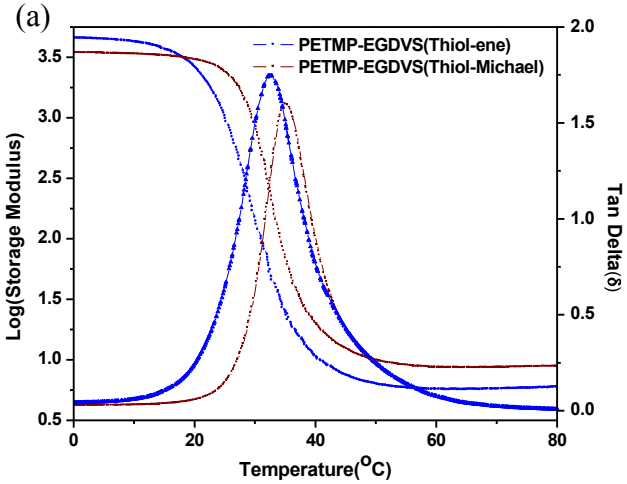


Fig. S2 Reaction kinetics of a series of divinyl-PETMP crosslinking polymerizations: (a) diacrylate HDDA/PETMP; (b) divinyl sulfonate/PETMP; (c) divinyl sulfone/PETMP; (d) divinyl sulfonamide/PETMP. The systems in a, b and c were cured with 20 mW/cm^2 UV light in the range of 320-390 nm with 0.2 wt. % of DMPA as radical photoinitiator. The system in d was cured with 100 mW/cm^2 UV light in the range of 320-390 nm with 0.5 wt. % of DMPA.

11. DMA

(a)


PETMP-EGDVS(Thiol-ene)
PETMP-EGDVS(Thiol-Michael)
Log(Storage Modulus)
Tan Delta(δ)
Temperature(°C)

(b)

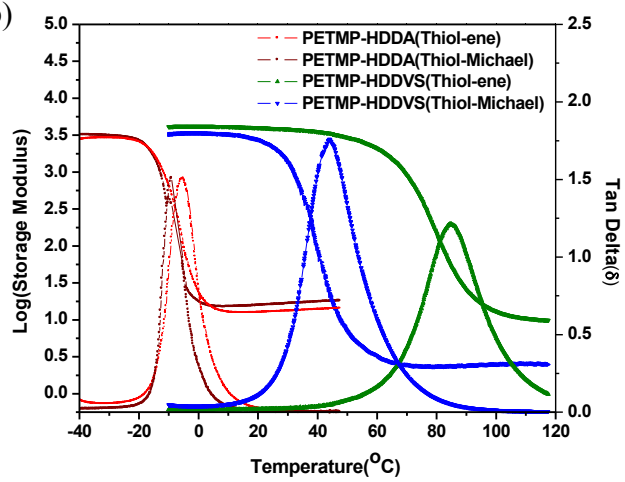

PETMP-HDDA(Thiol-ene)
PETMP-HDDA(Thiol-Michael)
PETMP-HDDVS(Thiol-ene)
PETMP-HDDVS(Thiol-Michael)
Log(Storage Modulus)
Tan Delta(δ)
Temperature(°C)

Fig. S3 Storage modulus and tan delta plots for neat network polymer with PETMP as thiol monomer (a) Thiol Michael network and Thiol-ene network polymer of thiol-vinylsulfonate (PETMP/EGDVS). (b) Comparison of Thiol Michael network and Thiol-ene network polymer of thiol-acrylate and thiol-vinylsulfonate (PETMP/HDDA) and (PETMP/HDDVS). The monomer ratios are: thiol:vinyl = 1:1 based on the functional group content.

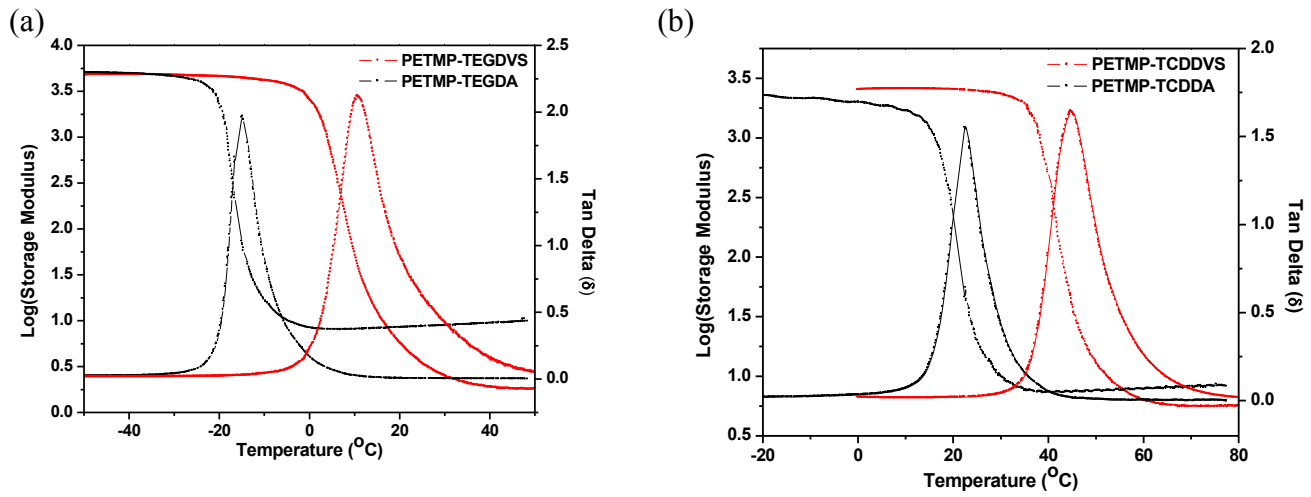


Fig. S4 Storage modulus and tan delta plots for neat network polymer (a) Comparison of Thiol Michael network polymer of thiol- vinylsulfonate (PETMP/TEGDVS) and thiol-acrylate (PETMP/TEGDA). (b) Comparison of Thiol Michael network polymer of thiol-vinylsulfonate (PETMP/TCDDVS) and thiol-acrylate (PETMP/TCDDA). The monomer ratios are: thiol:vinyl = 1:1 based on the functional group content.

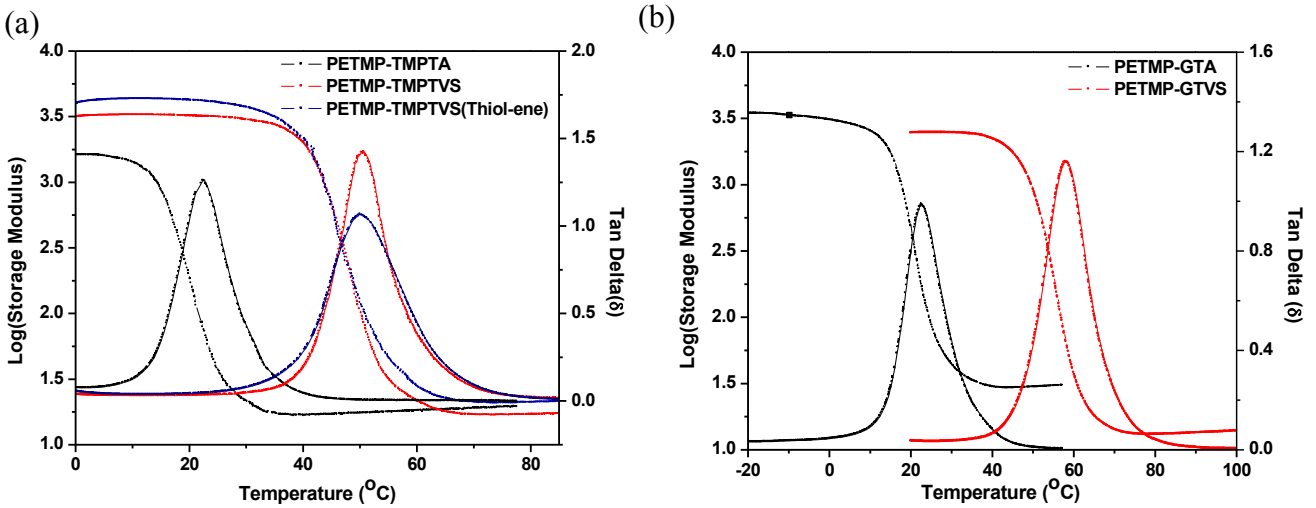


Fig. S5 Storage modulus and tan delta plots for neat (a) Comparison of Thiol michael network polymer of thiol-acrylate (PETMP/TMPTA) and thiol-vinyl sulfonate (PETMP/TMPTVS) and thiol-ene network polymer of (PETMP/TMPTVS). (b) Comparison of Thiol Michael network polymer of thiol-acrylate (PETMP/GTA) and thiol-vinylsulfonate (PETMP/GTVS). The monomer ratios are: thiol:vinyl = 1:1 based on the functional group content.

Resin System	T_g (°C)	Rubbery Modulus (MPa)
EGDA/PETMP	-5.1(0.8)	5(0)
HDDA/PETMP	-9(0)	15(0)
TEGDA/PETMP	-15.7(0.8)	9(0.7)
TCDDA/PETMP	22(1)	7(0.01)
TMPTA/PETMP	22.4(0)	17(0.4)
GTA/PETMP	23(2)	30(0.06)
EGDVS/PETMP	35(2)	8(0.07)
HDDVS/PETMP	43(3)	2(0.1)
TEGDVS/PETMP	11(0.8)	2(0.06)
TCDDVS/PETMP	45(0.7)	6(0.05)
TMPTVS/PETMP	50(2)	17(0.2)
GTVS/PETMP	58(3)	13(0.3)
HMDVSA/PETMP	46(3)	16(0.05)
HMDVSA/SiTSH	58(6)	17(0.2)
DMHDVSA/PETMP	34(1)	8(0.3)
DMHDVSA/SiTSH	29(3)	11(0)
DMPDVSA/SiTSH	57(0.6)	18(0.1)
HPDVSA/SiTSH	95(0.3)	17(0.4)

12. MTS

Resin System	Young's Modulus (GPa)	Toughness (J/m^3)	Stress@break (MPa)	Stress@break (%)
GTVS/PETMP	0.58(0.07)	0.6(0.2)	19(2)	4.5(0.3)
TCDDVS/PETMP	0.37(0.06)	11(3)	15(5)	94(11)
DMPDVSA/SiTSH	0.47(0.09)	4(1)	14(4)	27(3)

13. NMR Spectra

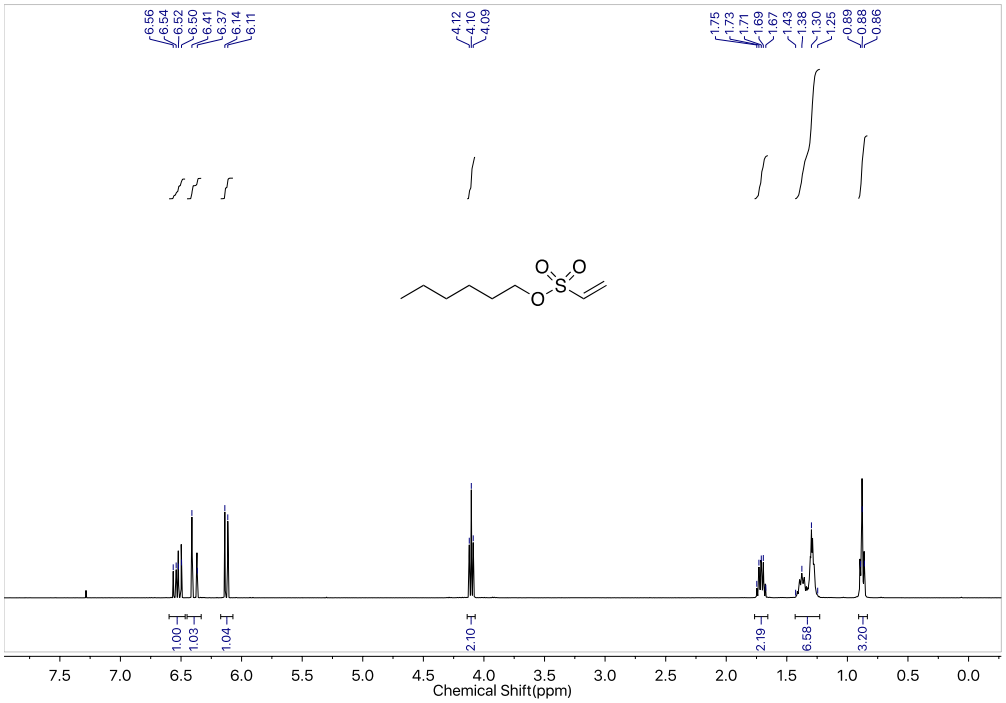


Fig. S6 [1]H NMR of N-Hexyl vinyl sulfonate

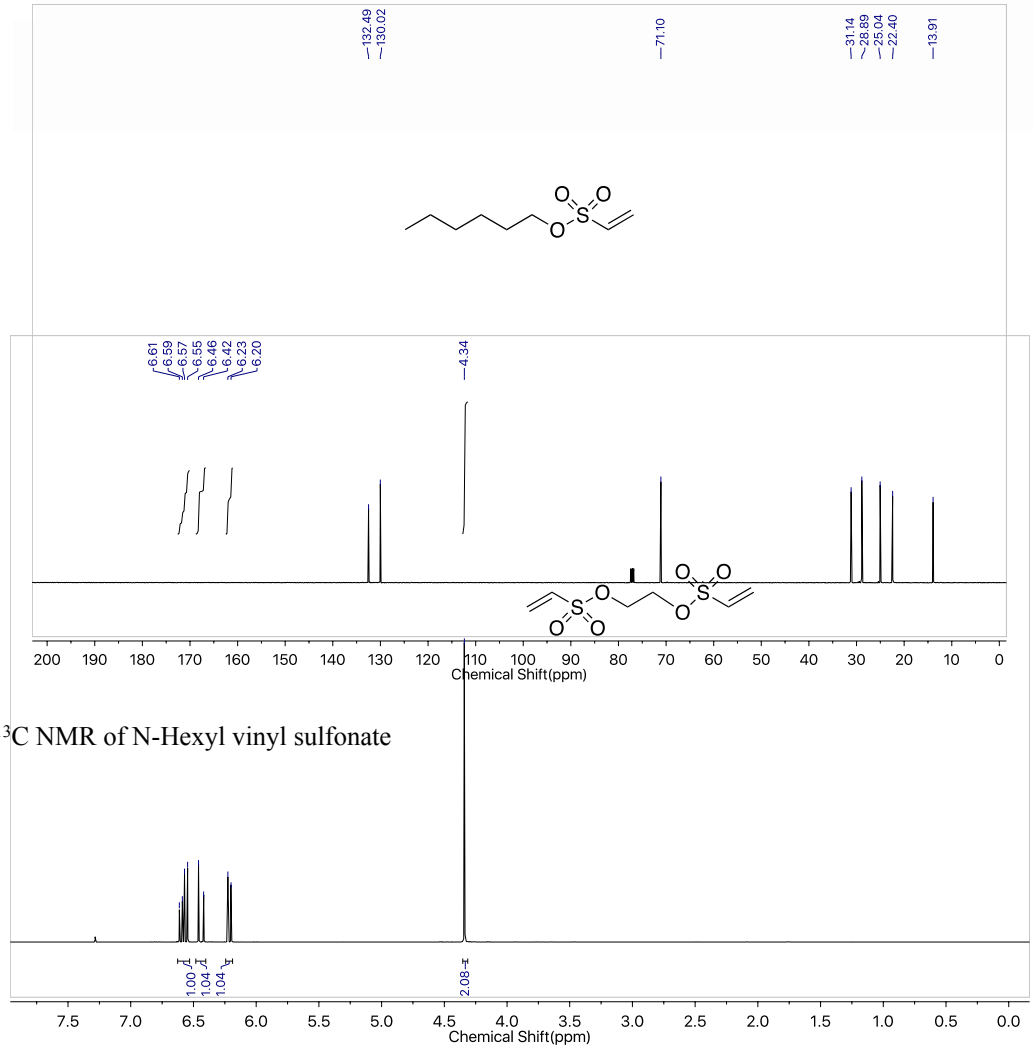


Fig. S7 [13]C NMR of N-Hexyl vinyl sulfonate

Fig. S8 ^{1}H NMR of Ethylene glycol di(vinyl sulfonate)

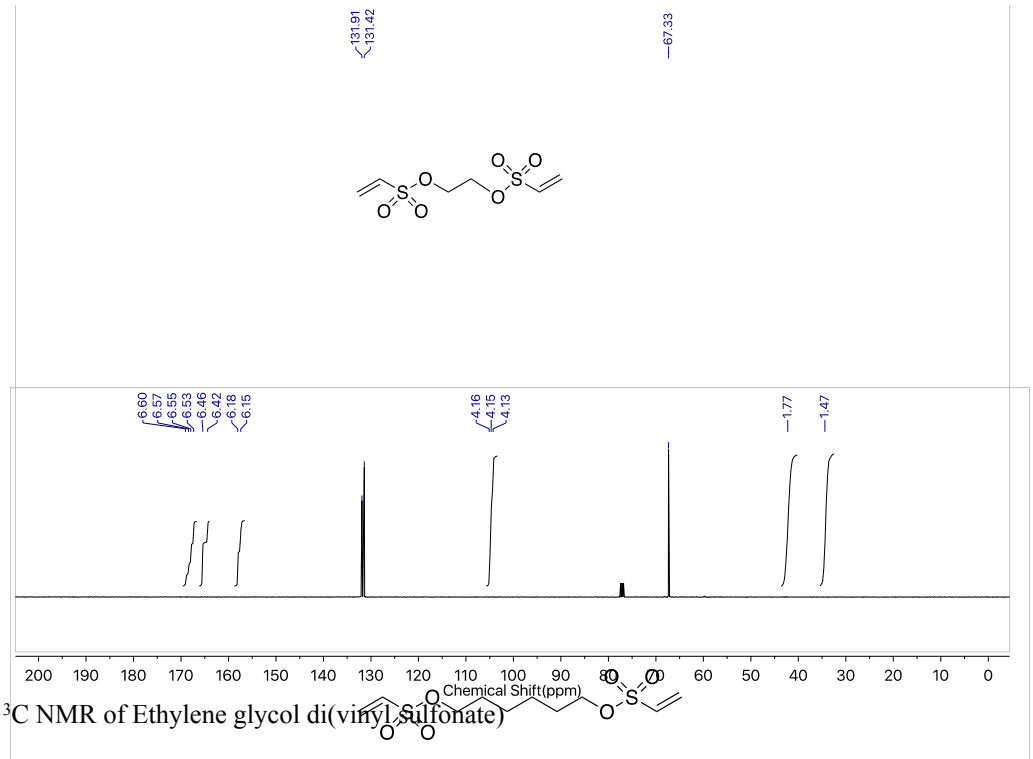


Fig. S9 ^{13}C NMR of Ethylene glycol di(vinyl sulfonate)

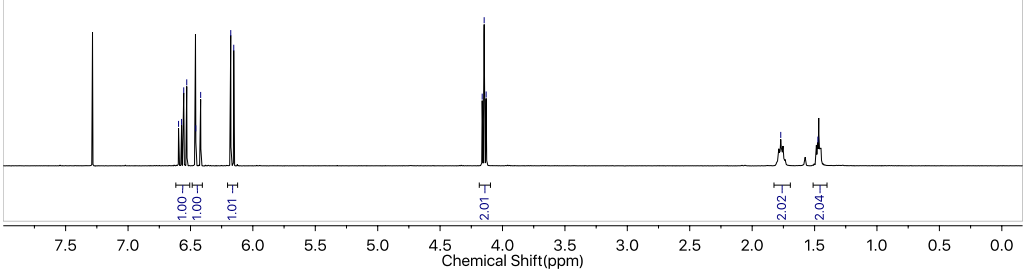


Fig. S10 [1]H NMR of 1,6-Hexanediol di(vinyl sulfonate)

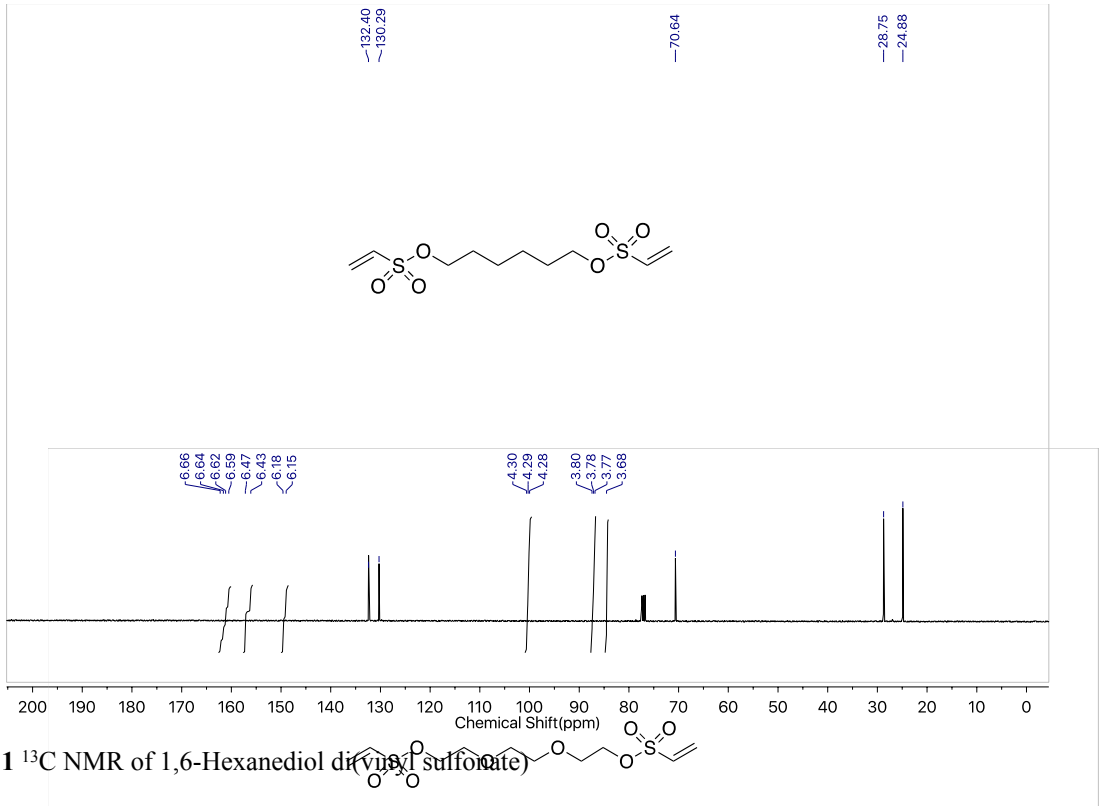


Fig. S11 [13]C NMR of 1,6-Hexanediol di(vinyl sulfonate)

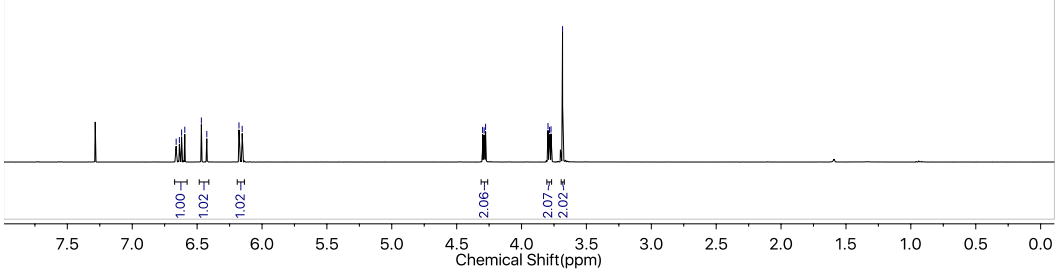


Fig. S12 [1]H NMR of Triethylene glycol di(vinyl sulfonate)

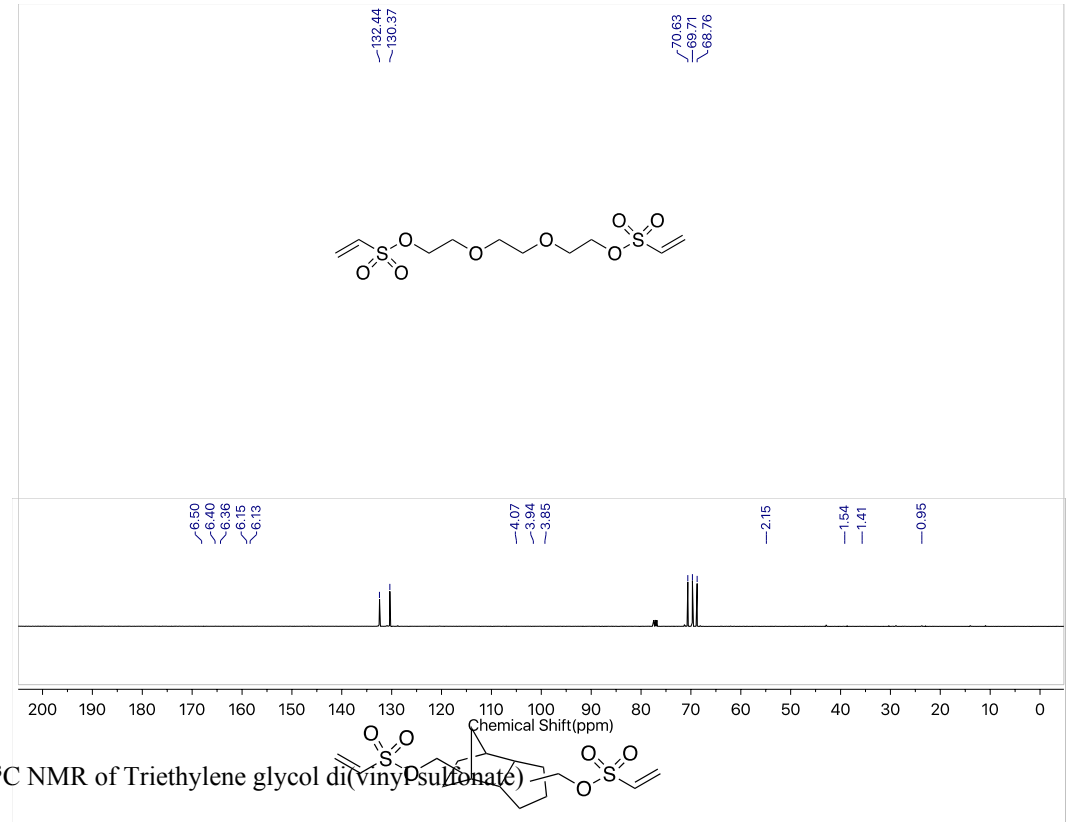


Fig. S13 [13]C NMR of Triethylene glycol di(vinyl sulfonate)

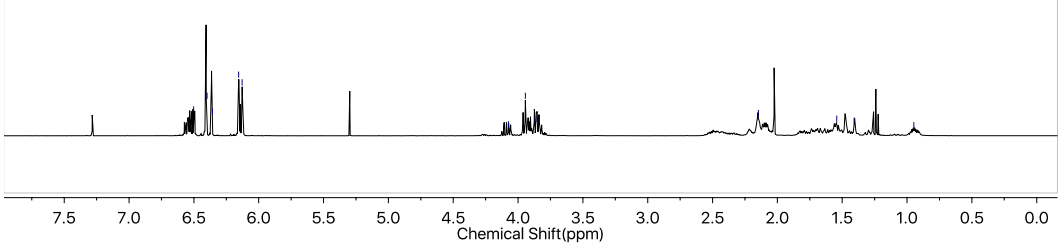


Fig. S14 [1]H NMR of Tricyclo[5.2.1.0^{2,6}]decane-4,8-dimethanol di(vinyl sulfonate)

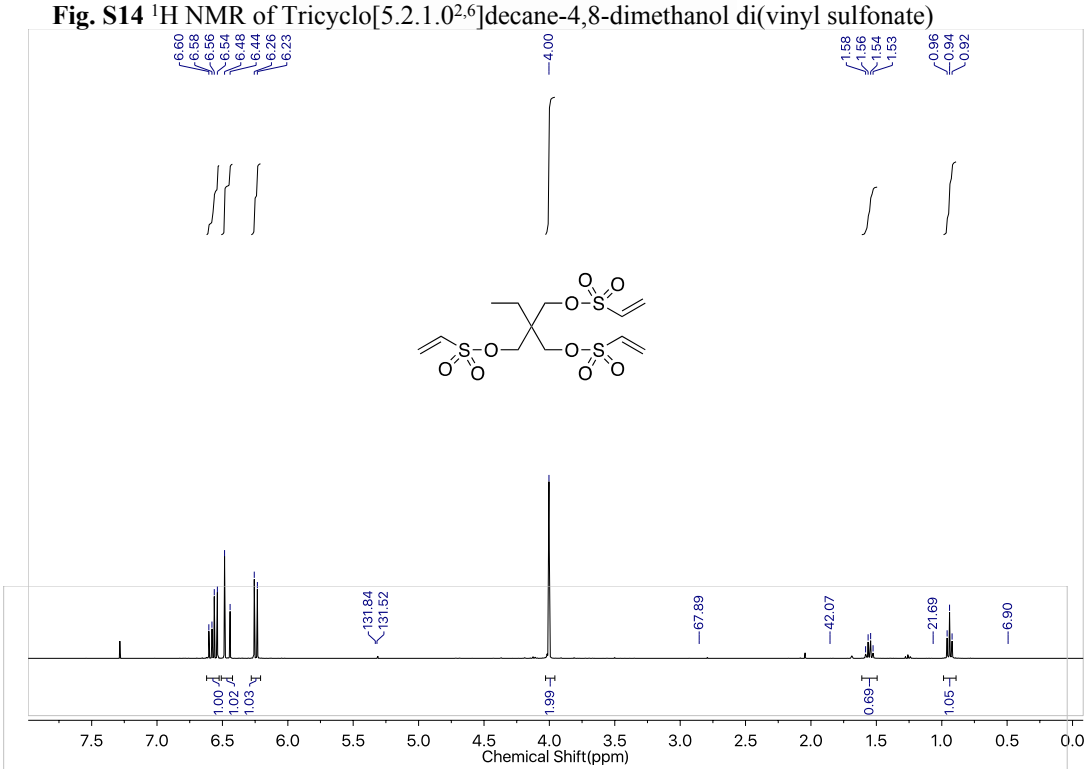


Fig. S15 [1]H NMR of Trimethylolpropane tri(vinyl sulfonate)

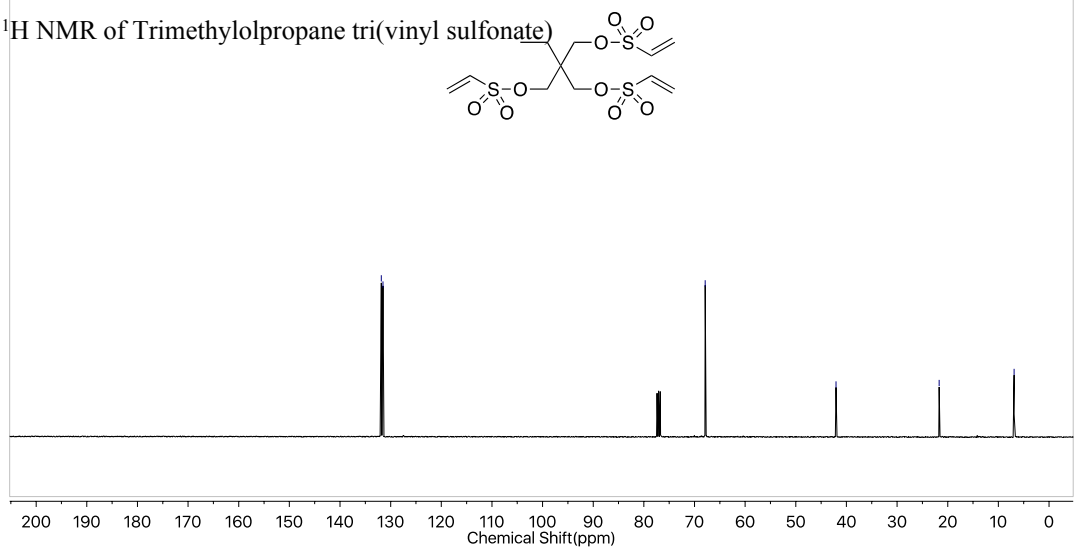


Fig. S16 ^{13}C NMR of Trimethylolpropane tri(vinyl sulfonate)

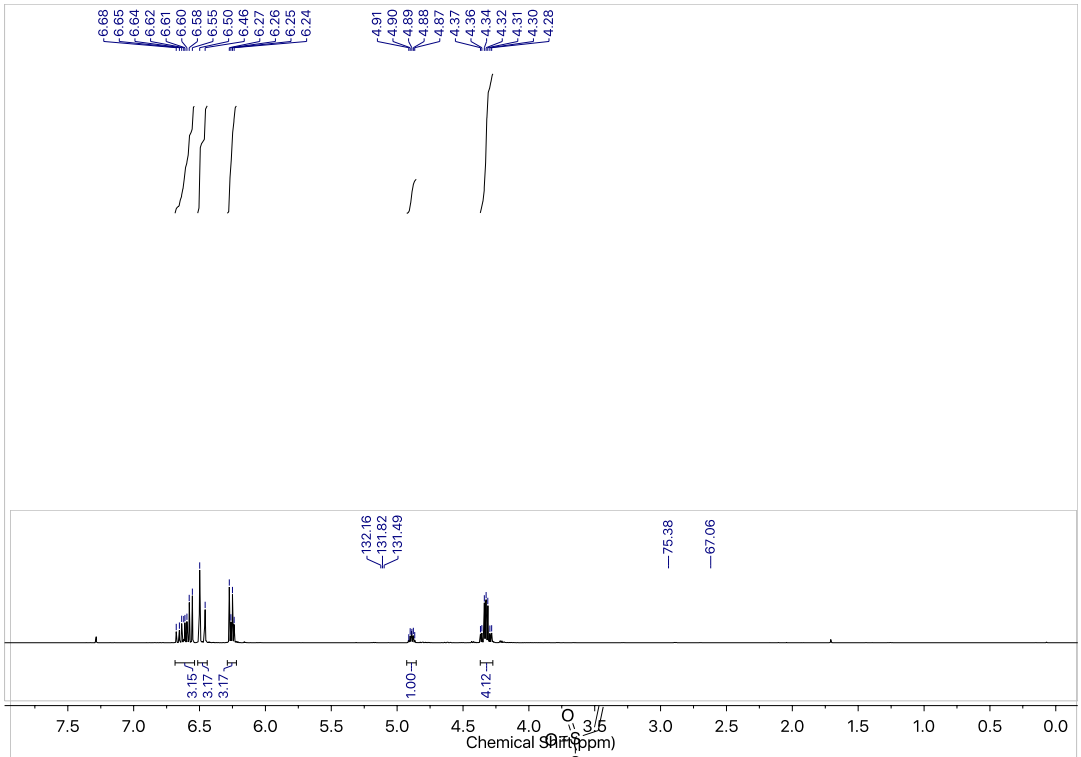


Fig. S17 ^{1}H NMR of Glycerol tri(vinyl sulfonate)

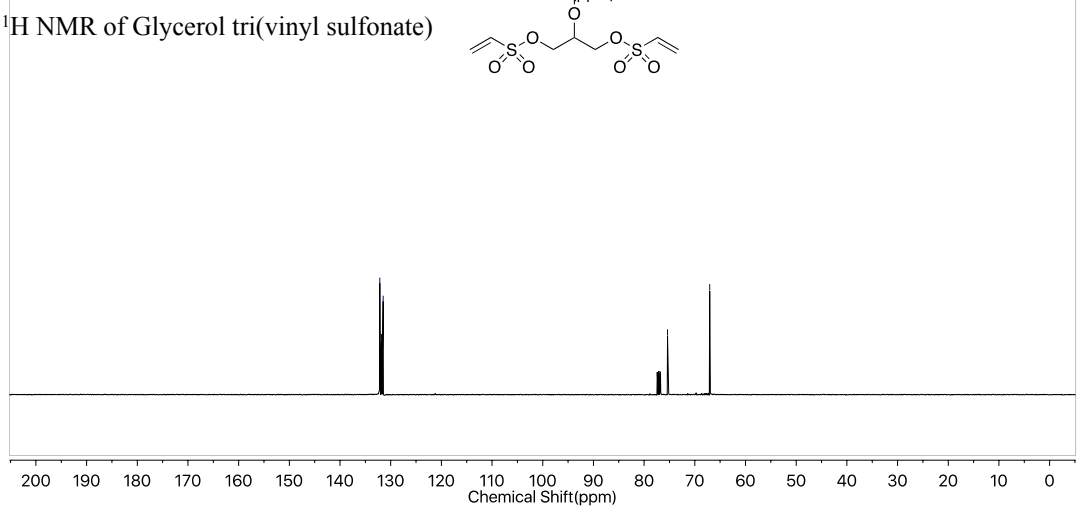


Fig. S18 ^{13}C NMR of Glycerol tri(vinyl sulfonate)

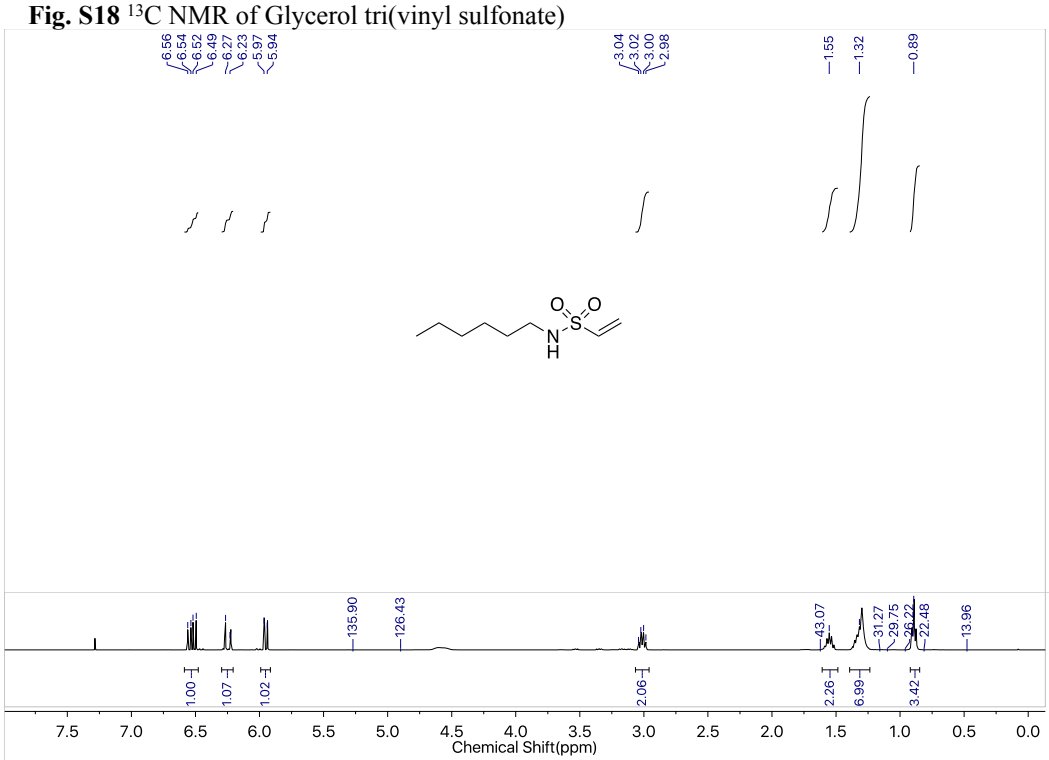


Fig. S19 ^{1}H NMR of N-Hexyl vinyl sulfonamide

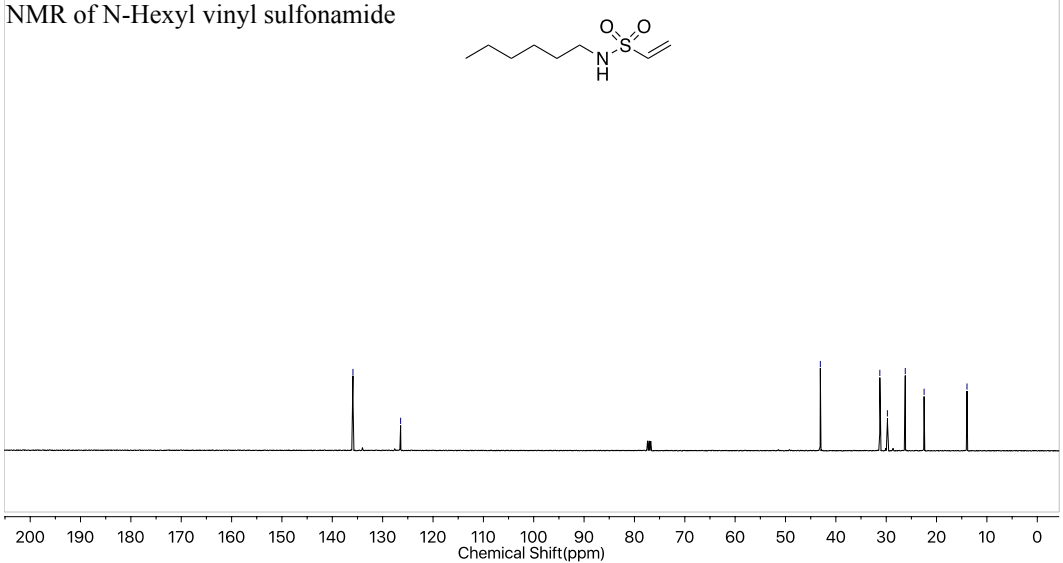


Fig. S20 ^{13}C NMR of N-Hexyl vinyl sulfonamide

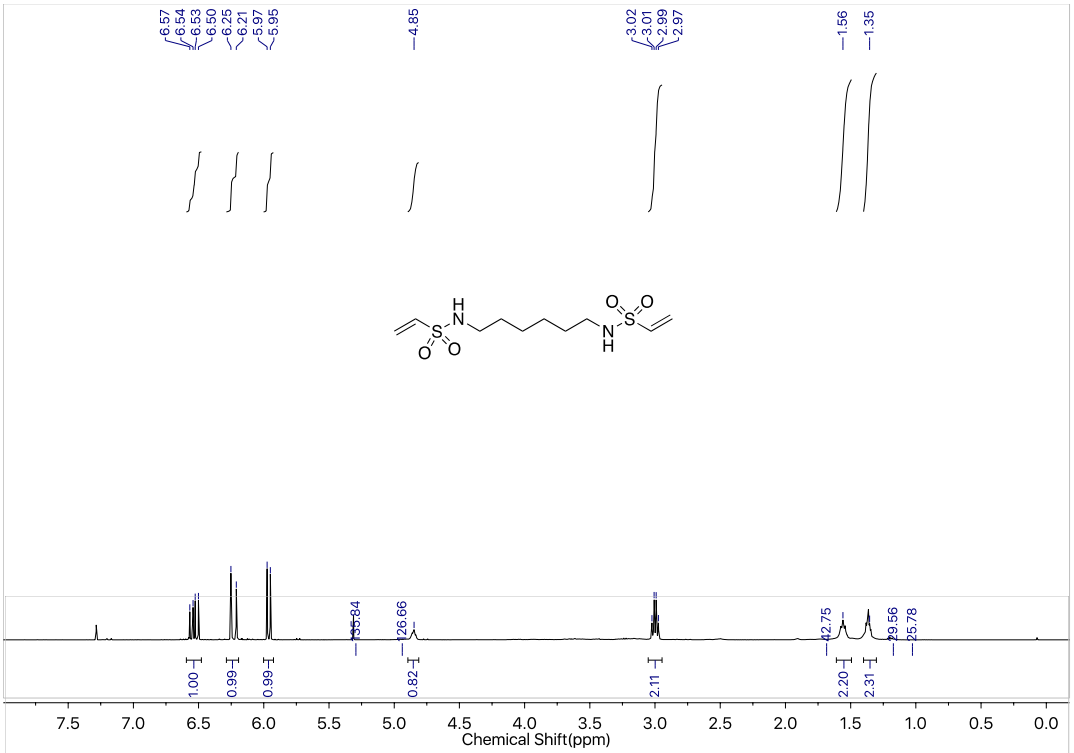


Fig. S21 ^{1}H NMR of *N*,*N*'-Hexamethylene bis(vinyl sulfonamide)

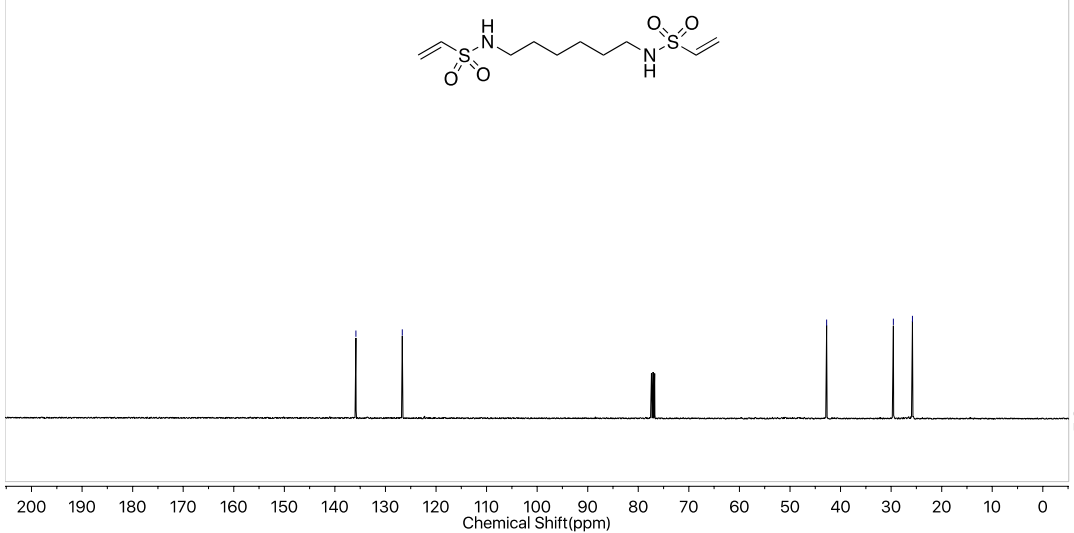


Fig. S22 ^{13}C NMR of *N*,*N*'-Hexamethylene bis(vinyl sulfonamide)

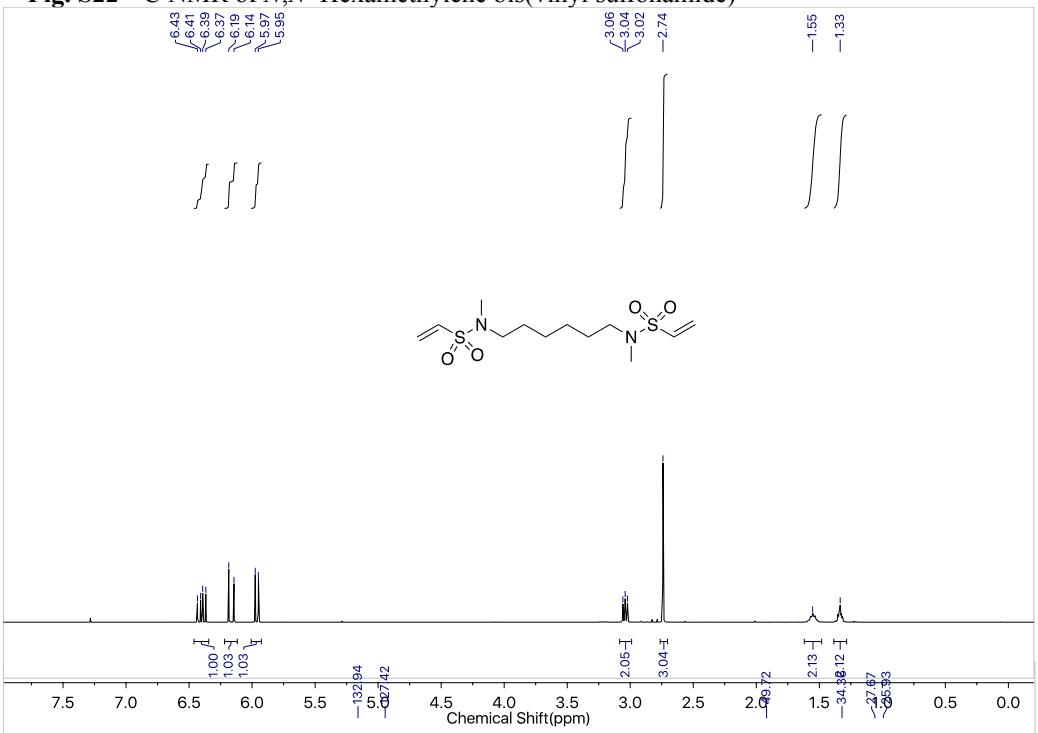


Fig. S23 ^{1}H NMR of N, N'-Dimethyl-1,6-hexane di(vinyl sulfonamide)

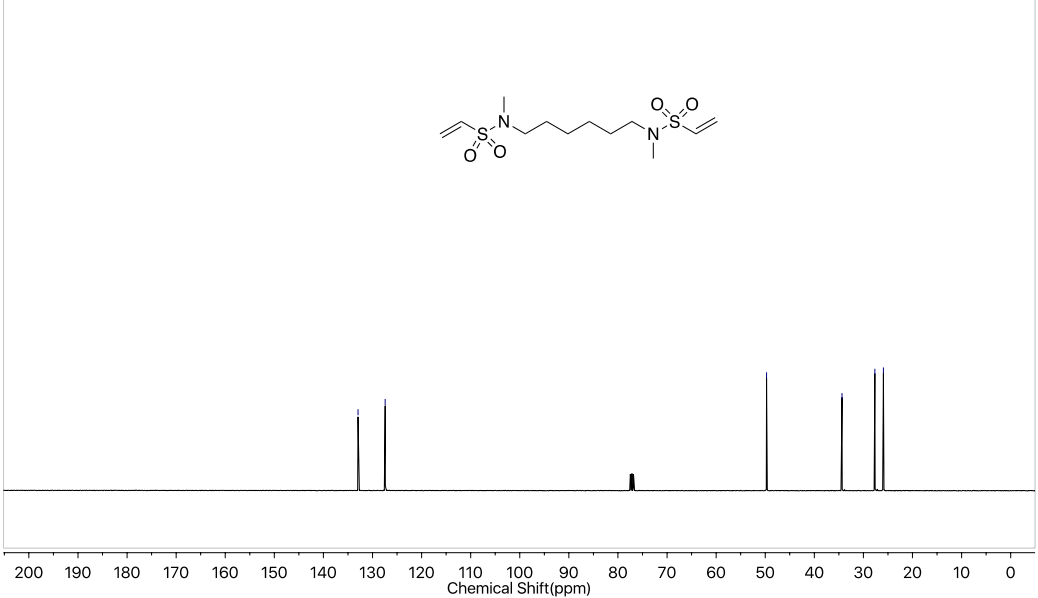


Fig. S24 ^{13}C NMR of N, N'-Dimethyl-1,6-hexane di(vinyl sulfonamide)

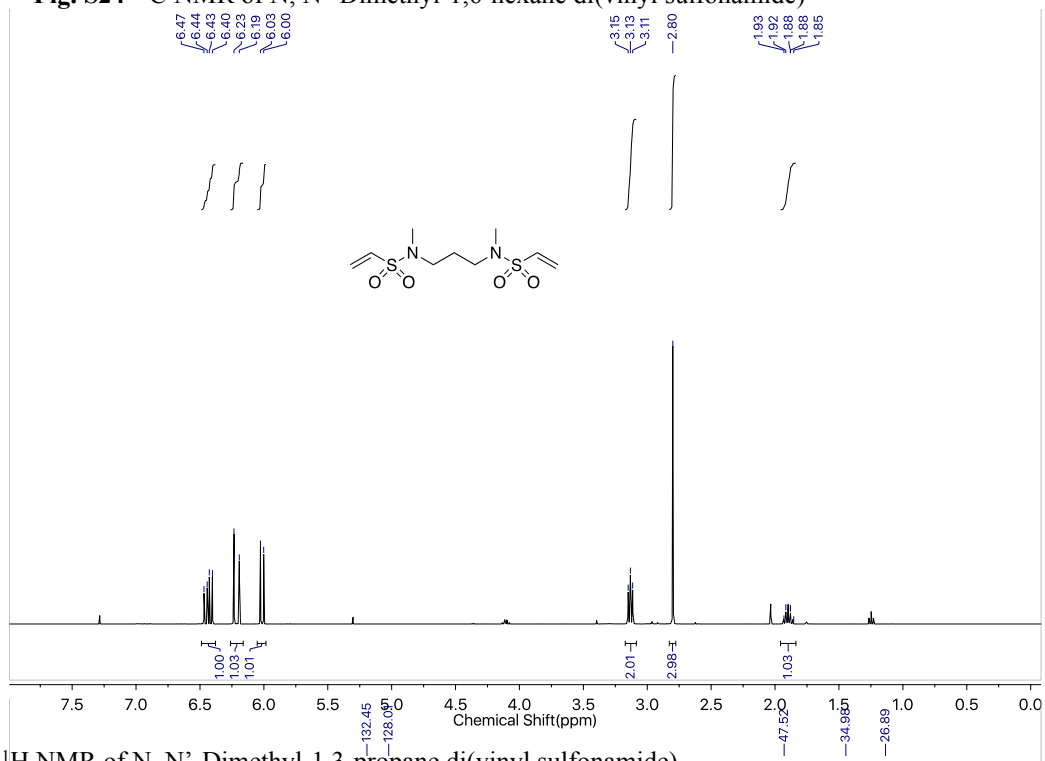


Fig. S25 ^{1}H NMR of N, N'-Dimethyl-1,3-propane di(vinyl sulfonamide)

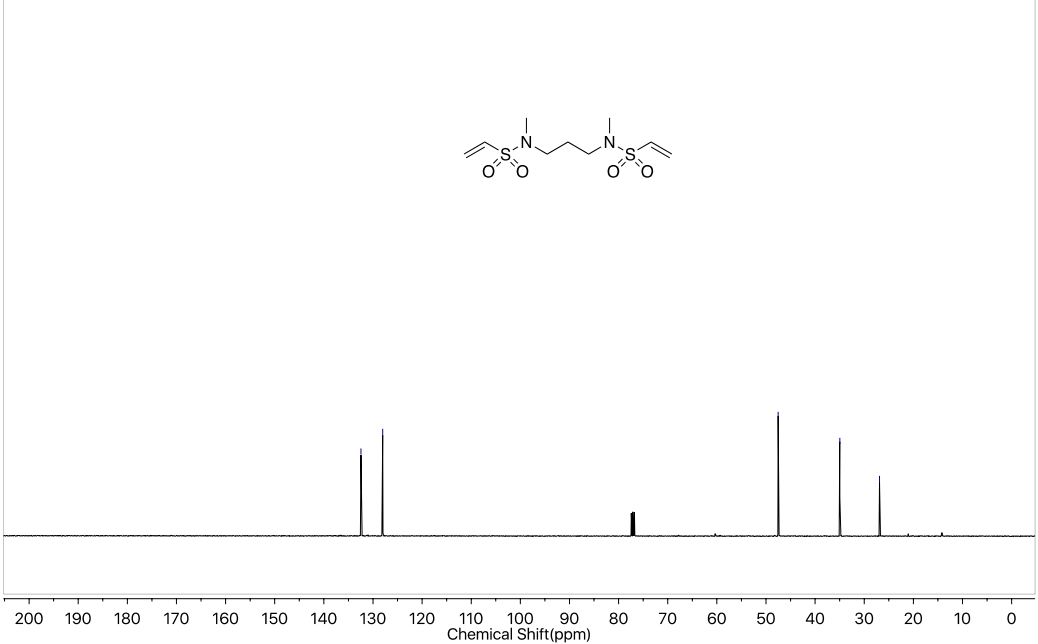


Fig. S26 ^{13}C NMR of N, N'-Dimethyl-1,3-propane di(vinyl sulfonamide)

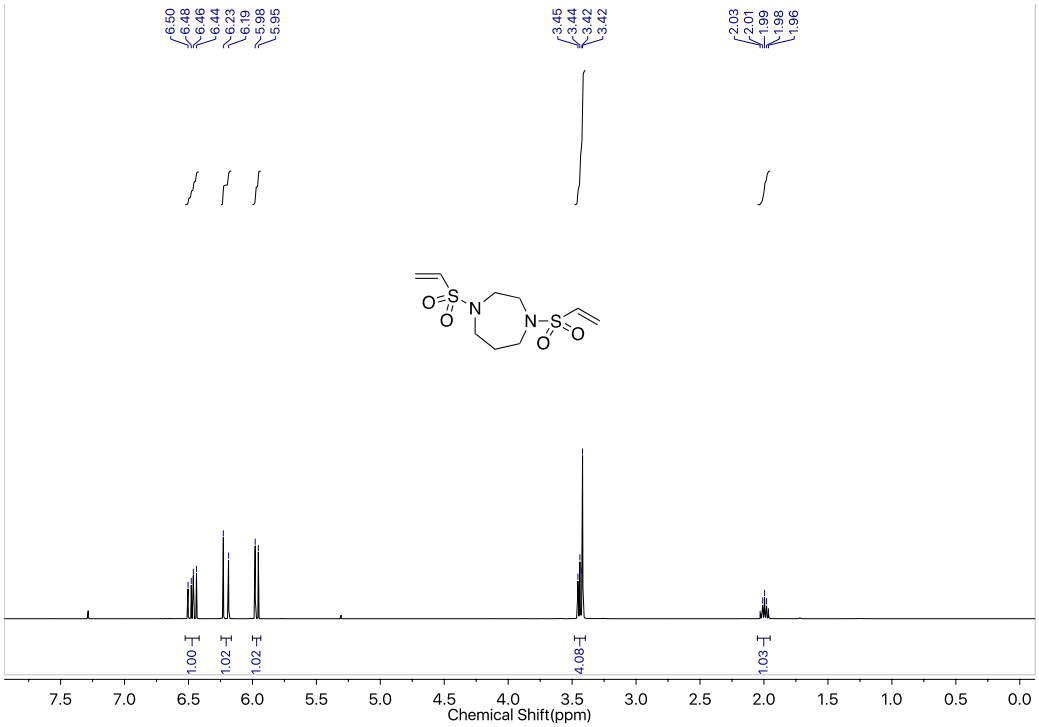


Fig. S27 ^{1}H NMR of Homopiperazine-1,4-bis(vinyl sulfonamide)

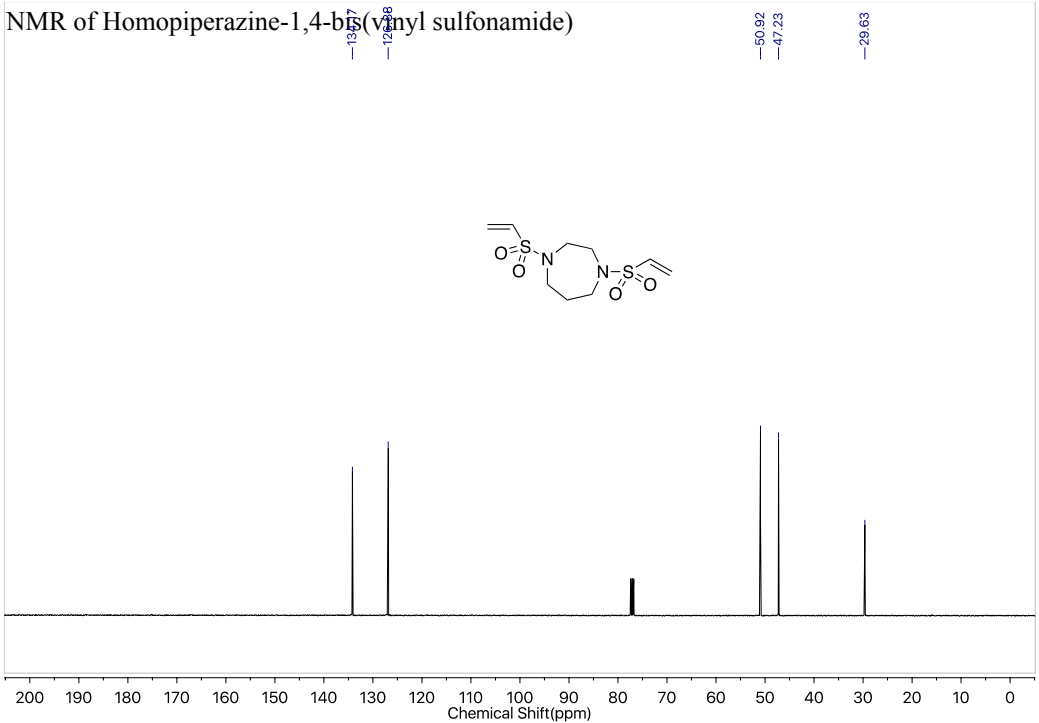


Fig. S28 ^{13}C NMR of Homopiperazine-1,4-bis(vinyl sulfonamide).

14. Reference:

1. W. Xi, H. Peng, A. Aguirre-Soto, C. J. Kloxin, J. W. Stansbury and C. N. Bowman, *Macromolecules*, 2014, **47**, 6159-6165.
2. M. Podgorski, E. Becka, M. Claudino, A. Flores, P. K. Shah, J. W. Stansbury and C. N. Bowman, *Dent. Mater.*, 2015, **31**, 1255-1262.
3. C. M. Cruz, M. Ortega-Munoz, F. J. Lopez-Jaramillo, F. Hernandez-Mateo, V. Blanco and F. Santoyo-Gonzalez, *Adv. Synth. Catal.*, 2016, **358**, 3394-3413.
4. J. Dadová, M. Vrábel, M. Adámik, M. Brazdová, R. Pohl, M. Fojta and M. Hocek, *Chem. Eur. J.*, 2015, **21**, 16091-16102.