Electronic Supplementary Material (ESI) for Polymer Chemistry

SUPPORTING INFORMATION

Kinetic Comparison of 13 Homogeneous Thiol-X Reactions

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Contents

I. Methods

Time-resolved online ATR FT-IR spectra were recorded on a React-IR 4000 Instrument (Mettler Toledo AutoChem ReactIR) equipped with a silicon ATR probe (SiComp, optical range 4400–650 cm-1). For online monitoring, the silicon probe was introduced into a two-necked glass flask containing the reaction mixture under stirring and spectra were recorded every minute or every 15 seconds. A few spectra were recorded before initiation of reactions by addition of catalyst or UV irradiation. The solvent spectrum was recorded and subtracted to enhance the signal of the reaction species. ^{1}H NMR spectra were recorded on a Bruker Avance 300 at 300 MHz. An Agilent technologies 1100 series LC/MSD system equipped with a diode array detector and single quad MS detector (VL) with an electrospray source (ESI-MS) was used for classic reversed phase LC-MS (liquid chromatography mass spectroscopy) analysis.

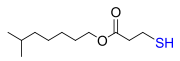
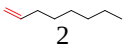
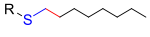
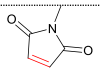
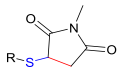
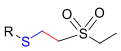
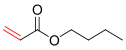
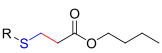
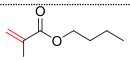
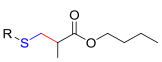
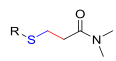
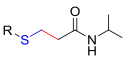
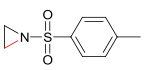
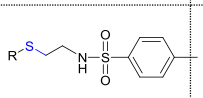
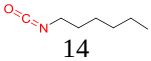
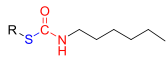
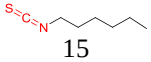
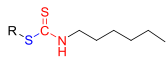
II. Reagents

Isooctyl 3-mercaptopropionate (the thiol, 1) (≥ 99%), 1-octene (2) (98%), 2-norbornene (3) (99%), *N*-methyl maleimide (4) (97%), ethyl vinyl sulfone (5) (98%), butyl acrylate (6) (≥99%, contains 10-60 ppm monomethyl ether hydroquinone as inhibitor), butyl methacrylate (7) (99%, contains 10 ppm monomethyl ether hydroquinone as inhibitor), *N*,*N*-dimethylacrylamide (8) (99%, contains 500 ppm monomethyl ether hydroquinone as inhibitor), 2-isopropenyl-2-oxazoline (10) (99%), methyl 2-bromopropionate (11) (99%), 1,2-epoxybutane (12) (99%), *N*-tosylaziridine (13) (98%), hexyl isocyanate (14) (97%), hexyl isothiocyanate (15) (95%), triethylamine (≥ 99%), dimethylphenylphosphine (99%), 2,2-dimethoxy-2-phenylacetophenone (photoinitiator, 99%), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, 98%), *n*-octylamine (99%), *N*,*N*-dimethylformamide (HPLC type, ≥ 99.9%), dimethyl sulfoxide (≥ 99.9%) and chloroform (≥ 99.9%) were purchased from Sigma-Aldrich and used as received. *N*-Isopropylacrylamide (9) (97%) was purchased from Aldrich and recrystallized twice.

III. Online FT-IR study

III. 1. Assignment of IR bands

Table S1. IR bands monitored during the thiol-X reactions

Thiol (1 eq)	Class	Reactant (1 eq)	Product	Band centers of monitored IR bands (cm^{-1}) And their tentatively assigned vibrations	
				Reactant	Product
 = R-SH 1 SH stretch 2550 cm^{-1}	Radical mediated	 2		1000, 919 CH_2=CH deformation (twist and wag)	1295 S-CH_2 out-of-plane bend
		 3		714 =CH wag	1300 S-CH_2 out-of-plane bend
	Michael addition	 4		834 =CH wag	1281 S-CH_2 out-of-plane bend
		 5		984, 799, 760 CH=CH_2 bend	1350 S-CH_2 out-of-plane bend
		 6		1297, 1278; 987, 968; 814 =CH rock; CH=CH_2 wag ; =CH_2 twist	1343, 1242 S-CH_2 out-of-plane bend
		 7		946 =CH_2 wag	1239 S-CH_2 out-of-plane bend
		 8		984,961,799 CH=CH_2 out-of-plane deformation	-
		 9		991, 960 CH=CH_2 out-of-plane deformation	-
		 10		990, 930 =CH_2 out-of-plane deformation	-
	S_N2	 11		-	-
	Three memb. ring	 12		-	-
		 13		910, 713, 695 ring deformation and CH_2 rock	-
	Iso(thio)cyanate	 14		2280 N=C=O stretch	1536, 1214 amide II (mainly δN-H, νC-N), amide III (δN-H, νC-C)
		 15		2179-2105 N=C=S stretch	1540, 964-931 thioamide (mainly νC-N), thioamide (δN-H)

-signals that are blended under other bands in the fingerprint region and thus cannot be distinguished.

III. 2. Illustration of FT-IR waterfall plots

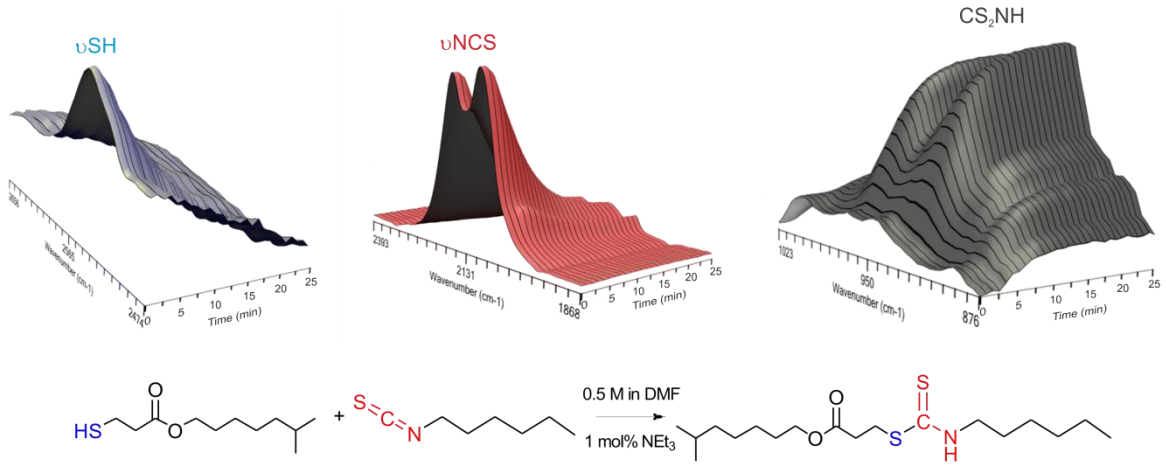


Fig. S1. Illustration of the online FT-IR waterfall plots for the thiol-isothiocyanate reaction.

III. 3. FT-IR spectra of thiol-X reactions

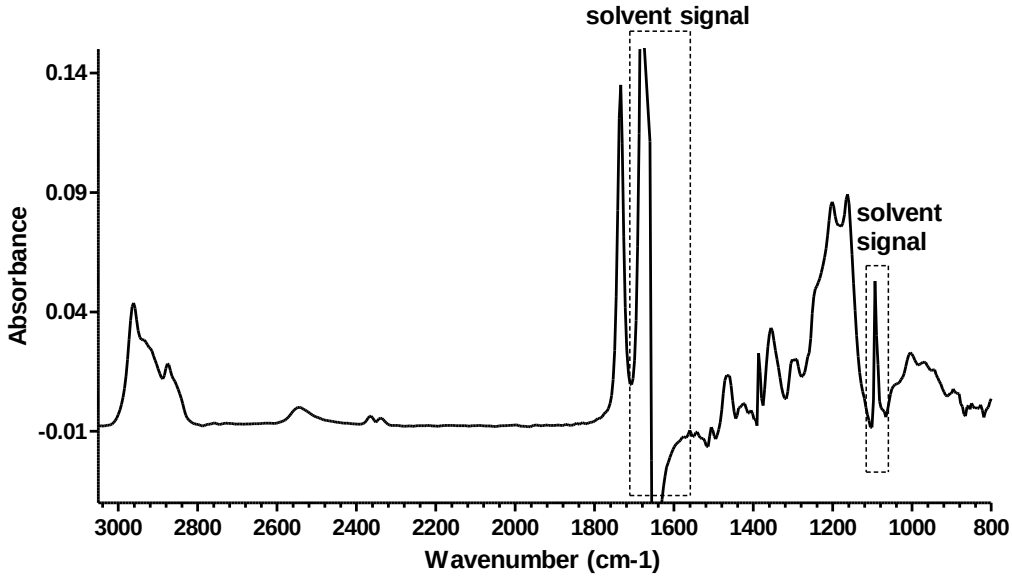


Fig. S2. IR spectrum of a 0.5 M solution of the thiol in DMF after solvent signal subtraction. Because of the high absorption of the solvent signals at 1715-1600 and 1100-1070 cm^{-1}, these signals still appear in the subtracted spectrum.

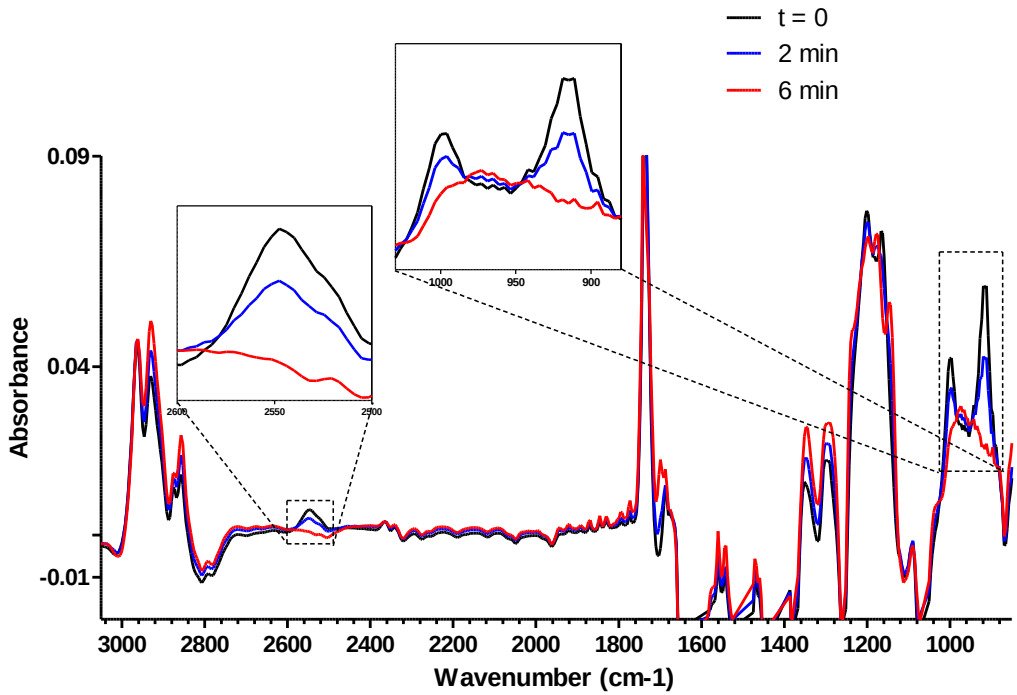


Fig. S3. Illustration of online IR spectra for the reaction between the thiol (1) and 1-octene (2) at 0.5 M concentration in DMF with 1 mol% of photoinitiator. Insets: zooms of the thiol and double bond peak regions.

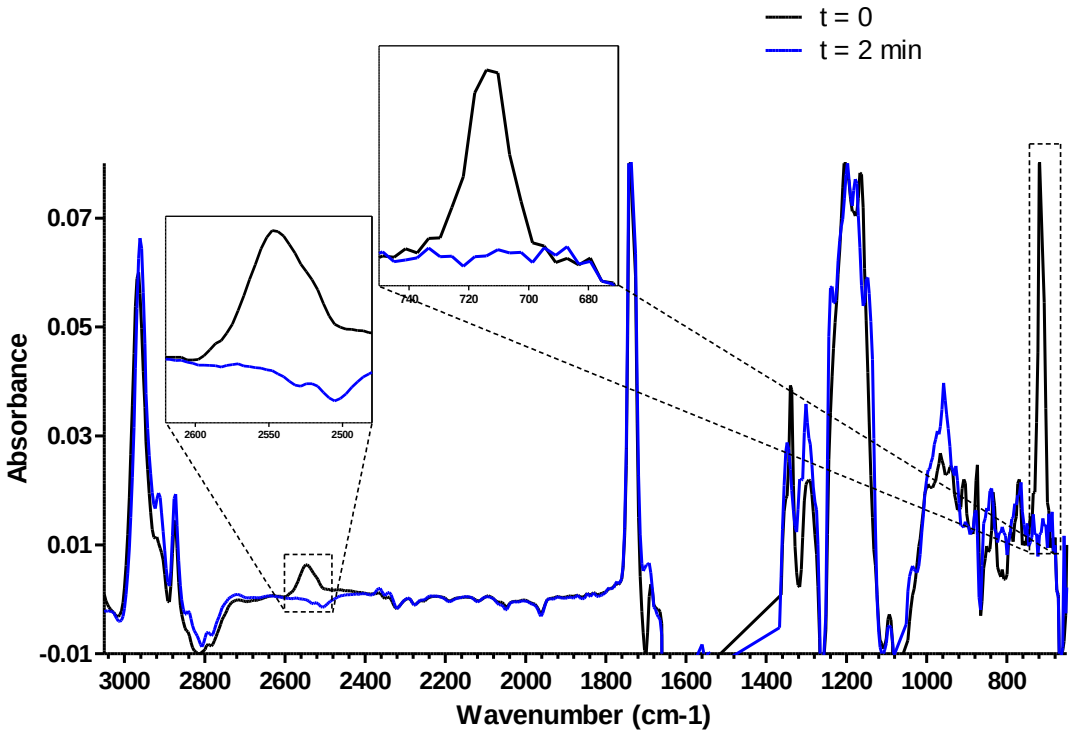


Fig. S4. Illustration of online IR spectra for the reaction between the thiol (1) and 2-norbornene (3) at 0.5 M concentration in DMF with 1 mol% photoinitiator. Insets: zooms of the thiol and double bond peak regions.

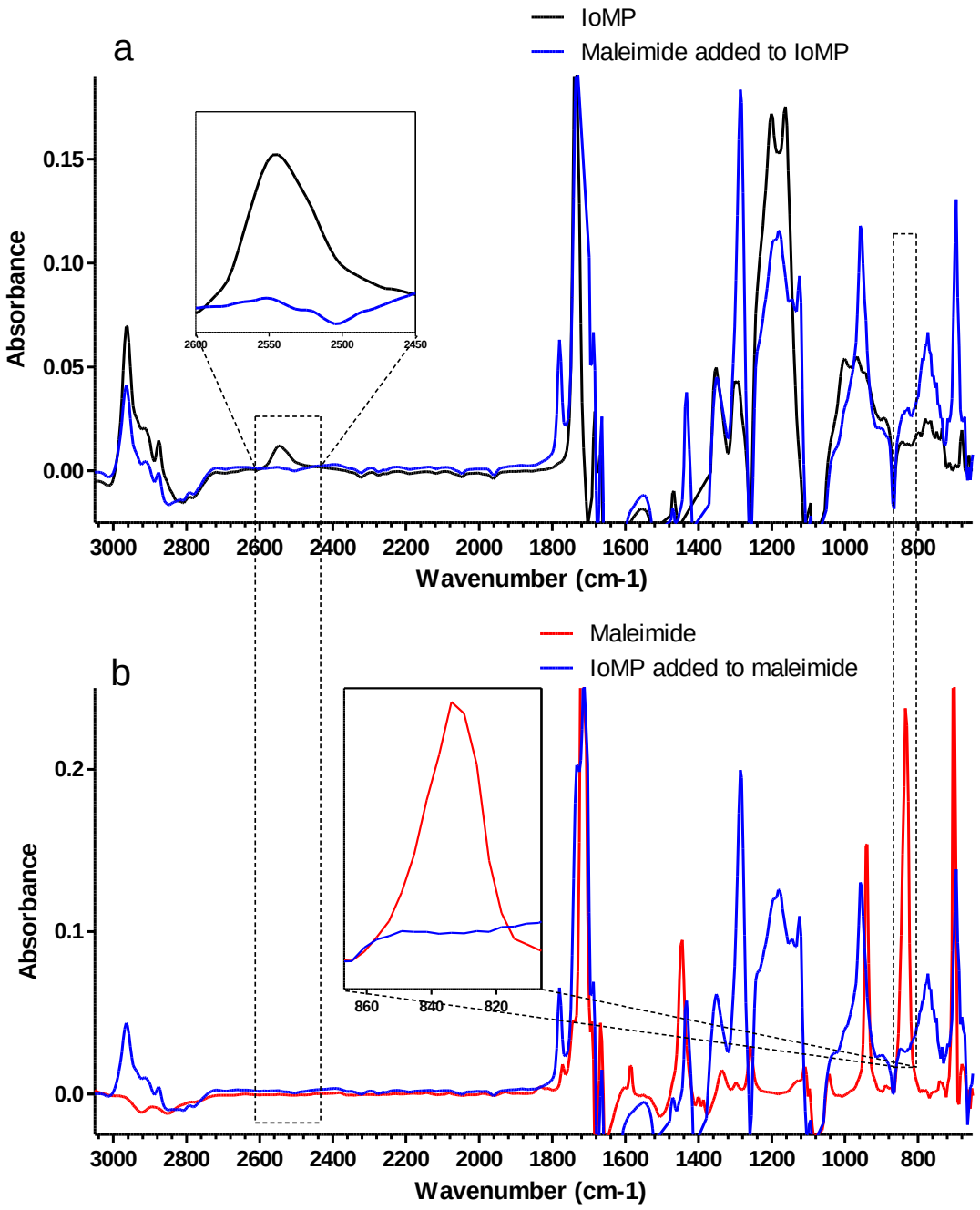


Fig. S5. IR spectra for the reaction between the thiol (1) and maleimide (4) in a 0.5 M solution of IoMP in DMF without any catalyst before and right after addition of the second reactant: a) maleimide added to thiol and b) thiol added to maleimide. In both cases the reaction was complete before the kinetic profile could be measured (spectra were recorded every minute). Insets: zooms of the thiol and double bond peak regions.

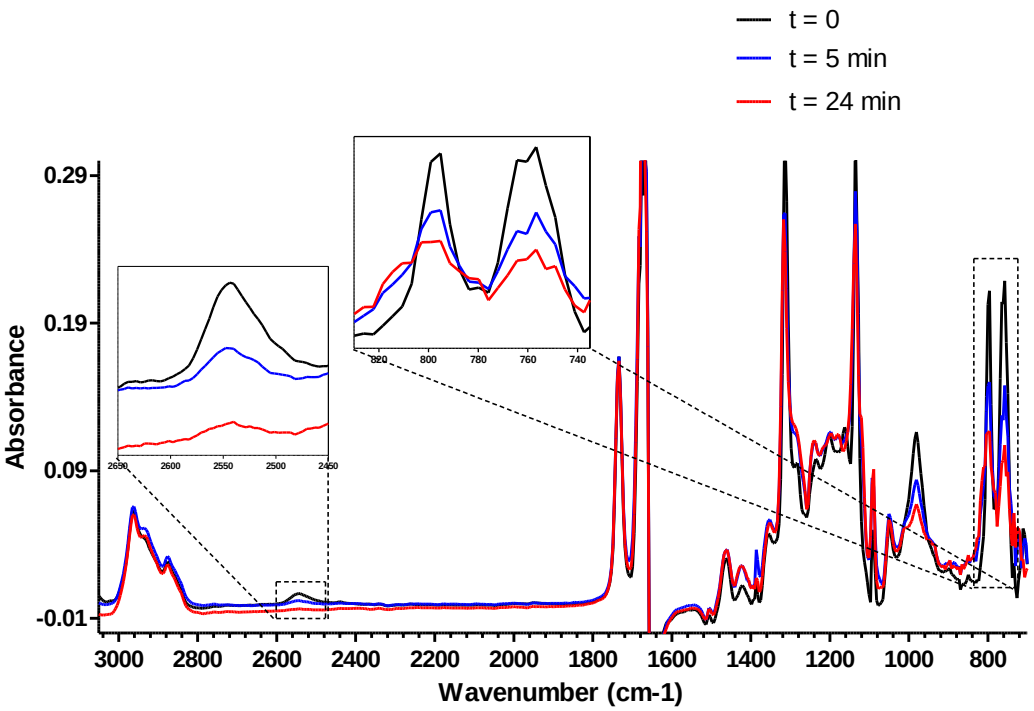


Fig. S6. Illustration of online IR spectra for the reaction between the thiol (1) and vinyl sulfone (5) at 0.5 M concentration in DMF with 1 mol% of NEt_3. Insets: zooms of the thiol and double bond peak regions.

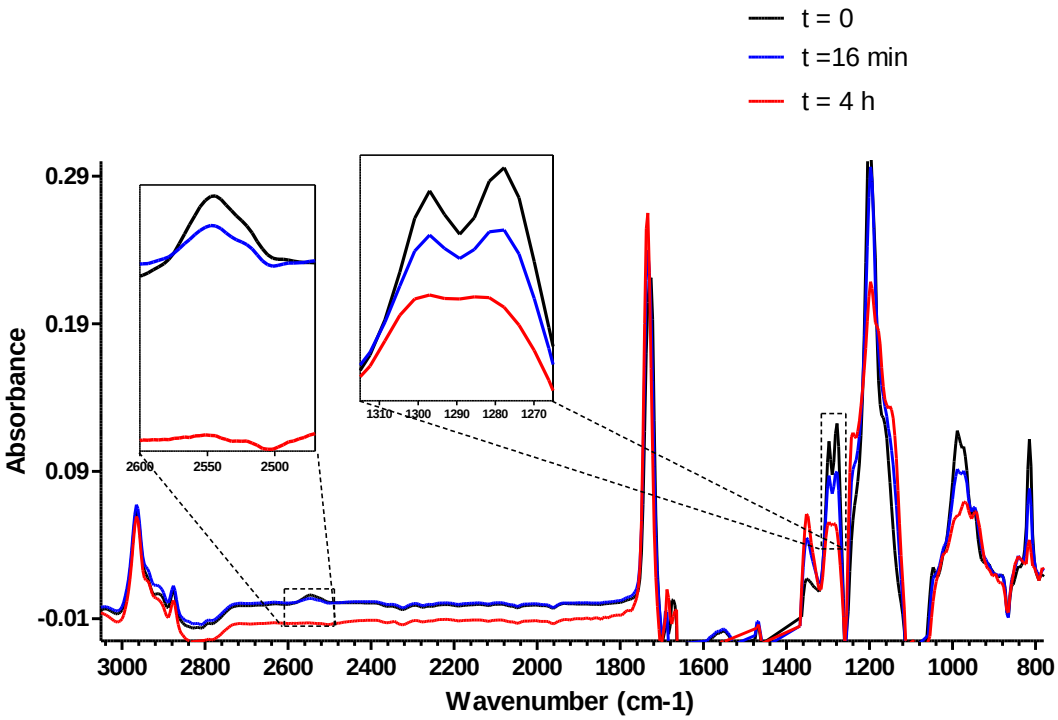


Fig. S7. Illustration of online IR spectra for the reaction between the thiol (1) and acrylate (6) in a 0.5 M solution of the thiol in DMF with 1 mol% of NEt_3. Insets: zooms of the thiol and double bond peak regions.

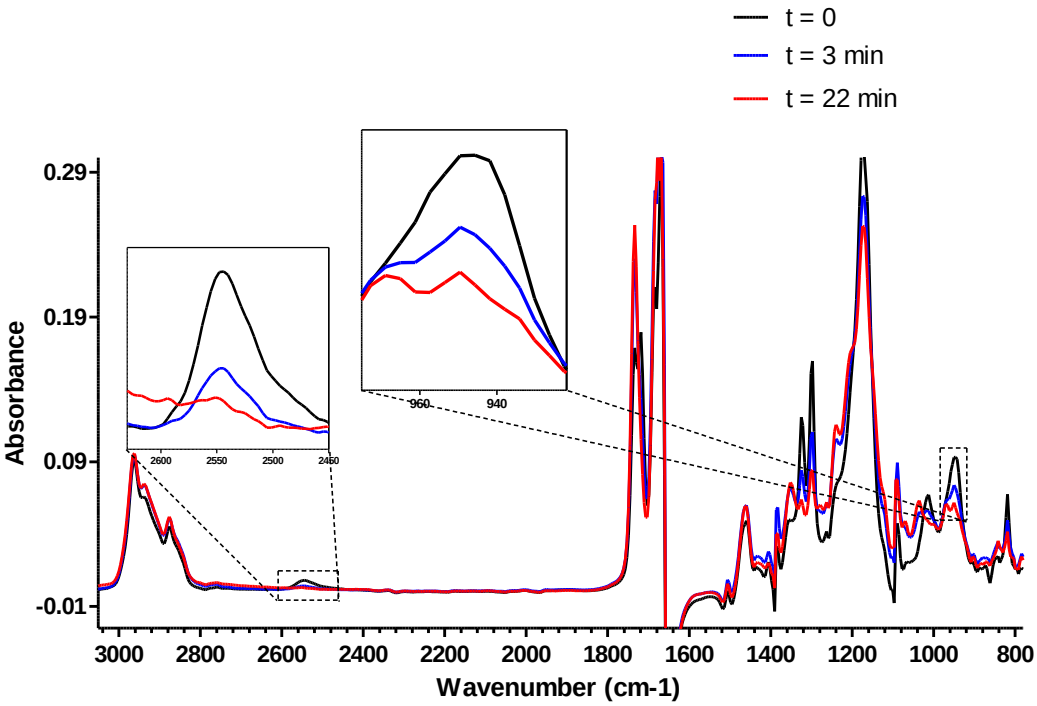


Fig. S8. Illustration of online IR spectra for the reaction between the thiol (1) and methacrylate (7) in a 0.5 M solution of the thiol in DMF with 1 mol% of DBU. Insets: zooms of the thiol and double bond peak regions.

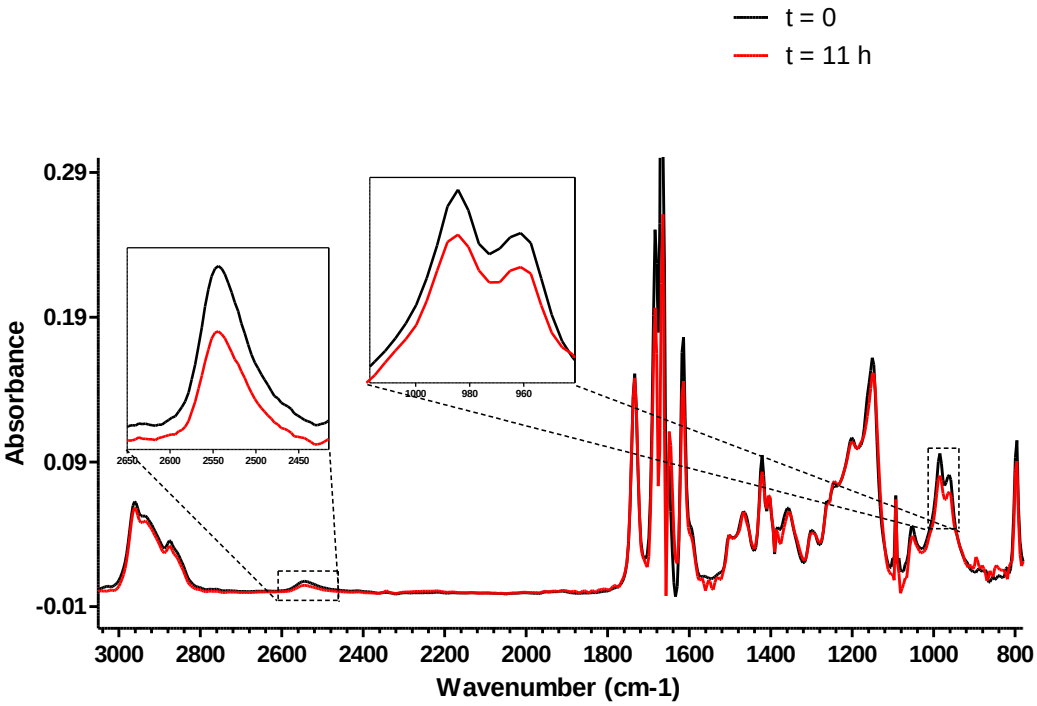


Fig. S9. Illustration of online IR spectra for the reaction between the thiol (1) and *N*,*N*-dimethylacrylamide (8) at 0.5 M concentration in DMF with 1 mol% of NEt_3. Insets: zooms of the thiol and double bond peak regions.

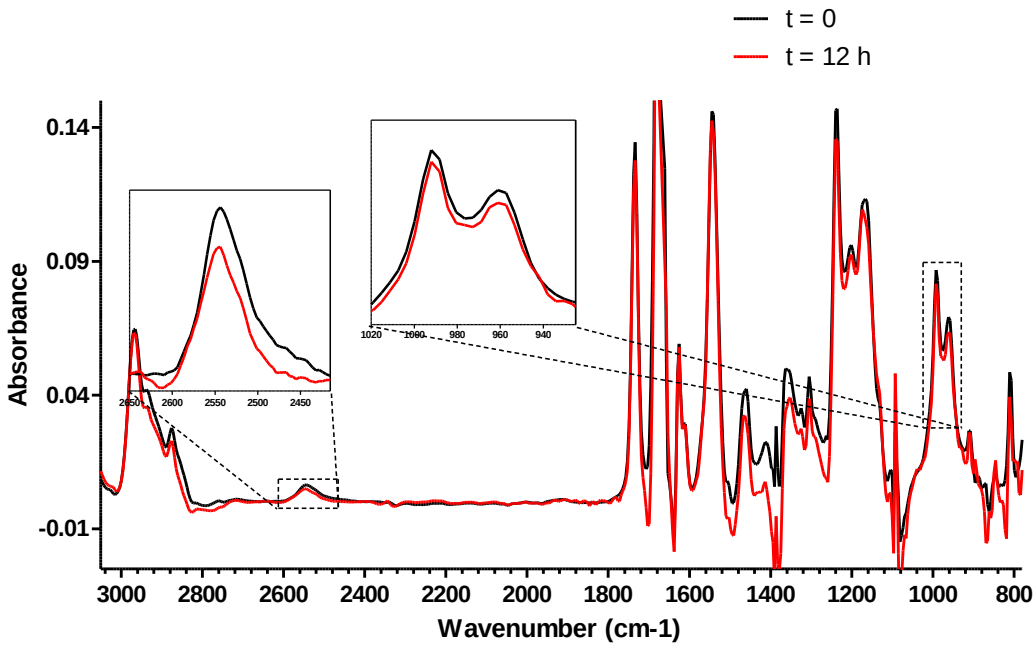


Fig. S10. Illustration of online IR spectra for the reaction between the thiol (1) and *N*-isopropylacrylamide (9) at 0.5 M concentration in DMF with 1 mol% of NEt_3. Insets: zooms of the thiol and double bond peak regions.

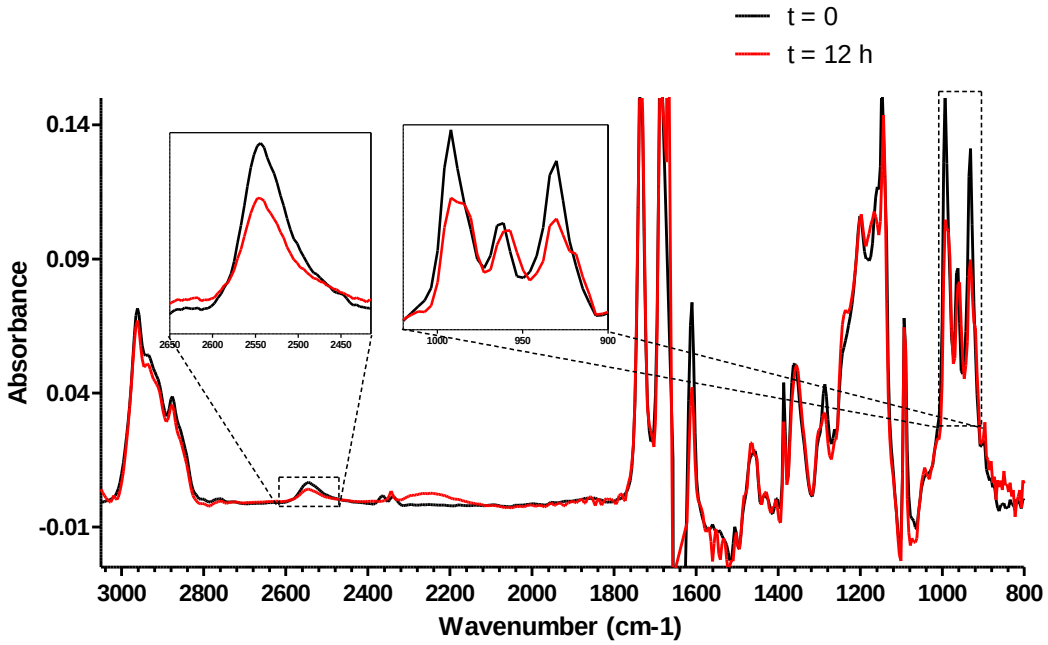


Fig. S11. Illustration of online IR spectra for the reaction between the thiol (1) and isopropenyl oxazoline (10) in at 0.5 M concentration in DMF with 1 mol% of the phosphine. Insets: zooms of the thiol and double bond peak regions.

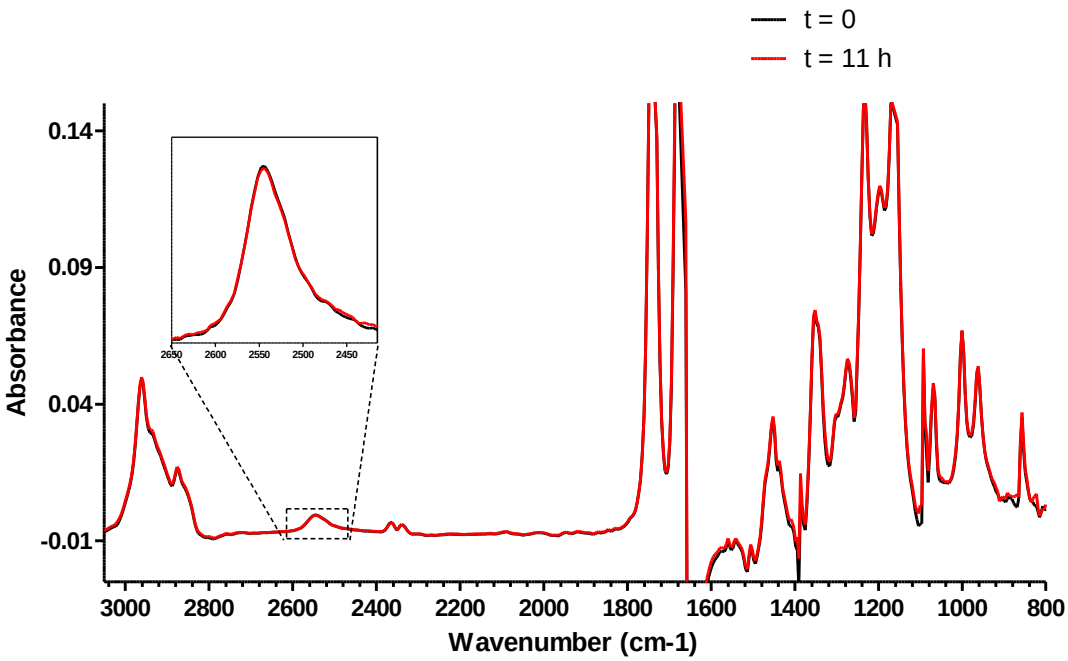


Fig. S12. Illustration of online IR spectra for the reaction between the thiol and methyl α-bromopropionate (11) at 0.5 M concentration in DMF with 1 mol% of DBU. Inset: zoom of the thiol peak region.

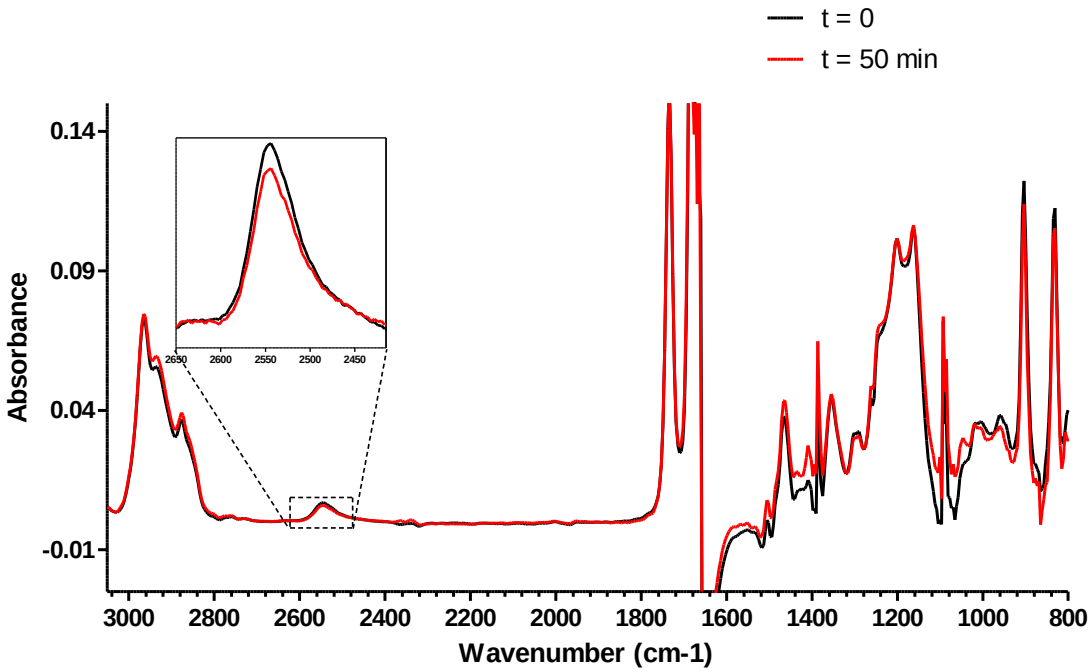


Fig. S13. Illustration of online IR spectra for the reaction between the thiol (1) and epoxy (12) at 0.5 M concentration in DMF with 1 mol% of DBU. Inset: zoom of the thiol peak region.

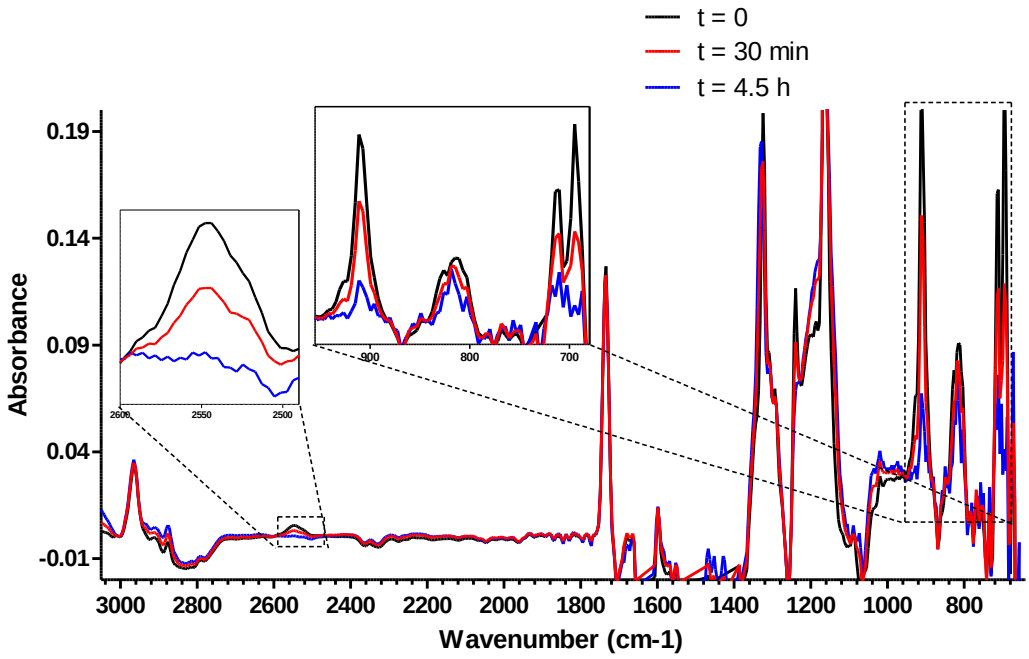


Fig. S14. Illustration of online IR spectra for the reaction between the thiol (1) and *N*-tosyl aziridine (13) at 0.5 M concentration in DMF with 1 mol% of phosphine. Insets: zooms of the thiol and aziridine ring peak region.

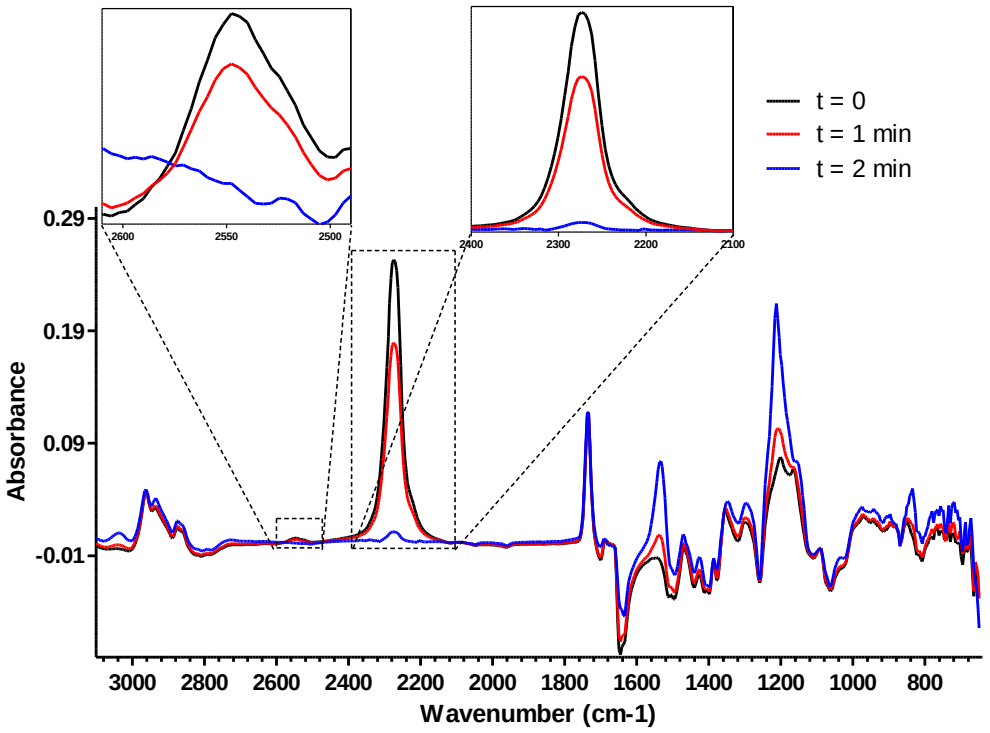


Fig. S15. Illustration of online IR spectra for the reaction between the thiol (1) and isocyanate (14) at 0.5 M concentration in DMF with 1 mol% of NEt_3. Insets: zooms of the thiol and NCO peak region.

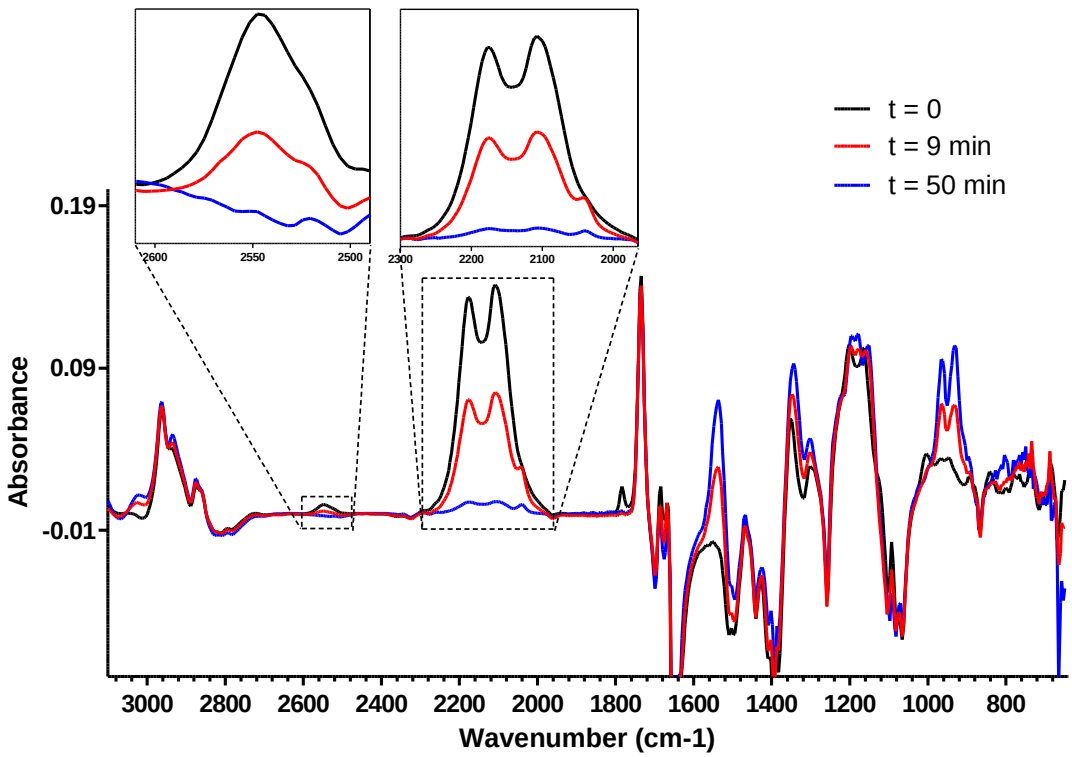


Fig. S16. Illustration of online IR spectra for the reaction between the thiol (1) and isothiocyanate (15) at 0.5 M concentration in DMF with 1 mol% of NEt_3. Insets: zooms of the thiol and NCS peak region.

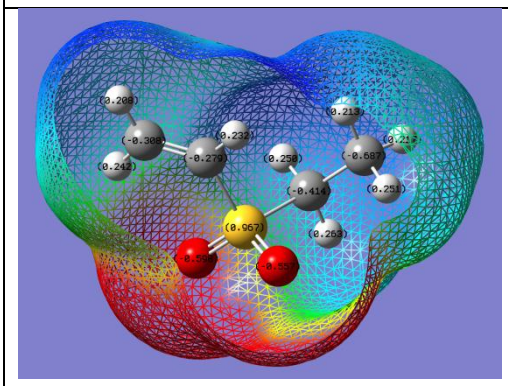
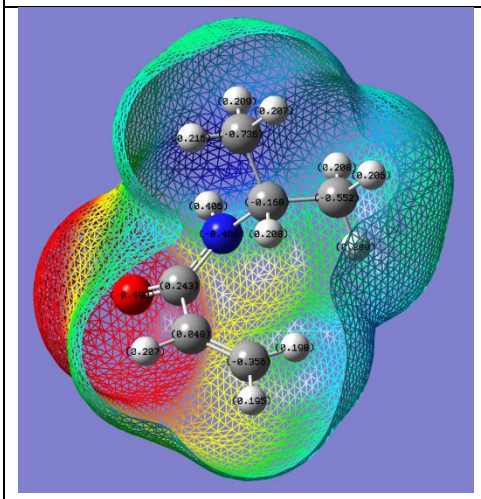
IV. Electrophilic indexes

The simulated electrophilic index of acrylamide is higher than those of ethyl methacrylate and methyl acrylate, as reported by LoPachin et al.[1]

Though outside of the scope of this paper, our calculations by density functional theory using Gaussian 03 suggested that *N*-isopropylacrylamide has a smaller electrophilic index compared to ethyl vinyl sulfone.

Calculations of the electrophilic indexes of N-isopropylacrylamide and ethyl vinyl sulfone

The structures of *N*-isopropylacrylamide and ethyl vinyl sulfone were optimized from ground state equilibrium with density functional theory calculations DFT B3LYP/6-31G(d) using the Gaussian 03 software. The calculation of the electronic chemical potential (μ) and the chemical hardness (η) were obtained from the expressions $\mu \approx (\varepsilon_{HOMO} + \varepsilon_{LUMO})/2$ and $\eta \approx \varepsilon_{LUMO} - \varepsilon_{LUMO}$. The electrophilicity index ω is calculated from $\omega = \mu^2/\eta$.[2]

Structures	Calculated ω (eV)
 Ethyl vinyl sulfone	1.264
 *N*-isopropylacrylamide	1.073

V. LC-MS spectra

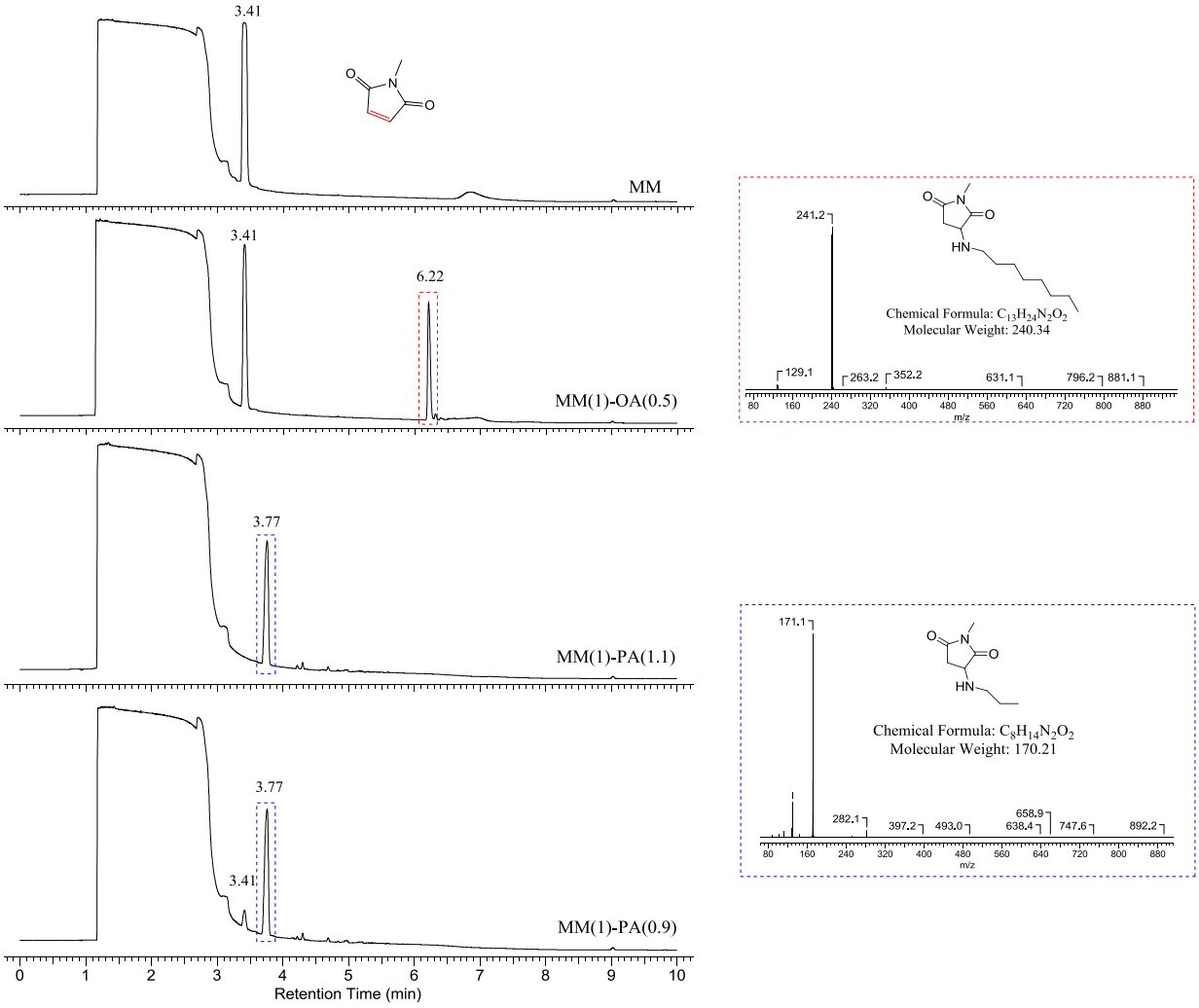


Fig. S17. LC-MS analysis of the reaction mixture of *N*-methyl maleimide (MM) with *n*-octylamine (OA) and *n*-propylamine (PA) in DMF (maleimide concentration of 0.5M) after 15 min, with maleimide:*n*-octylamine equal to 1:0.5 (MM(1)-OA(0.5)), and maleimide:*n*-propylamine equal to 1:1.1 and 1:0.9 (MM(1)-PA(1.1) and MM(1)-PA(0.9), respectively).

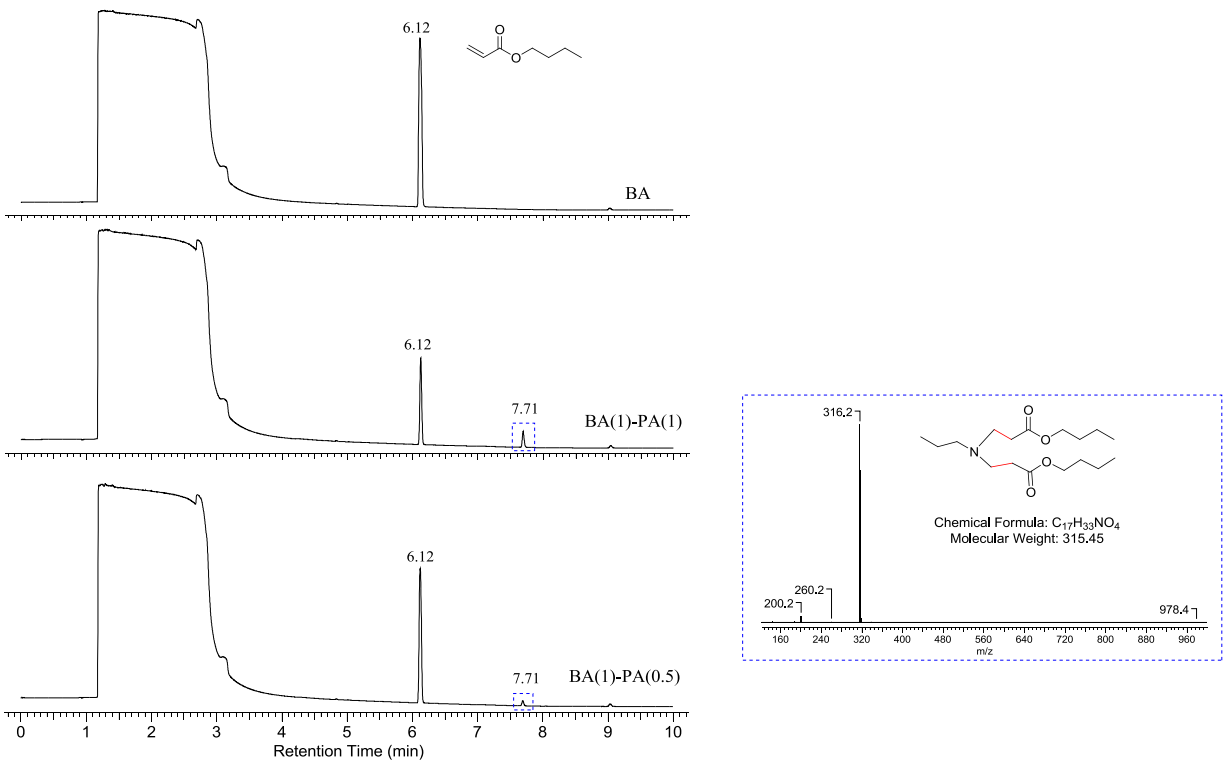


Fig. S18. LC-MS analysis of the reaction mixture of *n*-butyl acrylate (BA) with *n*-proylamine in DMF (BA concentration of 0.5M) after 14 hours, with acrylate:*n*-proylamine equal to 1:1 and 1:0.5 (BA(1)-PA(1) and BA(1)-PA(0.5), respectively).

VI. ^{1}H NMR spectra

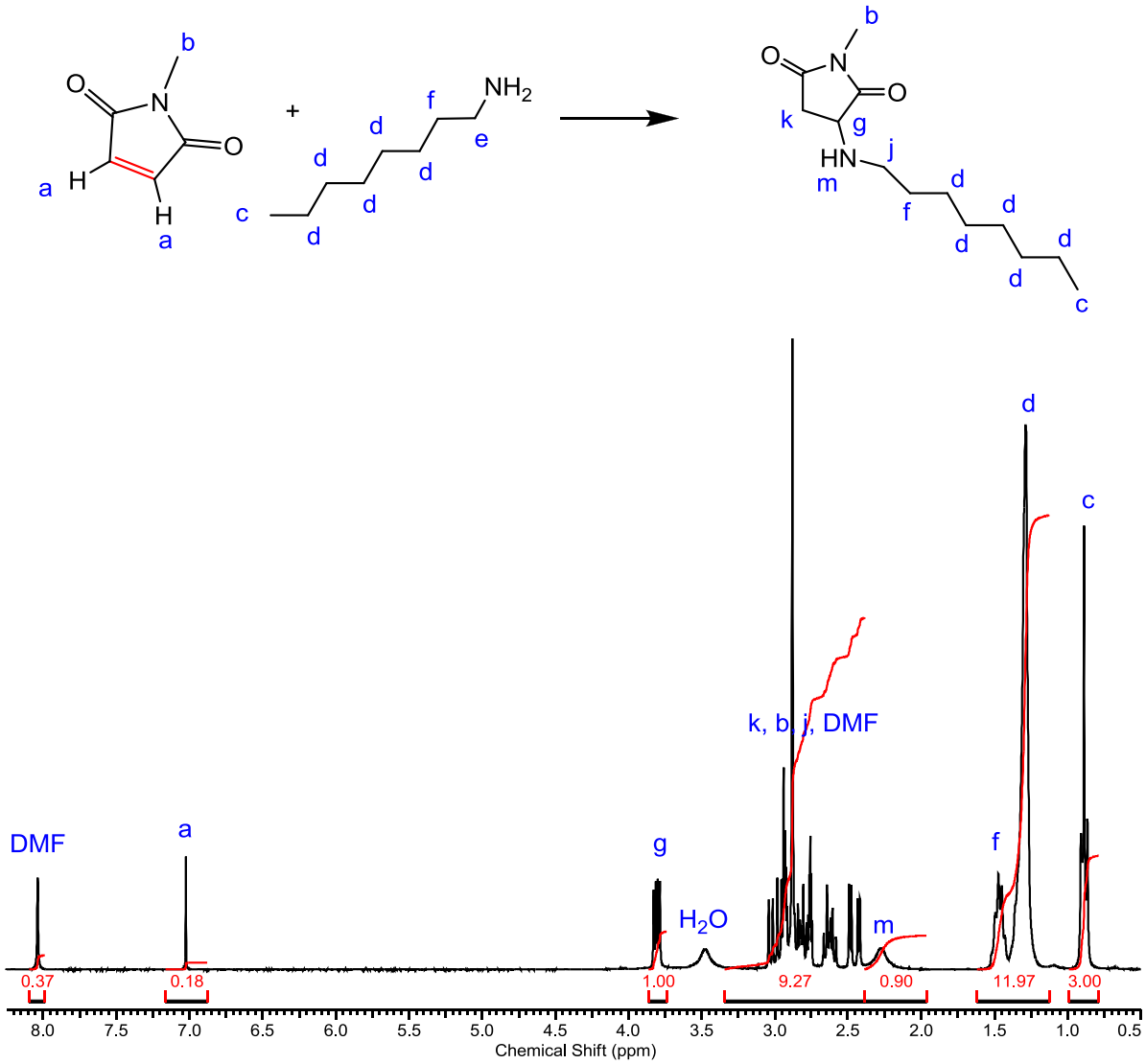


Fig. S19. ^{1}H NMR spectrum of the reaction mixture of maleimide and *n*-octylamine with maleimide:*n*-octylamine equal to 1:0.75 in DMF-d_7 (maleimide concentration of 0.5 M) after 30 minutes.

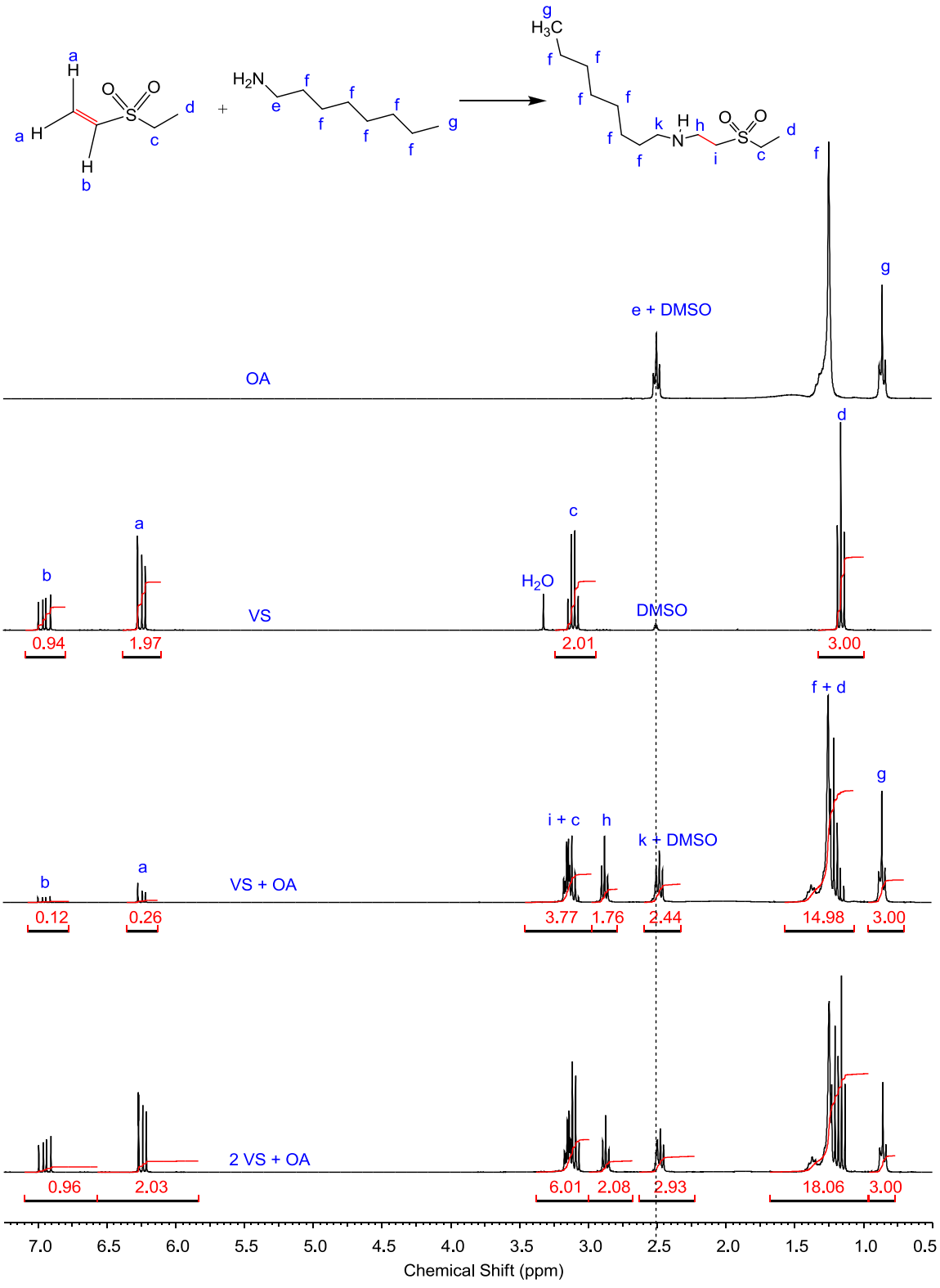


Fig. S20. ^{1}H NMR spectra of *n*-octylamine (OA), ethyl vinyl sulfone (VS), and the reaction mixture of ethyl vinyl sulfone and *n*-octylamine with vinyl sulfone:*n*-octylamine equal to 1:1 and 2:1 in DMSO-d_6 (VS concentration of 0.5M) after 4 hours. 90% and 50% of the vinyl groups were consumed for the (VA + OA) and (2 VA + OA) reactions, respectively.

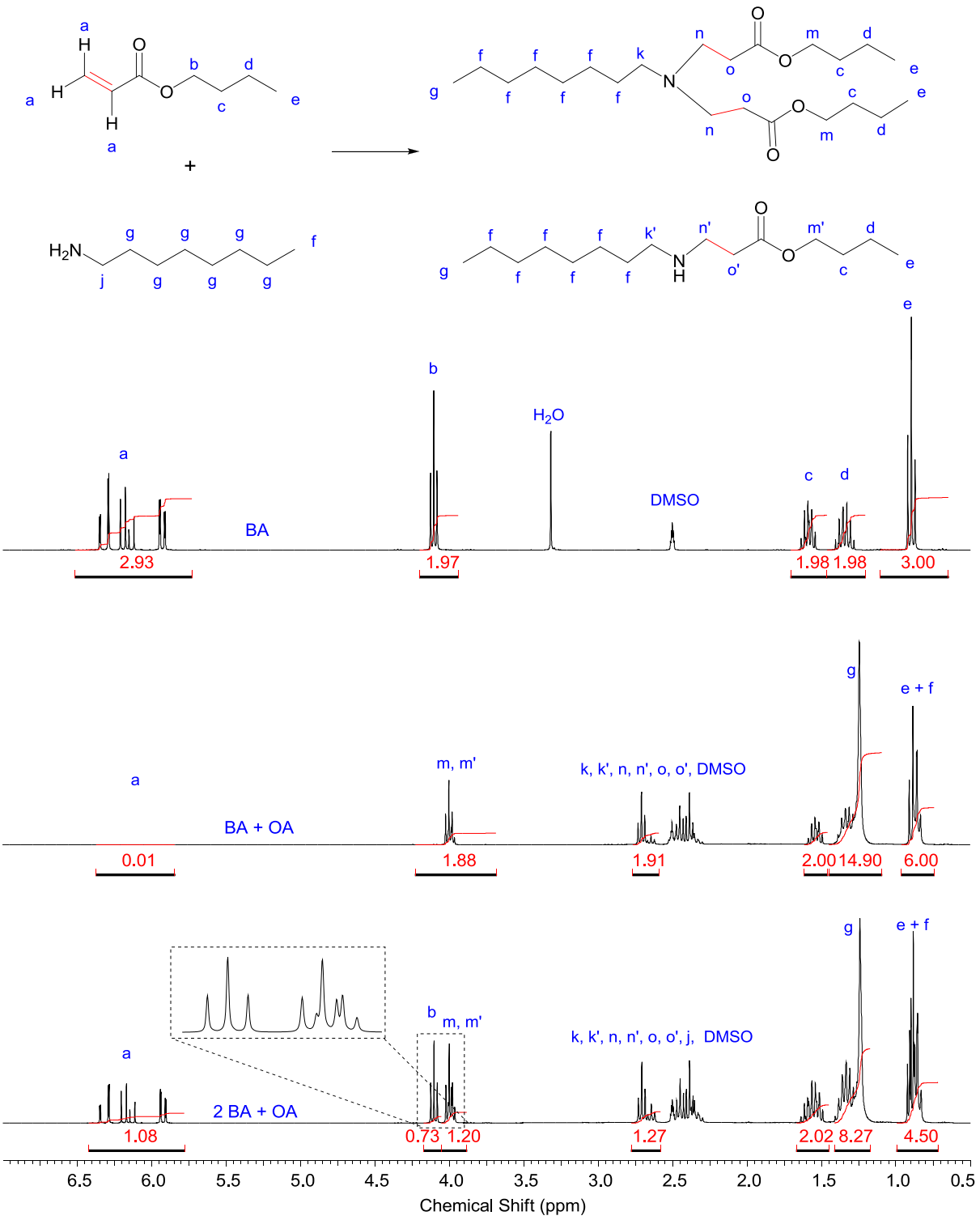


Fig. S21. ^{1}H NMR spectra of *n*-butyl acrylate (BA), and the reaction mixture of *n*-butyl acrylate and *n*-octylamine (OA) with *n*-butyl acrylate:*n*-octylamine equal to 1:1 and 2:1 in DMSO-d_6 (BA concentration of 0.5M) after 30 hours. 100% and 64% of the acrylate groups were consumed for the (BA + OA) and (2 BA + OA) reactions, respectively.

VII. Comparison of the rates of the reactions of *n*-octylamine with vinyl sulfone and acrylate in DMF and DMSO

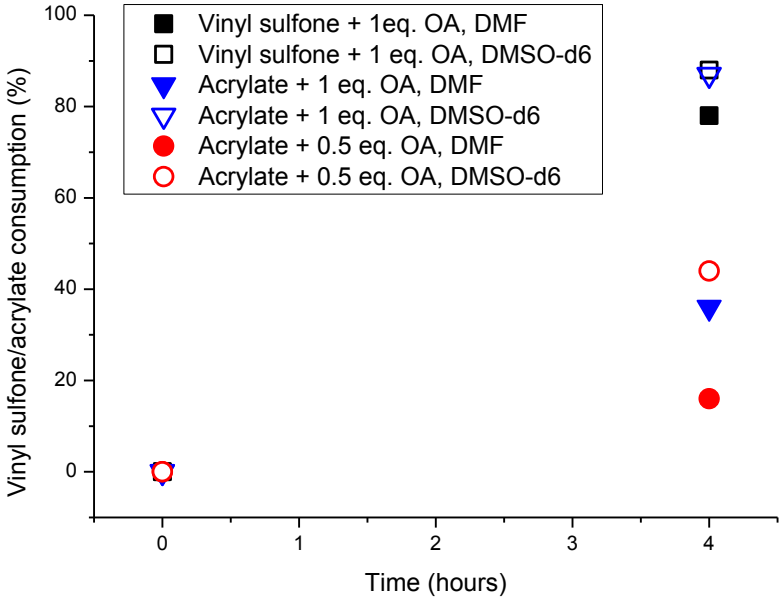


Fig. S22. Vinyl sulfone/acrylate consumption after 4 hours for the reactions of ethyl vinyl sulfone (5) and *n*-butyl acrylate (6) with *n*-octylamine (OA) conducted in DMF and DMSO-d_6. The vinyl sulfone/acrylate consumption was determined by online FT-IR and ^{1}H NMR for reactions performed in DMF and DMSO-d_6, respectively.

References

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