Supporting Information

Saccharin-Pendant Methacrylamide as a Unique Monomer in Radical Copolymerization: Peculiar Alternating Copolymerization with Styrene

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Contents

General Information

Materials

For synthesis: Saccharin (TCI, >99%), methacryloyl chloride (TCI, >90%), triethylamine (TCI, >99%), pivaloyl chloride (TCI, >98%), *n*-dibutylamine (TCI, >99%), *n*-hydroxy succinimide (TCI, >98.0%), trifluoroacetic acid (TCI, >99.0%), trimethylsilyl diazomethane (Aldrich, 2M solution in Et_2O), acetic acid (Wako, >99.9%), tetrahydrofuran (Wako, dehydrated), dichloromethane (CH_2Cl_2: Wako) and toluene (Wako, >99.5%) were used without purification. For dialysis, MWCO1000 (Spectra/PorVR7, diameter 29 mm), methanol (Wako, >99.5%) and acetone (Wako, >99.0%) were used.

For polymerization: 2,2'-azobis (isobutylonitrile) (TCI, >98%) and *N*-methyl methacrylamide (TCI, >98.0%) N-ethyl maleimide (TCI, 98.0%), were used as received without further purification. Styrene (TCI, 99.0%) methyl methacrylate (TCI, >99.8%), methyl acrylate (TCI, >99.0%) and vinyl acetate (TCI) were dried overnight over calcium chloride and purified by distillation under reduced pressure over calcium hydride. *p*-methoxy styrene was washed with 10% aqueous sodium hydroxide and then with saturated aqueous sodium chloride, dried overnight over sodium sulfate, and distilled under reduced pressure. p-nitrostyrene (TCI, >98.0%) was passed through inhibitor remover (Aldrich) column to remove inhibitor before use. Acetonitrile (Wako) was dried by molecular sieves 4A (Wako) and bubbled with dry nitrogen for more than 15 min before use. 1,4-dioxane (Wako, >99.5%) was bubbled with dry nitrogen for more than 15 min before use. For reprecipitation, Acetone (Wako, >99.0%) or methanol (Wako, >99.5%) were used.

Measurements

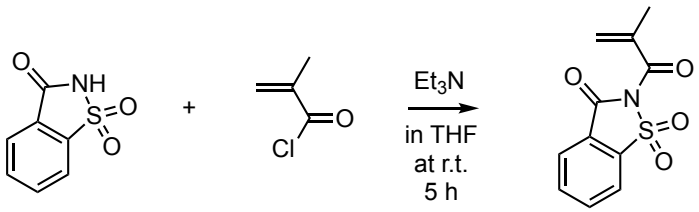
NMR spectra were measured on a JEOL JNM-ECA500 spectrometer operating at 500.16 MHz (^{1}H) and 125.04 MHz (^{13}C) at room temperature (^{13}C NMR of polymers were measured at 55˚C). Number-average molecular weight (M_n) and M_w/M_n ratio of polymers were measured by size exclusion chromatography (SEC) at 40℃ in in THF as an eluent on two polystyrene-gel columns (TOSOH TSKgel Super Multipore HZ-M). The columns were calibrated against standard polystyrene samples (TOSOH PStQuick series).

Computational Study

The Gaussian 16 program package3 was used for computation.[1] The density functional theory (DFT) was applied for the optimization of the structures and vibrational analysis at B3LYP/6-31G* level.

Experimental Section

Monomer Synthesis



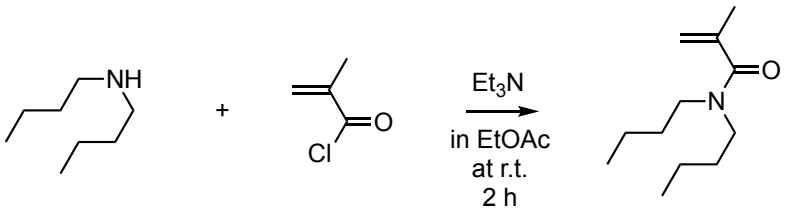
Scheme S1. Synthesis of saccharin methacrylamide (**1**)

Synthesis of Saccharin methacrylamide (1)

Saccharin (91.75 g, 500 mmol) was placed in round-bottom-flask under dry argon and dissolved in THF (1 L). Then, triethylamine (73.2 mL, 525 mmol) and methacryloyl chloride (47.8 mL, 510 mmol) were added at 0 ˚C and stirred for 5 hours at 0 ˚C. The reaction was quenched by methanol (1 mL). The reaction mixture was filtered and the filtrate was concentrated under reduced pressure. The resulting mixture was dissolved in CH_2Cl_2 and washed with saturated $NaHCO_3$ aq. and brine. The organic phase was dried over Na_2SO_4 and evaporated. The obtained solid were purified by recrystallization in toluene to yield **1** (93.87 g, 374 mmol, 75%) as a white solid (melting point: ~143 ˚C).

^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 8.14 (d, 1H), 8.01-7.88 (m, 3H), 5.80 (s, 1H), 5.79 (s, 1H), 2.09 (s, 3H)

^{13}C NMR (125 MHz, chloroform-d): δ (ppm) 167.10, 157.61, 139.46, 138.29, 136.51, 135.03, 126.36, 126,21, 125.67, 121.35, 18.00

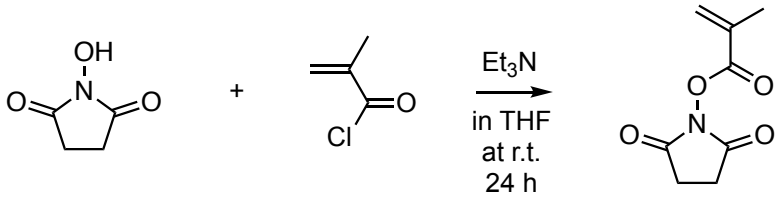


Scheme S2. Synthesis of N,N-dibutyl methacrylamide (**2**)

Synthesis of *N*,*N*-dibutyl methacrylamide (2)

Dibutylamine (4.25 mL, 25.0 mmol) and triethylamine (4.18 mL, 30.0 mmol) were dissolved in ethyl acetate in round-bottom-flask. Then, methacryloyl chloride (2.60 mL, 27.5 mmol) were added at 0 ˚C and stirred for 2 hours at room temperature. The reaction was quenched by methanol (3 mL). The reaction mixture washed with saturated $NaHCO_3$ aq. 3 times and brine. The organic phase was dried over Na_2SO_4 and evaporated. The obtained oil was purified with column chromatography (hexane; EtOAc = 3.1 as eluent) to yield 2 (3.94 g, 20.0 mmol, 80%) as a slightly yellow oil.

^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 5.10 (m, 1H), 4.98 (m, 1H), 3.31 (broad doublet, 4H), 1.95 (m, 1H), 1.52 (broad, 4H), 1.30 (broad, 4H), 0.92 (broad triplet, 6H)



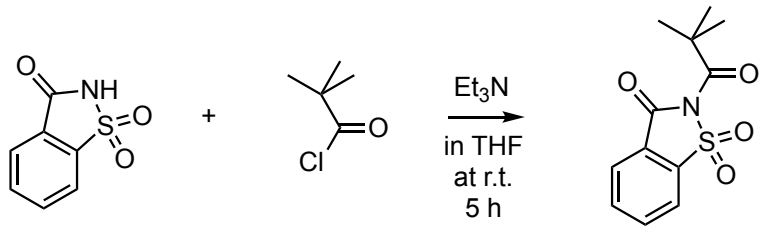
Scheme S3. Synthesis of *N*-hydroxysuccinimide methacrylate (**3**)

Synthesis of *N*-hydroxysuccinimide methacrylate (3)

N-hydroxysuccinimide (2.28 g, 20 mmol) was placed in round-bottom-flask under dry argon and dissolved in THF (20 mL). Then, triethylamine (3.35 mL, 24 mmol) and methacryloyl chloride (2.28 mL, 24 mmol) were added at 0 ˚C and stirred for 24 hours at room temperature. The reaction was quenched by water (1 mL). The reaction mixture was diluted with EtOAc and washed with saturated $NaHCO_3$ aq. two times and brine. The organic phase was dried over Na_2SO_4 and evaporated. The obtained solid were purified by recrystallization in mixed soluvent of hexane-AcOEt to yield 3 (3.08 g, 17 mmol, 85%) as a white crystal.

^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 6.41 (s, 1H), 5.88 (s, 1H), 2.85 (s, 4H), 2.05 (s, 3H).

Model compound Synthesis



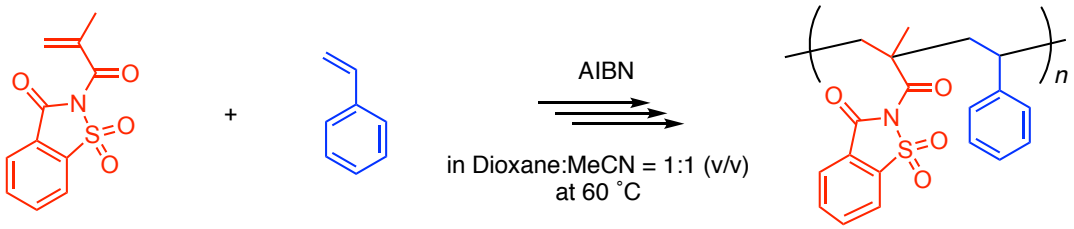
Scheme S4. Synthesis of model compound

Synthesis of Saccharin pivalamide

Saccharin (9.44 g, 51.5 mmol) was placed in round-bottom-flask under dry argon and dissolved in THF (150 mL). Then, triethylamine (8.62 mL, 61.8 mmol) and pivaloyl chloride (6.94 mL, 56.7 mmol) were added at 0 ˚C and stirred for 5 hours at room temperature. The reaction was quenched by methanol (1 mL). The reaction mixture was filtered. The filtrate was diluted with EtOAc and washed with saturated $NaHCO_3$ aq. and brine. The organic phase was dried over Na_2SO_4 and evaporated. The obtained solid were purified by recrystallization in toluene to yield saccharin pivalamide (3.35 g, 12.5 mmol, 24%) as a white solid.

^{1}H NMR (500 MHz, chloroform-d): δ (ppm) 8.14 (d, 1H), 7.98-7.86 (m, 3H), 1.44 (s, 9H)

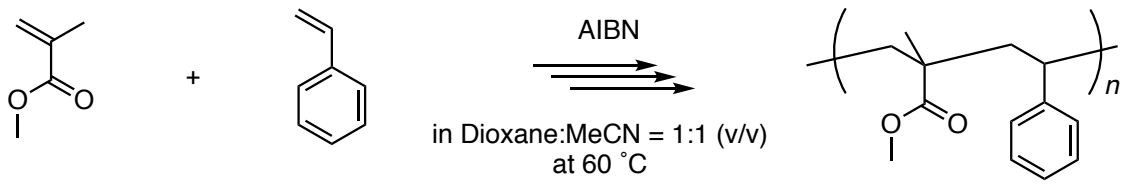
Polymerization



Scheme S5. Alternating copolymerization of **1** and styrene

Copolymerization of saccharin methacrylamide and styrene

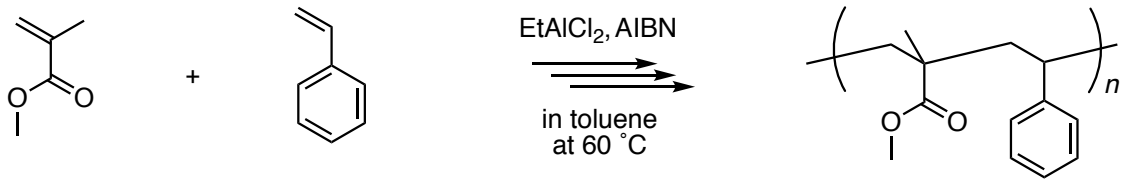
In a round bottom flask was placed AIBN (88.4 mg, 0.538 mmol) and SacM (10.87 g, 43.3 mmol) under argon. Degassed dioxane (18.83 mL), acetonitrile (18.83 mL), tetralin (0.5 mL) and styrene (4.97 mL, 43.3 mmol) were added at room temperature under argon. When the time-conversion plot was investigated, aliquots (ca. 0.7 mL each) of the solution were distributed with a syringe into glass tubes that were then sealed. The reaction mixture was placed in an oil bath kept at desired temperature. In predetermined intervals, the polymerization was terminated by cooling in dry ice-methanol. Monomer conversion was determined by ^{1}H NMR from the peak area of the olefinic protons of the monomer with tetralin as an internal standard. The quenched reaction solutions were poured into acetone to purify by reprecipitation. The copolymer of 1 and styrene were obtained as a colorless solid (5.62 g). Other polymerizations are performed in a similar procedure.



Scheme S6. Random copolymerization of MMA and styrene

Copolymerization of MMA and Styrene

In a round bottom flask was placed AIBN (13.9 mg, 0.0846 mmol). Degassed dioxane (3.43 mL), acetonitrile (3.43 mL), tetralin (0.08 mL), MMA (0.724 mL, 6.77 mmol) and styrene (0.778 mL, 6.77 mmol) were added at room temperature under argon. The reaction mixture was placed in an oil bath kept at desired temperature. After 24 h reaction, the polymerization was terminated by cooling in dry ice-methanol. Monomer conversion was determined by ^{1}H NMR from the peak area of the olefinic protons of the monomer with tetralin as an internal standard. The quenched reaction solutions were poured into methanol to purify by reprecipitation. The copolymer of MMA and styrene were obtained as a colorless solid (M_n = 16700, M_w/M_n = 1.45).

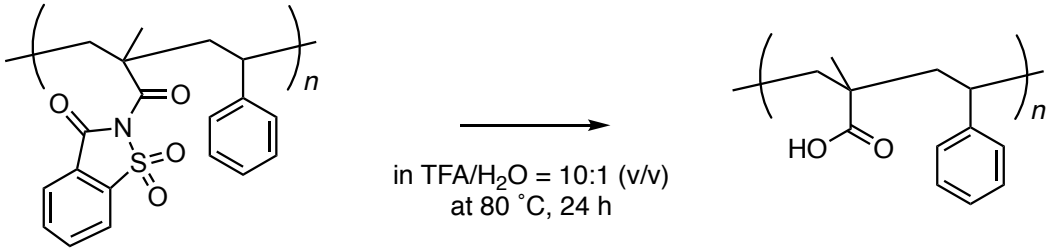


Scheme S7. Radical copolymerization of MMA and styrene in the presence of $EtAlCl_2$

Radical copolymerization of MMA and styrene in the presence of $EtAlCl_2$

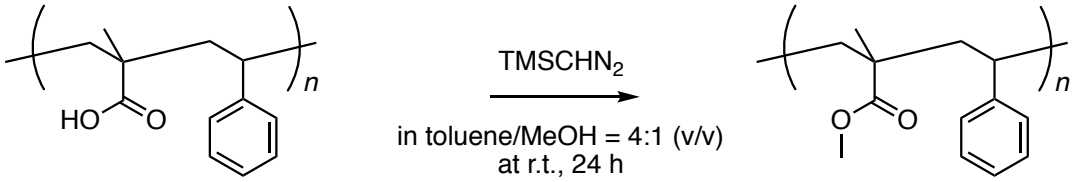
MMA (0.428 mg, 4 mmol) and $EtAlCl_2$ solution in toluene (1.8M, 0.889 mL, 1.60 mmol) were stirred for 8 h at room temperature under argon in a baked grass tube equipped with a three-way stopcock. In another grass tube, AIBN (12.2 mg, 0.0743 mmol), toluene, tetralin (0.20 mL), and styrene (1.858 mL, 16.2 mmol) were mixed under argon. The styrene solution (3.68 mL) was then added to the solution of MMA-$EtAlCl_2$. The reaction mixture was placed in an oil bath kept at 60 ˚C temperature. After 45 min reaction, the polymerization was terminated by cooling in dry ice-methanol. The quenched reaction solutions were diluted by dichloromethane, and poured into methanol to purify by reprecipitation. The copolymer of MMA and styrene were obtained as a colorless solid (M_n = 519700, M_w/M_n = 1.70).

Side-chain conversion



Scheme S8. Hydrolysis of side-chain

Alternating copolymer of **1** and styrene (1.03 g, mmol) was suspended in mixed solvent of TFA: H_2O = 10:1 (v/v) 22 mL. The mixture was stirred for 24 h at 80 ˚C. Then, the reaction mixture was poured into Et_2O to remove TFA. The precipitated mixture of polymer and saccharin was purified by dialysis with methanol: acetone = 9:1 (v/v) to obtain MAA-styrene alternating copolymer as slightly brown solid (0.502 g, 91%).



Scheme S9. Methylation of MAA unit

MAA-styrene alternating copolymer (83.4 mg, 0.438 mmol of carboxyl group) was dissolved in mixed solvent of toluene and methanol (10 mL, 4:1, v/v). Trimethyl silyl diazomethane (2 M in Et_2O, 0.329 mL, 0.657 mmol) was slowly added to the solution at room temperature. After 24h stirring, AcOH was slowly added in ice bath to quench the reaction. Resultant solution was diluted with toluene and washed with water 3 times and then brine, dried over Na_2SO_4, then evaporated. (M_n = 22300, M_w/M_n = 1.58)

Procedures to Determine Monomer Reactivity Ratio

The monomer reactivity ratio was calculated by setting **1** as M_1 and styrene as M_2. Copolymerizations of **1** and styrene were performed with AIBN by changing the injection ratio ($[M_1]_0$:$[M_2]_0$ = 900:100, 700:300, 500:500, 300:700, and 100:900 mM). Typical procedure of the copolymerization is as follows. In a Schlenk tube was placed 1 (381.9 mg, 1.52 mmol) under dry argon. Then, dioxane (1.33 mL), MeCN (1.33 mL), tetralin (internal standard, 0.03 mL), styrene (0.175 mL, 1.52mmol) and AIBN (0.304 mL of 100 mM stock solution in Dioxane-MeCN = 1:1 (v/v), 30.4 μmol) were added at room temperature under dry argon (5:5 injection condition). For immediately after mixing, aliquots (ca. 1.0 mL each) of the solution were distributed with a syringe into glass tubes that were then sealed. The tube was placed in an oil bath kept at 60℃ for 2 h. The reaction was terminated by cooling the solution to 0 ˚C. The composition ratio of copolymer [F = $DP_{n,1}/(DP_{n,1} + DP_{n,2})$] was determined from the conversion ratio [Conv.(M_1)/(Conv.(M_1) + Conv. (M_2))] by ^{1}H NMR (in $CDCl_3$) with tetralin as an internal standard. The actual monomer feed ratio [$f = [M_1]_0/([M_1]_0 + [M_2]_0)$] was also determined with by ^{1}H NMR spectrum (before heating). These values are listed in Table S1. The monomer reactivity ratios were then calculated via Kelen-Tüdős method[2] with the f and F values. The arbitrary constant for the method, α = 1.27.

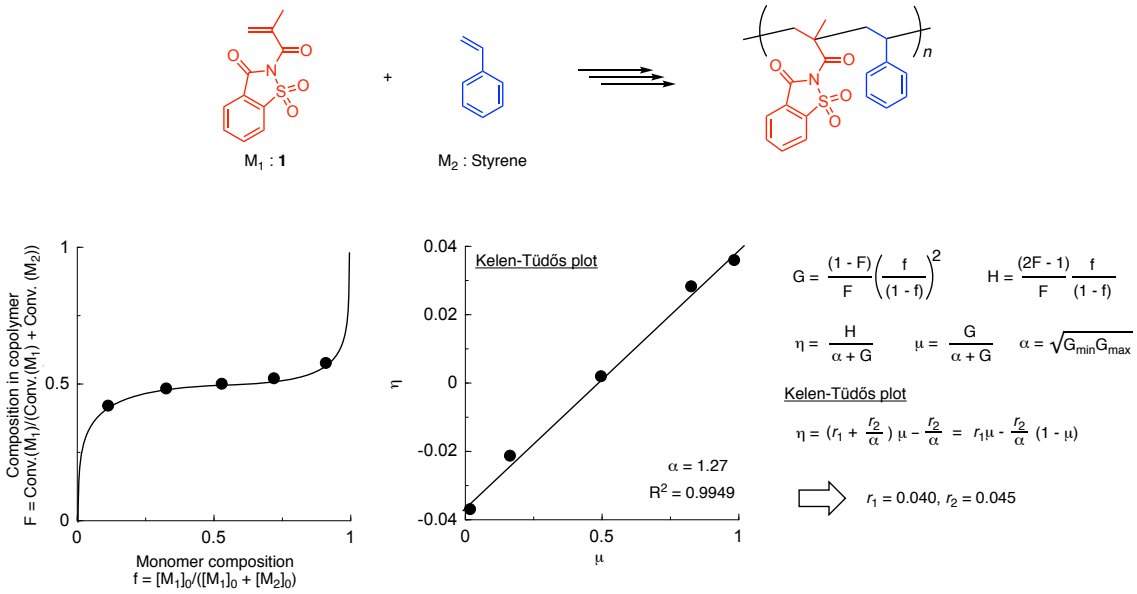


Figure S1. Determination of monomer reactivity ratio of 1 and styrene by Kelen-Tüdős method. Polymerization conditions: $[\text{total monomer}]_0/[\text{AIBN}]_0$ = 1000/10 mM in Dioxane-MeCN = 1:1 (v/v) at 60 ˚C

Table S1. Data for determine monomer reactivity ratio

Before polymn.		After polymn.		Conversion.			
1+St[a,b]	St[a,c]	**1**+St	St	**1**	St	f	F
473.74	22.65	456.81	18.11	2.746680263	20.04415011	0.908741111	0.577084304
474.80	77.70	438.38	66.23	6.283052128	14.76190476	0.718733032	0.520985592
363.85	112.37	317.12	96.84	12.40655321	13.8204147	0.528075259	0.501124317
403.49	205.59	358.10	189.80	14.95704901	7.680334647	0.324916267	0.483818241
401.05	319.88	368.48	306.61	23.77725761	4.148430661	0.112590681	0.421029668

a) Integration standard is benzyl proton of tetralin (2.7 ppm) as 100,

b) peaks at 5.6-5.8 ppm, sum of 2 protons of **1** and 1 proton of styrene,

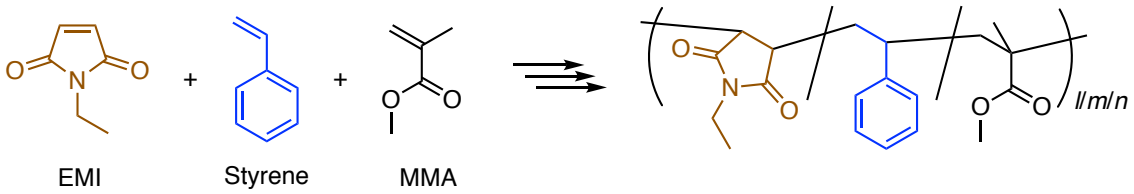
c) peaks at 5.1-5.2 ppm

Solubility of the alternating copolymer of 1 and styrene

Table S2. Solubility of the alternating copolymer of 1 and styrene

Solvent	Solubility	Solvent	Solubility
Water	Insoluble	THF	Insoluble (swollen)
Toluene	Insoluble (little swollen)	Dioxane	Insoluble (a little swollen)
Methanol	Insoluble	Acetonitrile	Insoluble
Acetone	Insoluble	Dioxane: Acetonitrile = 1:1	Soluble
DMF	Soluble (decomposition)	Ethyl acetate	Insoluble
DMSO	Soluble (decomposition)	Pyridine	Insoluble (swollen)
CH_2Cl_2	Insoluble (Swollen)	Acetic Acid	Insoluble
$CHCl_3$	Insoluble (little swollen)		

Terpolymerization of EMI, styrene and MMA



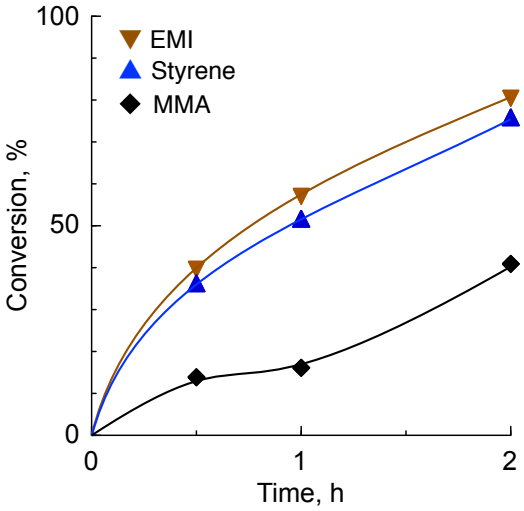


Figure S2. Time-conversion plot for terpolymerization of EMI, Styrene, and, MMA

Polymerization conditions: $[EMI]_0/[Styrene]_0/[MMA]_0/[AIBN]_0$ = 800/800/800/10 mM in Dioxane-MeCN = 1:1 (v/v) at 60 ˚C.

Bond Dissociation Energy

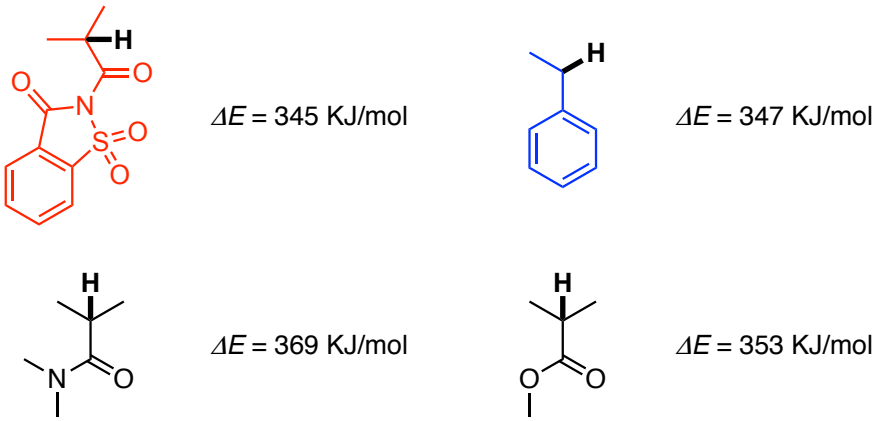


Figure S3. Bond dissociation energy for H_2 adduct of monomers

Model reaction of side-chain conversion

DMAP (21.5 mg, 0.176 mmol), MeOH (17.8 μL 0.440 mmol), and $CDCl_3$ (0.4 mL) were mixed in glass tube. The mixture was added $CDCl_3$ solution of saccharin pivalamide (200 mM, 0.440 mL, 0.088 mmol) at room temperature. The salt of saccharin and DMAP was precipitated. ^1H NMR was measured after 5 h reaction.

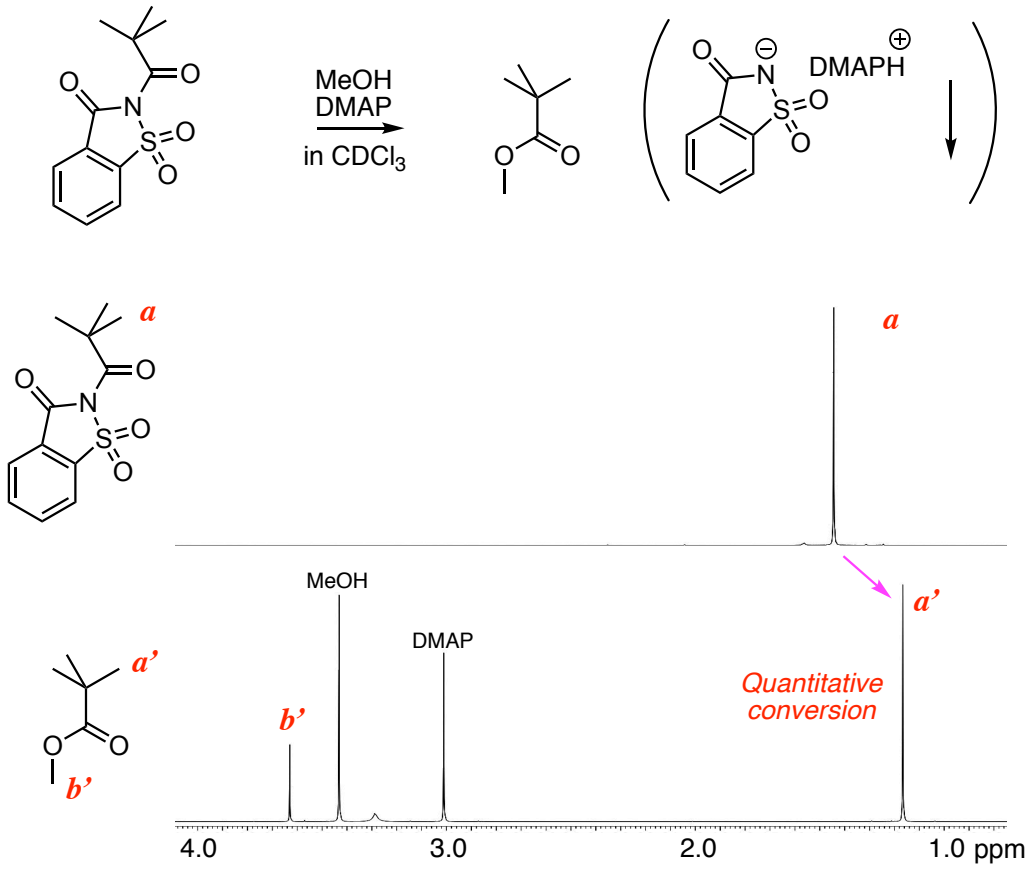


Figure S4. Model reaction for side-chain conversion: $[saccharin\ pivalamide]_0/[MeOH]_0/[DMAP]_0$ = 100/500/200 mM in $CDCl_3$ at room temperature.

^{1}H, ^{13}C NMR and FT-IR Spectra of the Products

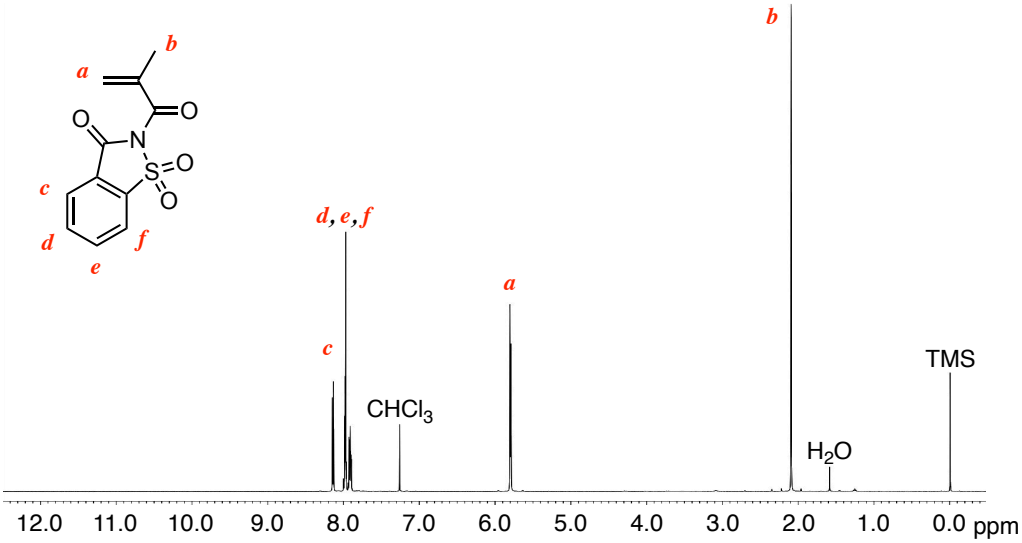


Figure S5. ^{1}H NMR spectrum (in $CDCl_3$ at room temperature) of **1**.

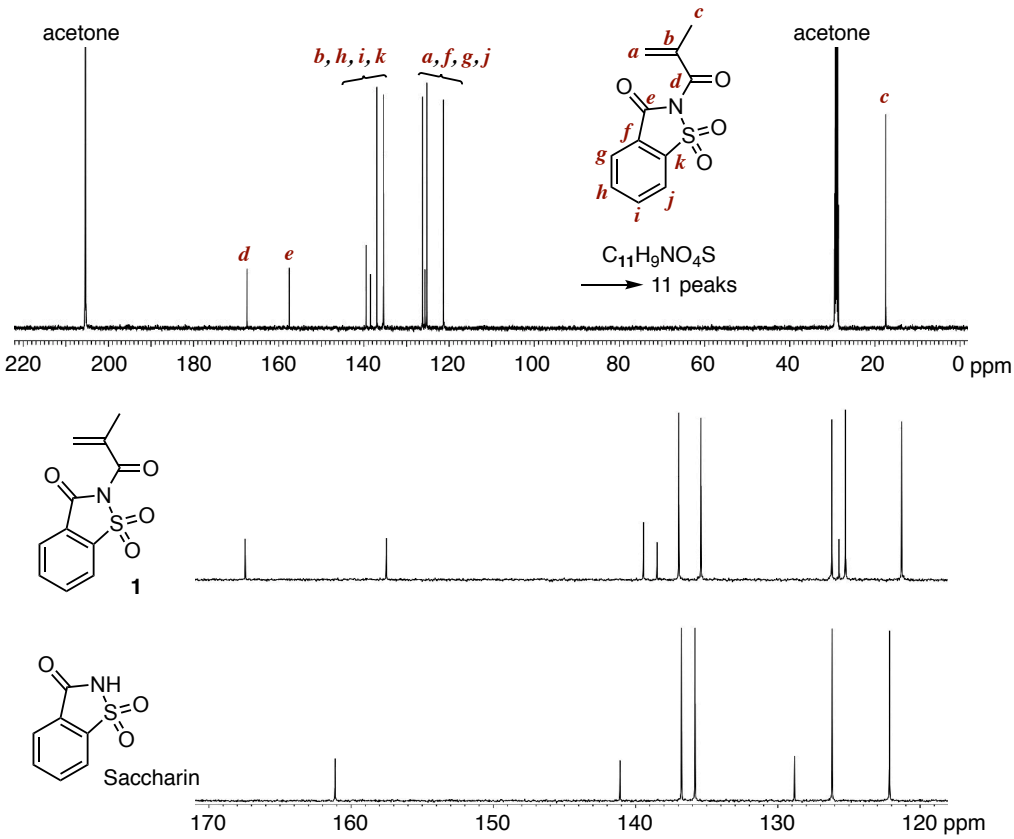


Figure S6. ^{13}C NMR spectra (in Acetone-d_6, at room temperature) of **1** in comparison with the precursor, saccharin.

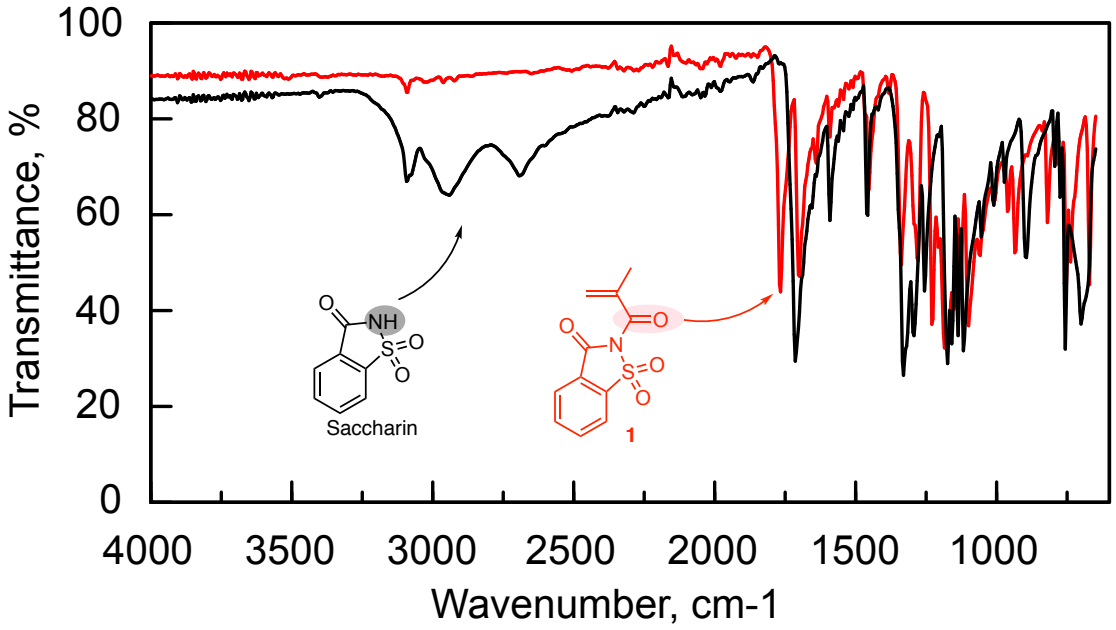


Figure S7. FT-IR Spectrum of **1** in comparison with saccharin.

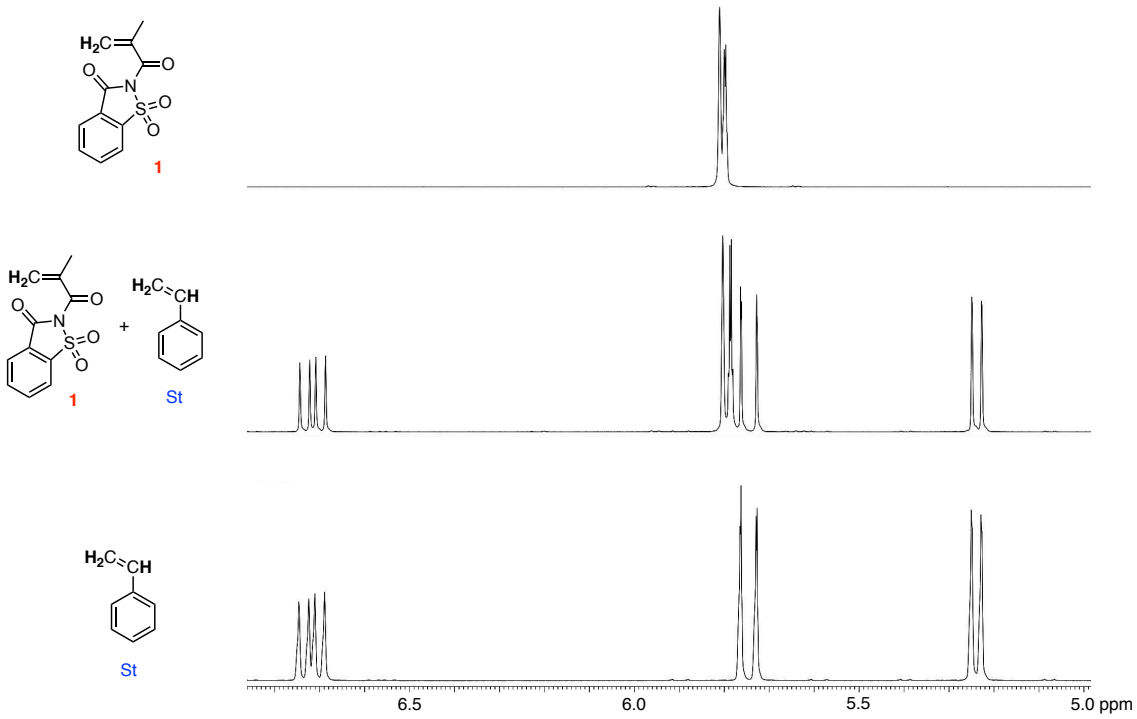


Figure S8. ^{1}H NMR spectrum (in $CDCl_3$, at room temperature) of the mixture of **1** and styrene (middle) in comparison with **1** (upper) and styrene (lower).

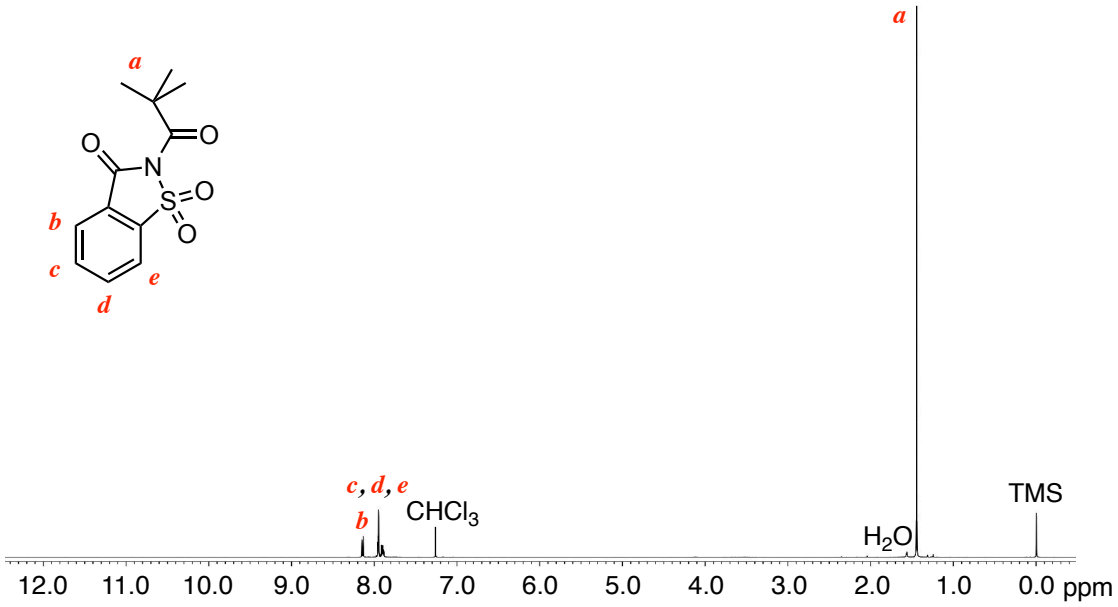


Figure S9. ^{1}H NMR spectrum (in $CDCl_3$ at room temperature) of saccharin pivalamide.

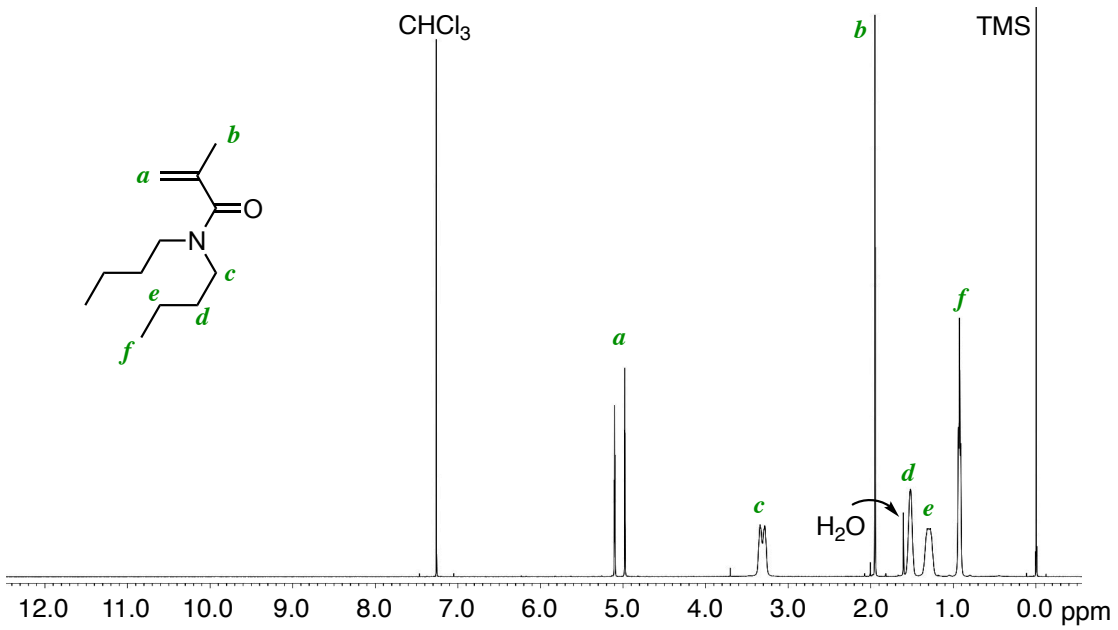


Figure S10. ^{1}H NMR spectrum (in $CDCl_3$ at room temperature) of **2**.

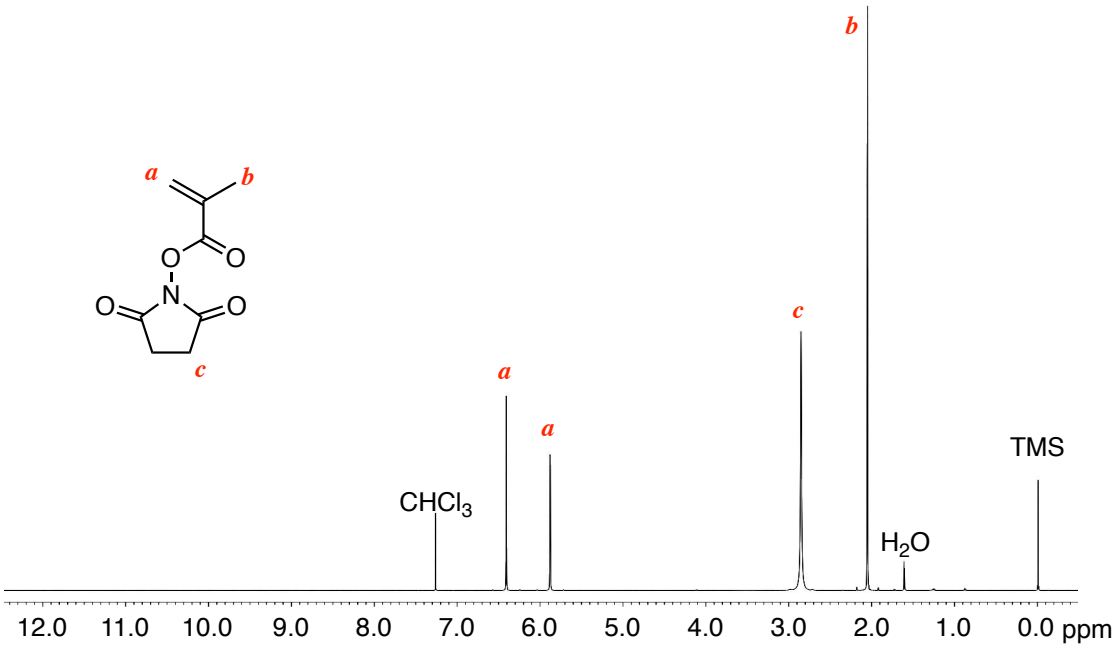


Figure S11. ^{1}H NMR spectrum (in $CDCl_3$ at room temperature) of **3**.

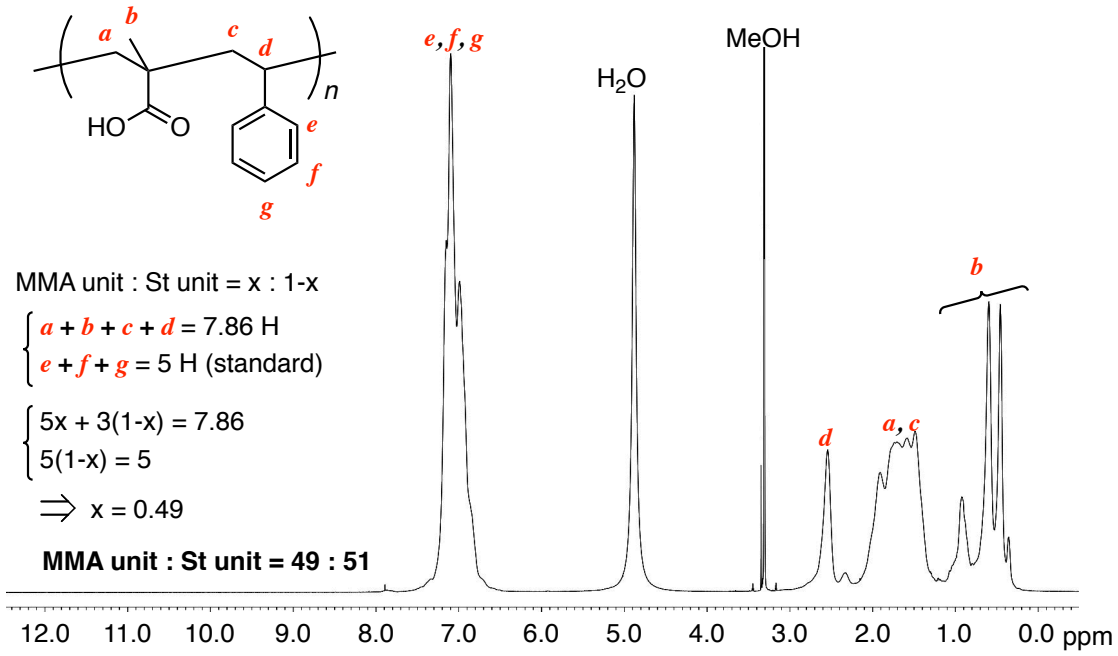
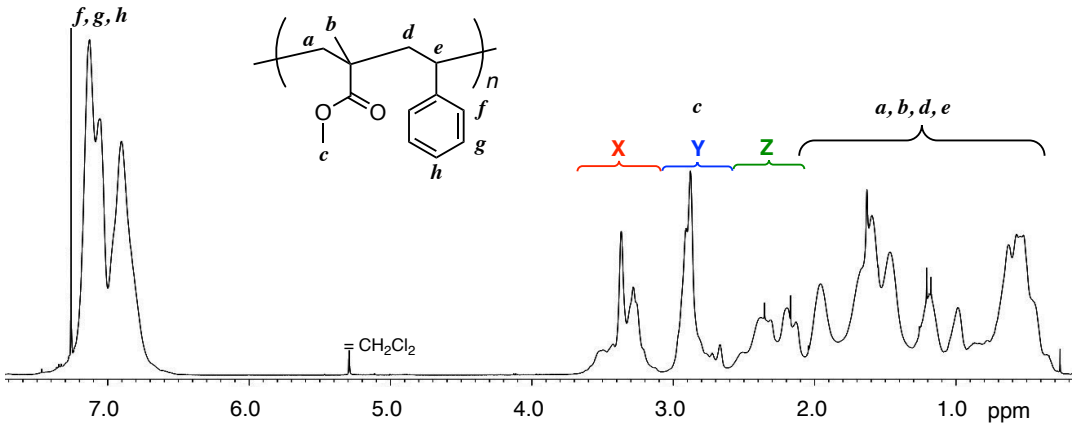


Figure S12. ^{1}H NMR spectrum (in CD_3OD at room temperature) and composition calculation of MAA-Styrene alternating copolymer synthesized from **1**.



Composition ratio

DP_{MMA} : DP_{St} = x : y

$\begin{cases} a+b+c+d+e = 10.66 \\ f+g+h = 5 \text{ (standard)} \end{cases}$

$\begin{cases} 8x + 3y = 10.66 \\ 5y = 5 \end{cases}$

$\Rightarrow$ x = 0.9575, y = 1

DP_{MMA} : DP_{St} = 49 : 51

Three regions of methoxy peak

The integration ratios of these regions are

$\begin{cases} \mathbf{X} = 1.15, \\ \mathbf{Y} = 1.24 \\ \mathbf{Z} : \text{overlapped with methine region} \end{cases}$

The total integration ratio of methoxy peak is

$\mathbf{X} + \mathbf{Y} + \mathbf{Z} = (10.66 - 3) \times \frac{3}{8} = 2.8725$

The fractions of region i (F_i) are

$\begin{cases} F_x = 0.400 \\ F_Y = 0.432 \\ F_Z = 1 - F_x - F_Y = 0.168 \end{cases}$

Coisotacticity parameter (σ)

$\sigma = (1 - F_x^{1/2})(1 + r_1 f_1 / f_2)$

$= (1 - 0.400^{1/2})(1 + 0.04 \times 1 / 1)$

$= 0.382$

r_1 is the reactivity ratio and f_i is the mole fraction of monomer i in the monomer feed (M_1 = **1**, M_2 = styrene)

The fraction of triad sequence (F_{MMM}, $2F_{MMS}$, F_{SMS})

$F_x = F_{MMM} + 2(1 - \sigma)F_{MMS} + (1 - \sigma)^2 F_{SMS} = 0.400$

$F_Y = 2\sigma F_{MMS} + 2\sigma(1 - \sigma)F_{SMS} = 0.432$

$F_Z = \sigma^2 F_{SMS} = 0.168$

$\Rightarrow$ $F_{MMM} = 0.14$, $2F_{MMS} = -0.29$, $F_{SMS} = 1.15$

Figure S13. Detailed sequence analysis of the MMA-Styrene copolymer synthesized from **1**.

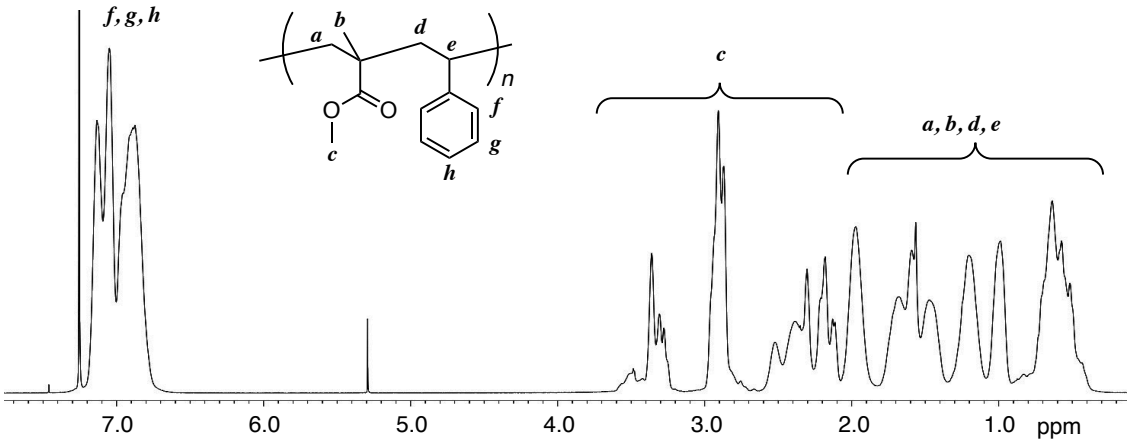


Figure S14. ^{1}H NMR spectrum (in $CDCl_3$ at room temperature) of MAA-Styrene alternating copolymer synthesized via radical copolymerization in presence of $EtAlCl_2$.

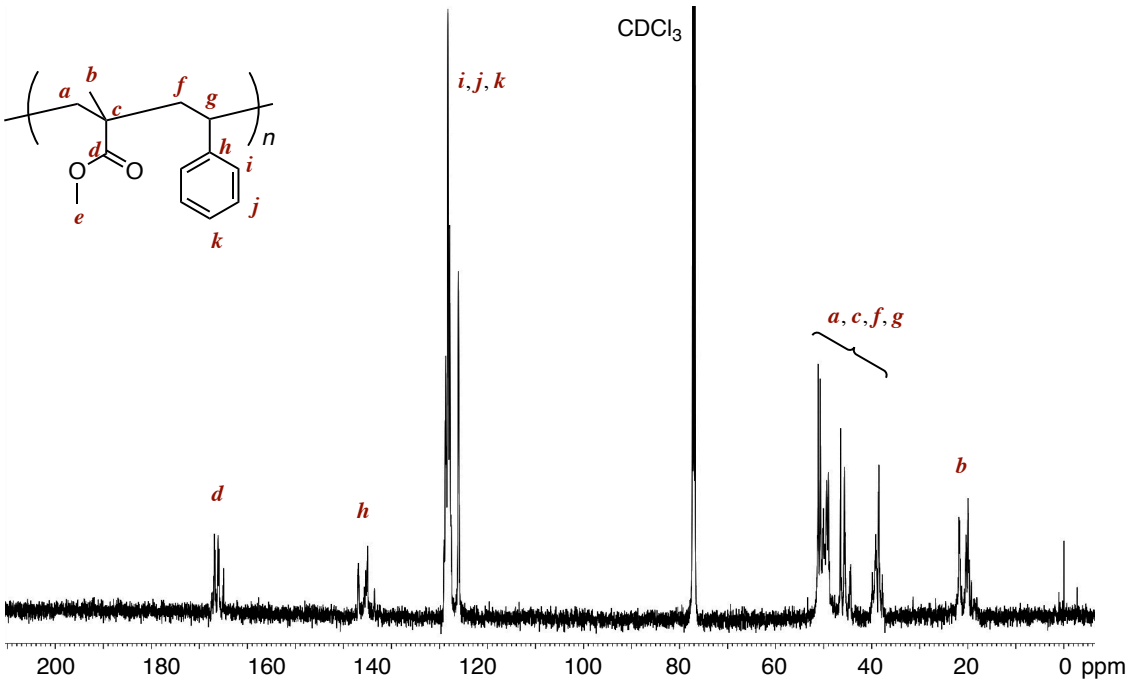


Figure S15. ^{13}C NMR spectrum (in $CDCl_3$ at 55 ˚C) of MAA-Styrene alternating copolymer synthesized from **1**.

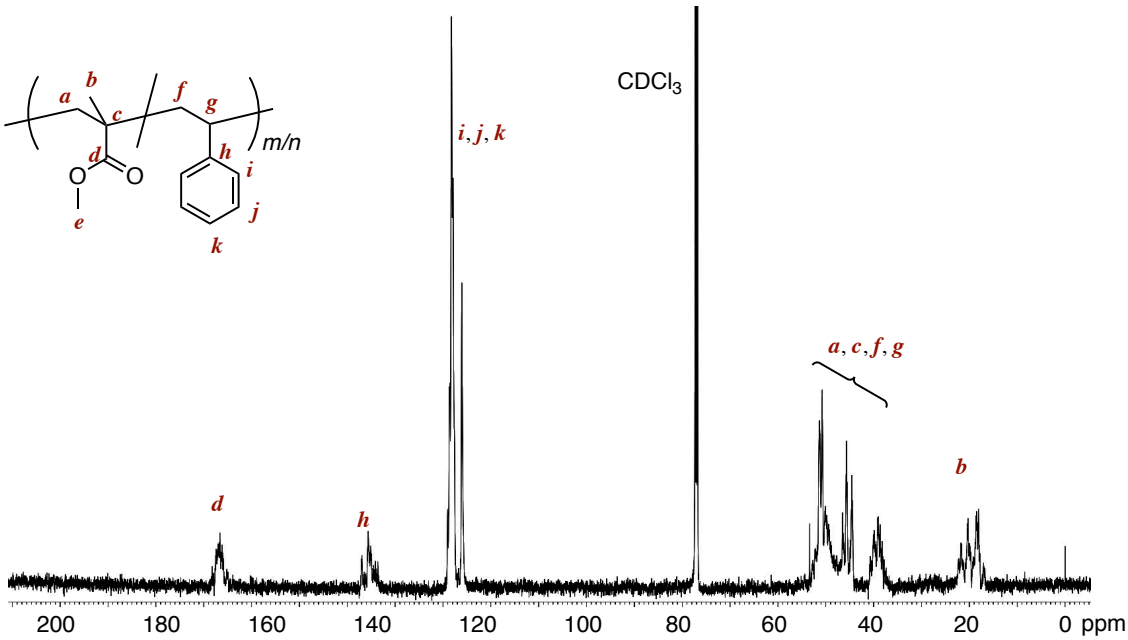


Figure S16. ^{13}C NMR spectrum (in $CDCl_3$ at 55 ˚C) of MAA-Styrene statistical copolymer.

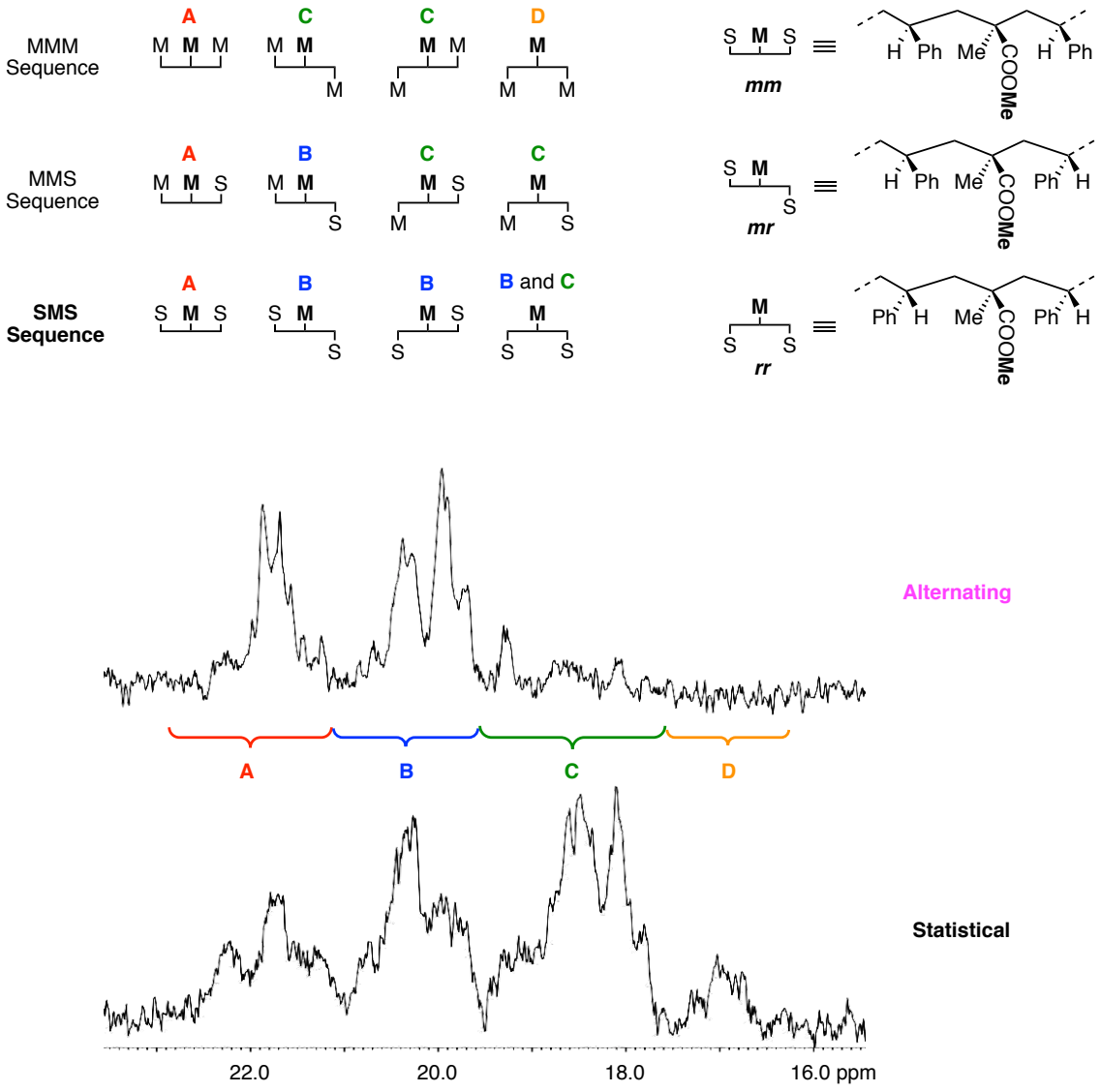


Figure S17. Sequence analysis by ^{13}C NMR spectra (in $CDCl_3$ at 55 ˚C).

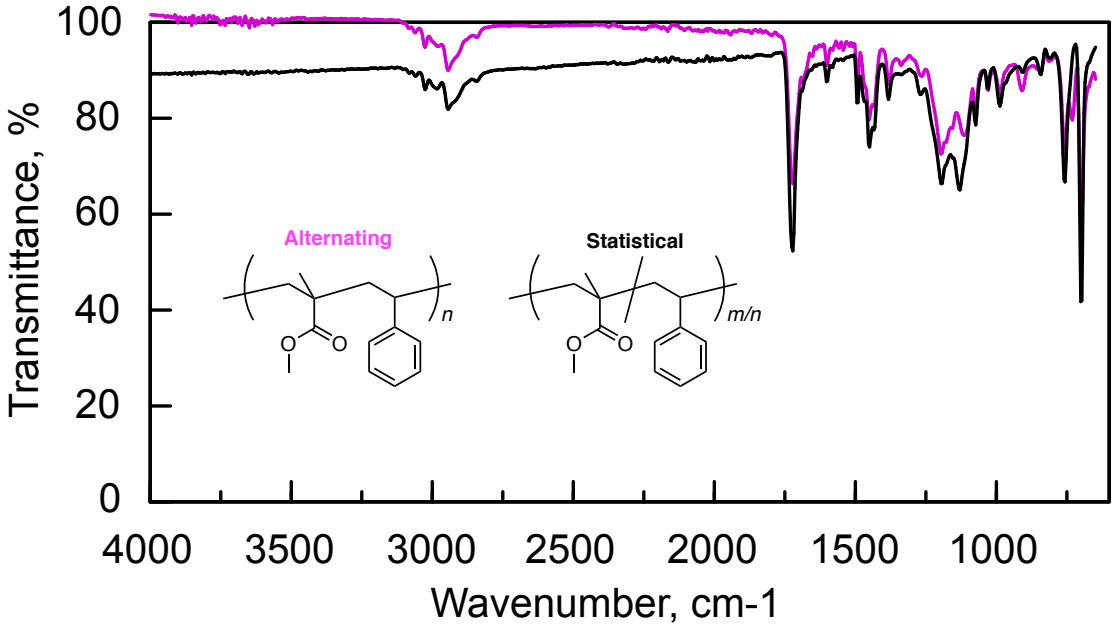


Figure S18. FT-IR Spectra of MMA-St copolymers.

DSC measurement

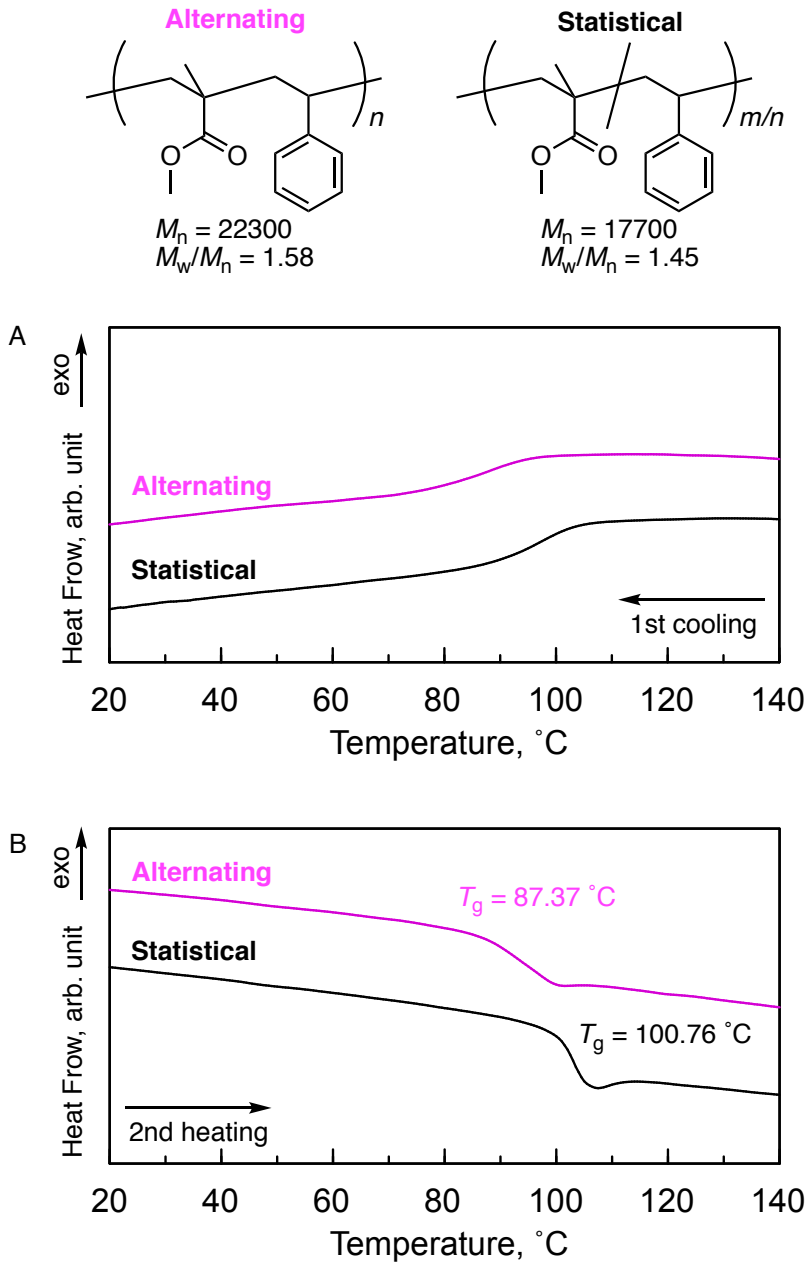
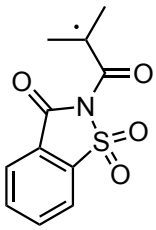
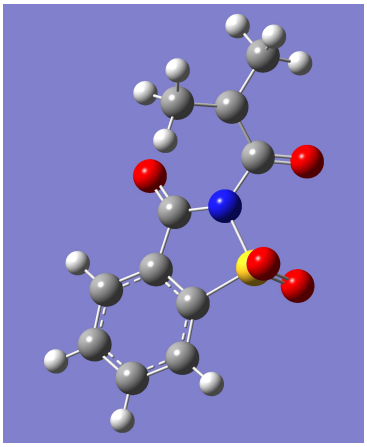


Figure S19. DSC profiles of the alternating copolymer of MMA and styrene obtained via radical copolymerization of **1** with styrene followed by side-chain conversion: Samples are kept at 150˚C for 10 min, cooled to 0˚C at 10 ˚C/min (A, 1st cooling), kept at 0˚C for 10 min, and then heated to 150 ˚C at 10 ˚C/min (B, 2nd heating).

Computational Study for Radical Polymerization Behavior

Model for chain end radical of saccharin methacrylamide





SOMO energy: -0.22838 eV

Sum of electronic and thermal Energies: -1178.718609 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.402558	1.913720	-0.312614
2	6	0	-3.733902	1.571615	-0.069240
3	6	0	-4.088108	0.257400	0.262633
4	6	0	-3.120211	-0.748014	0.355274
5	6	0	-1.802473	-0.383708	0.114280
6	6	0	-1.434314	0.917000	-0.214358
7	16	0	-0.383336	-1.471460	0.100164
8	7	0	0.693276	-0.096327	-0.153588
9	6	0	0.028037	1.107715	-0.421425
10	8	0	0.567776	2.144596	-0.758662
11	8	0	-0.448062	-2.337643	-1.069891
12	8	0	-0.094610	-2.022727	1.420977
13	6	0	2.112460	-0.343406	-0.295945
14	8	0	2.469484	-1.391777	-0.830191

15	6	0	3.029652	0.616170	0.267762
16	6	0	4.466669	0.502518	-0.127028
17	6	0	2.650258	1.647051	1.280252
18	1	0	-2.107303	2.925539	-0.570898
19	1	0	-4.505877	2.332261	-0.137588
20	1	0	-5.129675	0.012109	0.447906
21	1	0	-3.389500	-1.769111	0.604993
22	1	0	5.076462	0.185806	0.732406
23	1	0	4.855215	1.482364	-0.437840
24	1	0	4.608762	-0.219244	-0.932299
25	1	0	3.448108	1.748086	2.026009
26	1	0	2.515450	2.628612	0.805902
27	1	0	1.719033	1.403276	1.798489

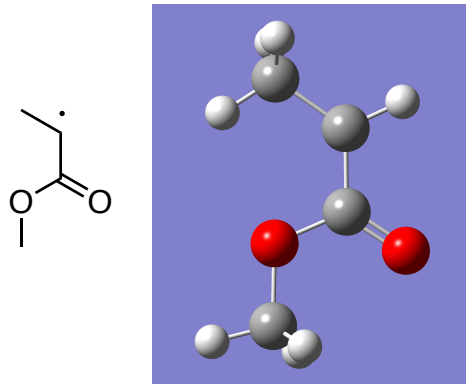
Mulliken charges and spin densities:

		1	2
1	C	-0.150574	0.000277
2	C	-0.133202	-0.000163
3	C	-0.111689	0.000414
4	C	-0.162162	-0.000279
5	C	-0.194806	0.000738
6	C	0.095483	-0.000511
7	S	1.233789	-0.000165
8	N	-0.727025	-0.002220
9	C	0.580947	0.002832
10	O	-0.483579	0.001809
11	O	-0.457988	0.000064
12	O	-0.480991	0.001541
13	C	0.545202	-0.057904
14	O	-0.439296	0.287993
15	C	0.165162	0.746840
16	C	-0.515827	-0.058271

17	C	-0.520573	-0.057971
18	H	0.176608	0.000032
19	H	0.157852	0.000002
20	H	0.159566	0.000001
21	H	0.182826	0.000031
22	H	0.173934	0.037201
23	H	0.169912	0.027898
24	H	0.198577	0.001141
25	H	0.165014	0.015534
26	H	0.201491	0.046199
27	H	0.171349	0.006938

Sum of Mulliken charges = 0.00000 1.00000

Model for chain end radical of methyl acrylate



SOMO energy: -0.22801 eV

Sum of electronic and thermal Energies: -306.934149 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

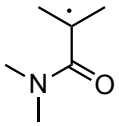
1	6	0	1.373191	0.514520	-0.000041
2	6	0	2.238686	-0.694720	-0.000057
3	6	0	-0.075563	0.520465	0.000031
4	1	0	1.824279	1.502091	0.000202
5	8	0	-0.756153	1.538802	-0.000018
6	8	0	-0.617164	-0.731323	0.000024
7	6	0	-2.048934	-0.769001	-0.000004
8	1	0	-2.315418	-1.826834	0.000636
9	1	0	-2.450220	-0.272280	0.888224
10	1	0	-2.450141	-0.273426	-0.888918
11	1	0	2.903634	-0.700052	-0.876845
12	1	0	2.899595	-0.702980	0.879822
13	1	0	1.650525	-1.613934	-0.002753

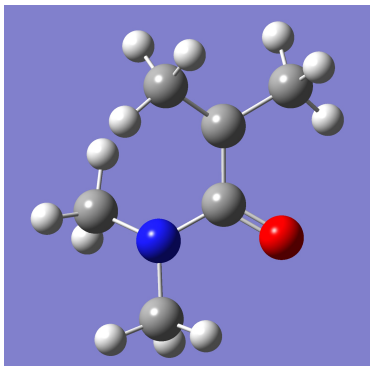
Mulliken charges and spin densities:

		1	2
1	C	-0.120513	0.891351
2	C	-0.499033	-0.067305
3	C	0.605100	-0.079283
4	H	0.163702	-0.042078
5	O	-0.491288	0.190637
6	O	-0.469732	0.025882
7	C	-0.214079	-0.002956
8	H	0.159452	0.000027
9	H	0.167961	0.001440
10	H	0.167933	0.001450
11	H	0.170759	0.039713
12	H	0.170834	0.039978
13	H	0.188903	0.001144

Sum of Mulliken charges = 0.00000 1.00000

Model for chain end radical of *N*,*N*-dimethyl methacrylamide





SOMO energy: -0.19682 eV

Sum of electronic and thermal Energies: -365.618539 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.265486	0.112395	-0.012050
2	6	0	0.036046	-0.575583	-0.036789
3	6	0	-1.515556	1.442191	-0.659552
4	6	0	-2.451634	-0.668283	0.457332
5	1	0	-0.637062	1.829145	-1.181841
6	1	0	-2.331894	1.354856	-1.392079
7	1	0	-1.844718	2.202686	0.066859
8	7	0	1.201955	0.182623	-0.070842
9	8	0	0.078504	-1.810617	-0.110239
10	6	0	1.347577	1.436075	0.655029
11	6	0	2.449358	-0.534429	-0.292752
12	1	0	2.878975	-0.913034	0.647396
13	1	0	2.264652	-1.384297	-0.948850
14	1	0	3.174859	0.143024	-0.757536
15	1	0	1.811024	2.208041	0.026850

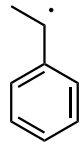
16	1	0	0.379665	1.799843	0.998966
17	1	0	1.984375	1.293844	1.541609
18	1	0	-3.062658	-0.074559	1.153281
19	1	0	-3.112326	-0.928747	-0.385067
20	1	0	-2.148446	-1.598426	0.940904

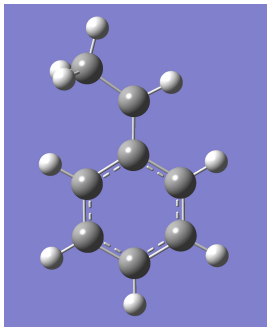
Mulliken charges and spin densities:

		1	2
1	C	0.094719	0.864963
2	C	0.533336	-0.065932
3	C	-0.513942	-0.070542
4	C	-0.497871	-0.069144
5	H	0.171107	0.002978
6	H	0.164052	0.031164
7	H	0.157037	0.045730
8	N	-0.415641	0.025576
9	O	-0.519690	0.152236
10	C	-0.319507	0.002803
11	C	-0.306044	-0.003521
12	H	0.148393	0.002535
13	H	0.190364	-0.000209
14	H	0.143788	0.002511
15	H	0.154592	-0.000560
16	H	0.169406	-0.000215
17	H	0.153121	0.003107
18	H	0.146512	0.029117
19	H	0.159522	0.045765
20	H	0.186747	0.001638

Sum of Mulliken charges = 0.00000 1.00000

Model for chain end radical of Styrene





SOMO energy: -0.16957 eV

Sum of electronic and thermal Energies: -1178.718609 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.015479	1.057670	0.000017
2	6	0	-1.337872	1.365857	0.000024
3	6	0	-2.302073	0.349594	-0.000015
4	6	0	-1.889618	-0.990818	-0.000012
5	6	0	-0.540999	-1.309477	0.000000
6	6	0	0.461452	-0.295782	-0.000050
7	6	0	1.833140	-0.646777	-0.000098
8	6	0	2.965447	0.332473	-0.000078
9	1	0	0.747858	1.859641	0.000190
10	1	0	-1.650590	2.407184	0.000101
11	1	0	-3.359712	0.597622	-0.000016
12	1	0	-2.631106	-1.785850	-0.000008
13	1	0	-0.228211	-2.351258	-0.000007
14	1	0	2.076100	-1.706802	0.000855
15	1	0	3.931010	-0.181298	-0.006864
16	1	0	2.938520	0.996717	-0.877149

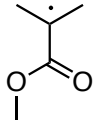
17	1	0	2.946396	0.987604	0.884170

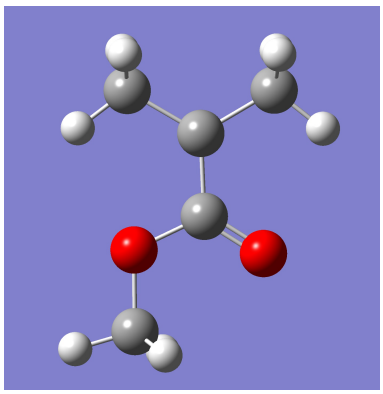
Mulliken charges and spin densities:

		1	2
1	C	-0.194015	0.245002
2	C	-0.124836	-0.129602
3	C	-0.135486	0.262709
4	C	-0.127434	-0.127997
5	C	-0.190161	0.232730
6	C	0.205346	-0.196478
7	C	-0.183677	0.768276
8	C	-0.490093	-0.063436
9	H	0.124196	-0.011439
10	H	0.127254	0.004965
11	H	0.127248	-0.012803
12	H	0.127544	0.004905
13	H	0.123806	-0.010724
14	H	0.131253	-0.038346
15	H	0.154715	0.001309
16	H	0.162138	0.035209
17	H	0.162203	0.035721

Sum of Mulliken charges = 0.00000 1.00000

Model for chain end radical of methyl methacrylate





SOMO energy: -0.21076 eV

Sum of electronic and thermal Energies: -346.227137 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.092002	0.119907	0.002134
2	6	0	-1.426240	1.577561	0.000803
3	6	0	0.283079	-0.356896	0.001385
4	6	0	-2.189799	-0.891373	-0.002322
5	8	0	0.616035	-1.536949	0.002039
6	8	0	1.195427	0.658712	-0.000753
7	6	0	2.564445	0.239747	-0.001415
8	1	0	-2.837803	-0.762459	-0.882593
9	1	0	-1.789121	-1.906426	-0.003987
10	1	0	-2.841397	-0.766794	0.875899
11	1	0	3.152976	1.158417	-0.004132
12	1	0	2.789195	-0.356148	0.888091
13	1	0	2.787108	-0.360145	-0.888735
14	1	0	-2.023566	1.843214	0.885157
15	1	0	-0.531632	2.203613	-0.006165
16	1	0	-2.034351	1.838944	-0.877328

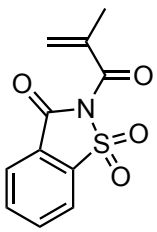
Mulliken charges and spin densities:

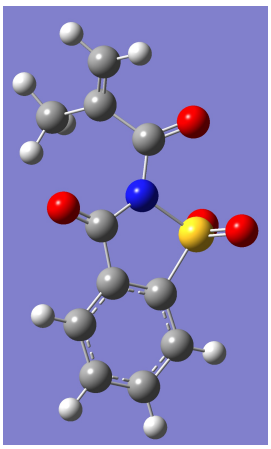
		1	2
1	C	0.117281	0.832845
2	C	-0.517721	-0.066666

3	C	0.579403	-0.062696
4	C	-0.514580	-0.066951
5	O	-0.500466	0.180993
6	O	-0.473076	0.029020
7	C	-0.211695	-0.003289
8	H	0.160070	0.037231
9	H	0.195248	0.001044
10	H	0.160070	0.037232
11	H	0.158253	0.000024
12	H	0.166696	0.001644
13	H	0.166696	0.001645
14	H	0.162664	0.038314
15	H	0.188498	0.001307
16	H	0.162659	0.038304

Sum of Mulliken charges = 0.00000 1.00000

Saccharin methacrylamide



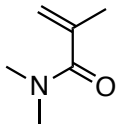


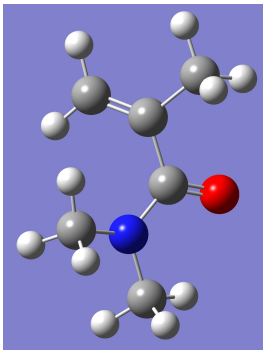
Sum of electronic and thermal Energies: -1178.140626 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.303719	-1.976162	-0.246871
2	6	0	-3.650958	-1.655745	-0.075587
3	6	0	-4.048858	-0.334562	0.169120
4	6	0	-3.109597	0.698549	0.244352
5	6	0	-1.774625	0.356096	0.074848
6	6	0	-1.363322	-0.950575	-0.165802
7	16	0	-0.388099	1.482405	0.061665
8	7	0	0.743431	0.112570	-0.076696
9	6	0	0.107312	-1.124219	-0.304912
10	8	0	0.671323	-2.167164	-0.568152
11	8	0	-0.190367	2.108881	1.363061
12	8	0	-0.415816	2.268692	-1.164424
13	6	0	2.135627	0.434995	-0.146883
14	8	0	2.442171	1.584107	-0.387717
15	6	0	3.135095	-0.642824	0.144982
16	6	0	2.954919	-1.524009	1.357072
17	6	0	4.210863	-0.681048	-0.649949
18	1	0	-1.974318	-2.992666	-0.436002
19	1	0	-4.401458	-2.438466	-0.131746
20	1	0	-5.102479	-0.106331	0.299833
21	1	0	-3.412439	1.724230	0.427973
22	1	0	2.759974	-0.922033	2.253306
23	1	0	2.126413	-2.225646	1.232358
24	1	0	3.866771	-2.102515	1.531815
25	1	0	5.007656	-1.400419	-0.482537
26	1	0	4.320530	-0.001747	-1.489134

***N*,*N*-dimethyl methacrylamide**





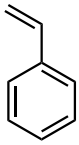
Sum of electronic and thermal Energies: -365.050270 (Hartree/Particle)

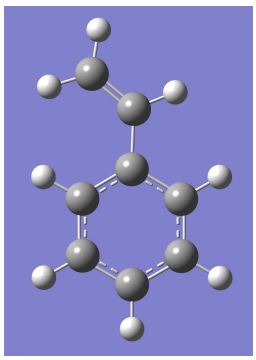
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.317804	0.187797	-0.099142
2	6	0	-0.004368	-0.544369	-0.126301
3	6	0	2.391363	-0.487474	0.714708
4	6	0	1.545508	1.249965	-0.880362
5	1	0	2.139352	-0.487172	1.783463
6	1	0	2.480875	-1.535037	0.410174
7	1	0	3.357599	0.009777	0.588524
8	1	0	0.766657	1.691924	-1.495703
9	1	0	2.534163	1.697264	-0.952150
10	7	0	-1.174048	0.164716	0.024749
11	8	0	0.002142	-1.758529	-0.325909
12	6	0	-1.287089	1.504429	0.581297
13	6	0	-2.434884	-0.549538	-0.124528
14	1	0	-3.126742	0.045158	-0.733428
15	1	0	-2.241109	-1.506006	-0.607463

16	1	0	-2.904170	-0.731922	0.852715
17	1	0	-1.893054	1.478070	1.497935
18	1	0	-0.303961	1.903282	0.823290
19	1	0	-1.778417	2.185017	-0.127365

Styrene





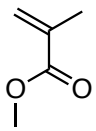
Sum of electronic and thermal Energies: -309.507775 (Hartree/Particle)

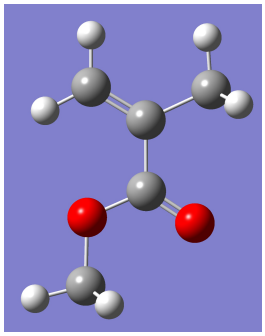
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.008885	1.092559	-0.000145
2	6	0	1.362256	1.329576	-0.000070
3	6	0	2.265327	0.261769	0.000064
4	6	0	1.780871	-1.046246	0.000136
5	6	0	0.406446	-1.281306	0.000037
6	6	0	-0.515191	-0.220383	-0.000090
7	6	0	-1.954781	-0.529364	-0.000222
8	6	0	-2.977340	0.334929	0.000271
9	1	0	-0.693975	1.935443	-0.000211

10	1	0	1.730505	2.352271	-0.000143
11	1	0	3.335444	0.450486	0.000060
12	1	0	2.472014	-1.885048	0.000296
13	1	0	0.034973	-2.303736	0.000067
14	1	0	-2.186267	-1.594744	-0.000856
15	1	0	-4.004483	-0.016890	0.000020
16	1	0	-2.840425	1.413013	0.000880

Methyl methacrylate





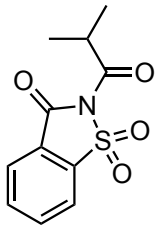
Sum of electronic and thermal Energies: -345.654568 (Hartree/Particle)

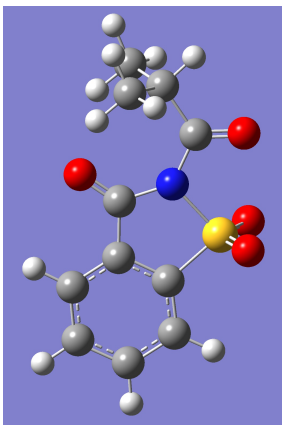
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.144799	0.259798	-0.000042
2	6	0	1.362187	1.581019	0.000029
3	6	0	-0.241203	-0.299429	-0.000261
4	6	0	2.240533	-0.773507	0.000077
5	8	0	-0.483471	-1.491386	-0.000054
6	8	0	-1.207219	0.648604	-0.000029

7	6	0	-2.552174	0.149353	0.000144
8	1	0	2.372329	1.982057	0.000166
9	1	0	0.544541	2.292740	-0.000059
10	1	0	3.225323	-0.297851	0.000233
11	1	0	2.162626	-1.425966	0.877040
12	1	0	2.162872	-1.425904	-0.876954
13	1	0	-3.191815	1.032704	0.000491
14	1	0	-2.737793	-0.459240	-0.889154
15	1	0	-2.737414	-0.459679	0.889223

H_2 adduct of Saccharin methacrylamide



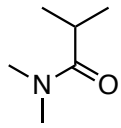


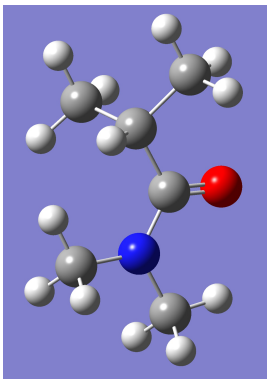
Sum of electronic and thermal Energies: -1179.348985 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.238591	-2.050231	-0.000023
2	6	0	-3.605213	-1.770884	0.000012
3	6	0	-4.067146	-0.447506	0.000028
4	6	0	-3.173245	0.627119	0.000019
5	6	0	-1.817495	0.324987	0.000000
6	6	0	-1.343591	-0.980848	-0.000022
7	16	0	-0.477067	1.501567	0.000010
8	7	0	0.725542	0.164220	-0.000104
9	6	0	0.137404	-1.114255	-0.000085
10	8	0	0.727792	-2.177666	-0.000195
11	8	0	-0.432073	2.206746	1.274331
12	8	0	-0.432158	2.206905	-1.274223
13	6	0	2.085990	0.611769	-0.000015
14	8	0	2.249116	1.814762	-0.000055
15	6	0	3.267921	-0.355051	0.000115
16	6	0	3.369063	-1.193831	1.288149
17	1	0	4.105419	0.350800	0.000249
18	1	0	-1.859517	-3.066915	-0.000043
19	1	0	-4.321267	-2.587178	0.000026
20	1	0	-5.135262	-0.251425	0.000046
21	1	0	-3.524512	1.653767	0.000024
22	1	0	3.327536	-0.555793	2.178035
23	1	0	2.578833	-1.943602	1.348636
24	1	0	4.333720	-1.713532	1.295877
25	6	0	3.369358	-1.193670	-1.288009
26	1	0	2.579118	-1.943408	-1.348756
27	1	0	3.328043	-0.555513	-2.177820
28	1	0	4.334011	-1.713381	-1.295575

H_2 adduct of *N*,*N*-dimethyl methacrylamide





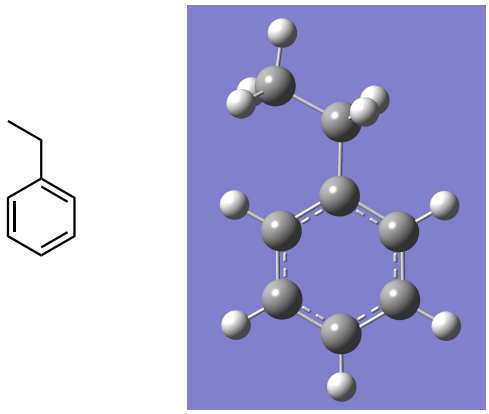
Sum of electronic and thermal Energies: -366.257758 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.227168	0.341862	-0.274824
2	6	0	0.030227	-0.493011	0.023736
3	6	0	-2.362624	-0.582364	-0.732629
4	6	0	-1.630283	1.131254	0.987605
5	1	0	-2.094711	-1.115742	-1.650659
6	1	0	-2.578917	-1.331710	0.032757
7	1	0	-3.269328	0.002062	-0.926844
8	7	0	1.268629	0.098761	-0.111884
9	8	0	-0.080691	-1.657326	0.400845
10	6	0	1.535881	1.476415	-0.486039
11	6	0	2.456512	-0.688879	0.187911
12	1	0	3.001180	-0.260281	1.040511
13	1	0	2.145162	-1.703700	0.429514

14	1	0	3.131830	-0.703773	-0.677948
15	1	0	2.128959	1.519628	-1.410626
16	1	0	0.617291	2.037839	-0.642066
17	1	0	2.111377	1.980377	0.303225
18	1	0	-2.545634	1.705240	0.804253
19	1	0	-1.821515	0.441134	1.816820
20	1	0	-0.850284	1.831676	1.307219
21	1	0	-1.025550	1.052870	-1.084294

H_2 adduct of styrene



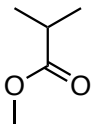
Sum of electronic and thermal Energies: -310.713752 (Hartree/Particle)

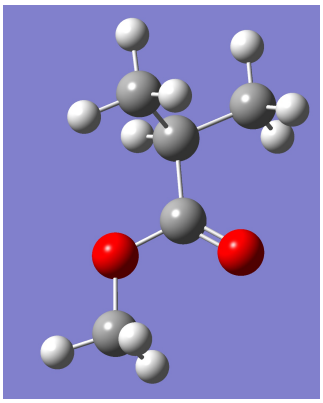
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.016320	1.042742	0.000030
2	6	0	1.377279	1.364152	0.000012
3	6	0	2.339025	0.355982	-0.000015
4	6	0	1.929423	-0.980373	-0.000025
5	6	0	0.572538	-1.294756	-0.000008
6	6	0	-0.408955	-0.290460	0.000021

7	6	0	-1.875955	-0.693220	0.000055
8	6	0	-2.896146	0.448023	-0.000061
9	1	0	-0.714691	1.845507	0.000051
10	1	0	1.681632	2.407878	0.000018
11	1	0	3.396780	0.605470	-0.000030
12	1	0	2.668720	-1.777490	-0.000048
13	1	0	0.263250	-2.338544	-0.000017
14	1	0	-3.914722	0.045526	-0.000053
15	1	0	-2.790909	1.084812	0.885730
16	1	0	-2.790863	1.084671	-0.885948
17	1	0	-2.060176	-1.335269	-0.873186
18	1	0	-2.060186	-1.335096	0.873423

H_2 adduct of methyl methacrylate





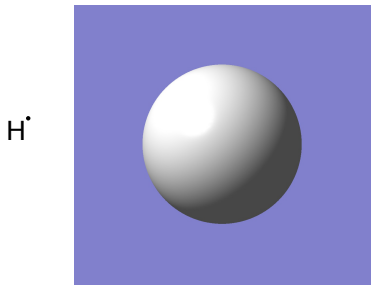
Sum of electronic and thermal Energies: -346.860557 (Hartree/Particle)

Standard orientation:

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	1.076737	0.219513	-0.396283
2	6	0	1.449452	1.427272	0.489032
3	6	0	-0.298574	-0.296624	0.005122
4	6	0	2.120159	-0.898057	-0.313126
5	8	0	-0.519783	-1.298881	0.650403
6	8	0	-1.276196	0.534207	-0.431006
7	6	0	-2.612500	0.159594	-0.061093
8	1	0	3.104632	-0.519654	-0.609336
9	1	0	2.188907	-1.287732	0.707094
10	1	0	1.861911	-1.735401	-0.969290
11	1	0	-3.260914	0.925863	-0.487427
12	1	0	-2.862515	-0.824371	-0.467040
13	1	0	-2.717675	0.129213	1.026894
14	1	0	2.422980	1.828575	0.187083
15	1	0	0.706483	2.225948	0.404255
16	1	0	1.519007	1.129499	1.541839
17	1	0	0.993375	0.575266	-1.431155

H radical



Sum of electronic and thermal Energies: -0.498857 (Hartree/Particle)

Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.000000	0.000000	0.000000

References

[1] Gaussian 16, Revision A.03, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, **2016**

[2] T. Kelen, F. Tüdős, B. Turcsányi, *Polymer Bull*. **1980**, *2*, 71-76.